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Theoretical Studies of Carbocations in Ion Pairs. Part 3. The *tert*-Butyl Cation in an Ionic Aggregate[1]

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The structure of the *tert*-butyl cation in the five-ion aggregate $Li^+{\bullet}H_3BF^-{\bullet}Me_3C^+{\bullet}FBH_3^-{\bullet}Li^+$ was studied by high level ab initio MO calculations, with electron correlation, at the MP2/6-31G** level. The aggregate size was defined by the distance L between two parallel planes. One Li^+ ion moves freely within each plane. At the first level of complexity, each Li..B..F group was collinear and normal to these planes, the angles between each of the three C^+-C bonds and an axis perpendicular to the planes were equal, and the ions in the central triple ion moved freely along this axis. Starting from the C_{3h} form preferred by the isolated carbocation, geometry optimization led to a C_s conformation, by methyl group rotation. The C_{3v} form of the cation maintained its conformation upon optimization. The stabilities of these two conformations cannot be fairly compared, because the interionic equilibrium distances are different. (The aggregate with a C_{3v} cation is lower in energy by 1.9 kcal/mol at $L = 12.658$ Å). At the second level of complexity, no restraint was placed upon carbocation orientation. The C_{3v} form did not change from the previous case, but in the C_s form the plane of the cation was tilted by 16−18° from the perpendicular orientation and the bond lengths and angles for the C−H's facing the closest anion were slightly changed. In the third stage, the Li..B..F axes could also tilt relative to the Li planes. The C_s aggregate geometry was unchanged, but the C_{3v} aggregate exhibited a very flat energy surface, optimizing ultimately with the cation within coordinating distance (1.655 Å) from the F atom of the nearest anion. Finally, the collinearity of the Li..B..F group was also released for the C_s aggregate. The oscillation between slightly different relative orientations of near-equal energy and with the same carbocation geometry occurred, but in the end optimization gave an aggregate with the same cation geometry and about the same relative orientation of ions as in the previous case. Thus, the geometry of the cation shows little sensitivity to the degree of freedom of movement of ions within the aggregate. Optimization of a triple ion with frozen interionic distances gave the same structure for the carbocation as the aggregate which got optimized to the same interionic distances, thus showing that geometry optimizations at fixed interionic distances give reliable structures for carbocations in ion pairs or aggregates.

Introduction

Some time ago we noticed that high-level theoretical calculations[2] routinely conducted on isolated carbocations in the gas phase fail sometimes to predict the behavior of carbocations intervening as reaction intermediates in media of moderate to low dielectric constant, but good anion-stabilizing properties (e.g., trifluoroacetic acid).[3] As in the cases which we investigated experimentally the outcome of the reactions was determined at the tight ion pair stage,[4] it was conceivable that an adjacent anion induces an alteration of structure and energy of the carbocation. Adding to our interest was the observation that on solid acid catalysts carbocations can appear, if at all, only as tight ion pairs with the anions of the acid sites.[5] Therefore, we embarked upon a study of structures and energies of carbocations in the presence of counterions by ab initio molecular orbital calculations. We have already reported on the effect of ion pairing on the geometry of the 2-propyl cation[6] and on the NMR spectrum of the same cation in the solid state.[1] It was found that the effect of the anion originates mostly in the electrostatic interaction with the positively charged atoms, especially hydrogens, in the cation. Thus, the presence of an anion, even at distances as long as 5 Å, changed the preferred conformation of the 2-propyl cation from 1,3-staggered (chiral 2-propyl cation, C_2 symmetry)[7] to 1,3-eclipsed (C_s symmetry),[6] because of the interaction 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^+-C-H bond angles are much reduced from the bond lengths and angles of the other methyl hydrogens.[6]

Studies of interconversion of the 1-propyl cation and hydronated cyclopropane,[8a] and of the 3-methyl-2-butyl cation and 2,3-dimethyl-1-hydronated cyclopropane[8b] have also been completed. Work on other systems is in progress and will be reported in due course.

The most important variables to be considered in the calculations were the nature of the anion and the interionic distance. It was found that the interionic distance has an important effect on the cation geometry and recombination of the ions occurs at different distances for different anions, because of the different nucleophilicities of the latter. At distances beyond the recombination range, the cation structure did not change, however, when the anion was changed.[6]

Because the cation−anion pair, $RR'R''C^+{\bullet}Z$ (**1**), was unstable toward recombination or elimination by hydron transfer, the anion was kept from "falling" or "tumbling" over the cation by

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fixing it in a given orientation and allowing it to move freely within a plane situated at a given distance (interionic distance, *d*) from the $C-C^{+}-C$ plane of the cation (plane-parallel movement). Otherwise, the cation and (in most cases) the anion were subjected to full geometry optimization, such that the calculation gave the most stable geometry of the carbocation in the field of the anion. Frequency analyses[2c] gave just three negative eigenvalues, identified[9] as the stretching of the $C^{+}\cdots Z^{-}$ "bond" and its bending in two perpendicular directions. We report here on an aggregate consisting of a 2-methyl-2-propyl cation, two anions, and two lithium cations (total charge +1), arrayed in the order $Li^{+}\cdot Z^{-}\cdot Me_3C^{+}\cdot Z^{-}\cdot Li^{+}$ ("double-decker sandwich," **2**), in which these constraints were released and the cation was allowed to "float" freely and find the equilibrium distances, d_{eq} and d'_{eq} from the two anions.

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, a C_1 form close to the C_{3h} form, was equal in energy to the C_s form.[10] The input geometry in our calculations was, therefore, the C_{3h} conformation with the geometric parameters obtained in the calculation for the isolated ion.[10]

Methods

The calculations were conducted with the program Gaussian 94,[11] as described before.[1,6] For the anion Z^{-} we used the trihydrofluoroborate anion (H_3BF^{-}, **A**),[1,6] which combined a size manageable for calculations with a realistic stability[12] and charge distribution. The strong interactions of the lithium cations with the negative hydrogens, which would be lost upon the reaction of one of the anions with the carbocation, were expected to prevent the latter process from occurring. At the same time, the difference in electronegativity makes the negative charge at the fluorine, which faces the carbocation, higher than at the hydrogens, leading to a model realistic for the aggregates containing the carbocation in a crystal or in solution. The overall size of the aggregate was determined by the distance between two parallel planes in which the two Li^{+} cations were allowed to move (*L*). By changing this distance, the interionic distances, d_{eq} and d'_{eq} could be varied somewhat, but could not be fully controlled, being fully optimized. As it turned out, the $Li^{+}...Li^{+}$ distance after optimization was usually equal to *L*.

To choose the appropriate level of theory, we noted that neglect of electron correlation had been found to give unreliable results,[3] but that the increase in size of the basis set beyond MP2/6-31G* up to MP2/6-311G** produced negligible changes in the optimized geometries.[3,6] We conducted the optimizations of the geometry of **2A** at the MP2/6-31G** level, the same as employed in the study of the isolated cation.[10]

We started the calculation with an imposed relative orientation of the ions, which was then relaxed in stages, as represented schematically in Figure 1. The anion was positioned with the fluorine facing the cation and, because of the size of the system, the bond lengths and the bond angles of the B−H bonds were frozen during optimization. In the first stage (Figure la), the Li...B...F groups were held collinear and perpendicular to the planes in which the Li cations were allowed to move. Each anion moves along the Li plane like a chandelier attached to a ceiling, with the point of attachment (the Li cation) free to glide on the ceiling. An axis of the cluster (aggregate) was defined as perpendicular to the planes containing the Li cations and passing through the central (*sp*^{2}) carbon. At this stage the three $C^{+}-C$ bonds were held at the same angle from axis of the cluster, but the cation was free to move up and down along it as well as sidewise between the two Li planes. This is described as *perpendicular orientation* (**p.o.**).

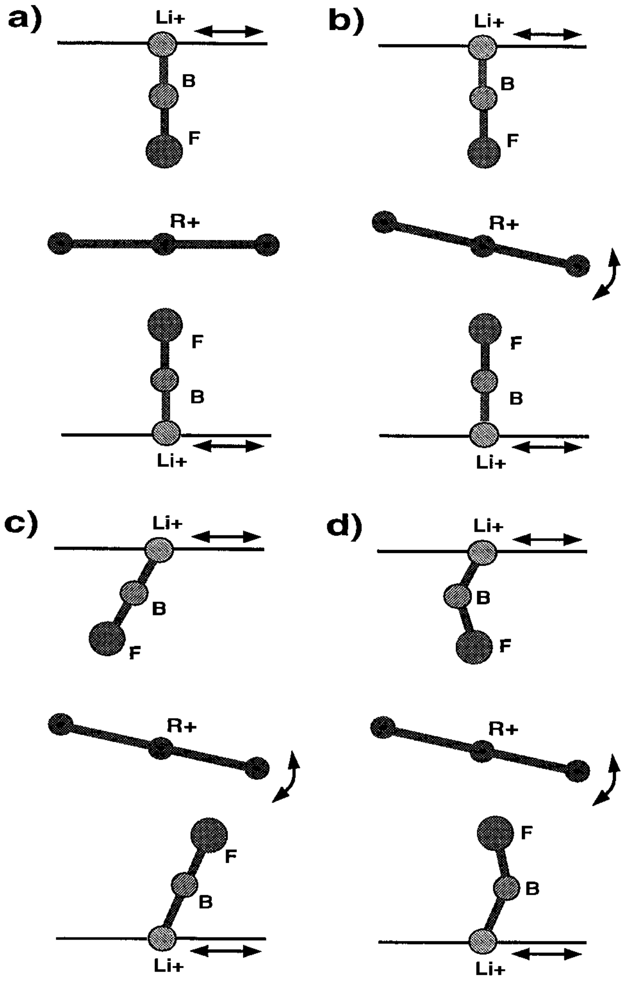

Figure 1. Schematic representation of the constraints upon orientation of ions in the aggregate released at successive stages of the calculations. (The drawings do not reflect the final values of the parameters illustrated.) (a) perpendicular orientation of the cation (**p.o.**); (b) free cation orientation (**f.c.o.**); (c) reduced restrictions on anion orientation (**r.r.**); (d) unrestricted orientation (**u.o.**).

In the next step, the constraint on the angles between the $C^{+}-C$ bonds and the axis of the cluster was removed. The cation was thus allowed to tilt freely in the center of the double-decker sandwich, with neither intramolecular nor intermolecular constraints (Figure lb). This is *the free cation orientation* (**f.c.o.**).

For a partial optimization of the orientation of the anion, the angle between each Li...B axis and the plane in which the Li cation was contained was optimized in the next stage (Figure 1c). The result was an aggregate with *reduced* level of orientation *restriction* (**r.r.**).

In the fourth stage, the last constraint on orientation of ions was removed, as the Li...B...F angles were optimized (Figure 1d). The result was an aggregate with *unrestricted orientation* (**u.o.**).

To achieve the optimization of the C_{3v} conformation of the cation in the system with reduced restriction of the anion orientation (**r.r.** see above), a system which exhibited a very flat energy surface, we relaxed somewhat one of the four optimization criteria, Maximum Force, from 0.000450 to

0.000650. The other three optimization criteria (RMS Force = 0.0000300, Max. Displacement = 0.00180, and RMS Displacement = 0.00120) were not altered.

In all cases the geometry was described in the calculations with the use of dummy atoms.[6] Frequency analyses[2c] were conducted by the DFT-B3LYP method,[13] with the same basis set as the geometry optimization. Optimization of **2A** was conducted at distances L between 12.25 and 13.5 Å, with the purpose of finding an arrangement for which the distances d_{eq} and d'_{eq} in the central triple ion would be at least close to the distances measured by Hollenstein and Laube for a crystalline *tert*-butyl salt (2.93 and 3.11 Å, respectively).[14]

Results and Discussion

Optimization of the C_{3h} form brought about in each case a rotation of the carbon−carbon bonds and led to the C_s conformation (**3**).[15] In this arrangement, two of the methyl groups point a hydrogen atom each toward an anion, as in the equilibrium form of the 2-propyl cation in ion pairs,[6] whereas the third methyl group points a hydrogen atom toward the other anion. The perpendicular orientation (**p.o.**) was examined first. The anions adopted a staggered conformation relative to the methyl groups, but kept twisting by ±30° around the B−F axes in opposite direction for 18 optimization cycles after the geometry of the cation and the total energy showed no perceptible variation. Such a behavior was not observed for the $Me_3C^{+\bullet}FBH_3^-$ ion pair.[16] Therefore, the rotational movement of the anions around the B−F bonds was frozen, enforcing one dihedral angle (φ(H,B,B′,H′) = 0°. Interestingly, it was found that two methyl hydrogens face the *nearest* anion for L = 13.458 Å (d_{eq} = 2.72 Å, d'_{eq} = 3.88 Å), but two methyl hydrogens face *the farthest* anion for L = 13.058 Å (d_{eq} = 2.69 Å, d'_{eq} = 3.41 Å) or 12.658 Å (d_{eq} = 2.67 Å, d'_{eq} = 3.08 Å). The axis of the cluster was in the end collinear with the Li^+...B−F....F−B ...Li^+ axis. The geometrical parameters of the carbocation changed in the expected manner with the change in L,[6] but the changes were not important within the limits of variation in L examined here. A representation of **3(p.o.)** at L = 13.058 Å is shown in two projections, front (**F**) and side (**S**), in Figure 2. The essentials of the cation geometry are presented in Table 1.

When the calculation was started with the form of C_{3v} symmetry of the cation[10] in **2A**, the conformation was retained after optimization, **4(p.o.)**. The interionic distances d_{eq} and d'_{eq} were in that case significantly different from each other: 2.13 and 3.15 Å at L = 12.258 Å, 2.20 and 3.45 Å at L = 12.658 Å, 1.94 and 4.17 Å at L = 13.058 Å, 1.80 and 4.74 Å at L = 13.458 Å. Two projections of the aggregate **4(p.o.)** at L = 12.658 Å are presented in Figure 3. The carbocation in this form deviates from planarity: the dihedral angle (φ(C,C^+,C,C) is 201.5°, instead of 180° (see Table 1). This distortion results from the interaction of the central carbon with the closest anion and from the interaction of three hydrogens, one in each methyl group, with the farthest anion. Deviations from planarity with the methyl groups moving toward the anion were found in calculations of the $Me_3C^{+\bullet}FBH_3^-$ ion pair at interionic distances between 2.95 and 4.0 Å.[16]

Conformation **4(p.o.)** was lower in energy than **3(p.o.)** by 1.9 kcal/mol at L = 12.658 Å. The difference represents the most likely electrostatic energy, because d_{eq} was shorter in the former than in the latter.

When the *tert*-butyl cation was placed in a triple ion $Z^{-\bullet}Me_3C^{+\bullet}Z^-$ (**5**, "simple sandwich"), recombination occurred. Optimization with the interionic distances frozen gave the same geometry for the carbocation as found for the "double-decker sandwich" optimized to the same interionic distances (d_{eq} and d'_{eq}).[16] This result shows that the calculations on an ion pair with frozen interionic distance provide a correct description of the carbocation in the field of the anion at the given interionic distance.

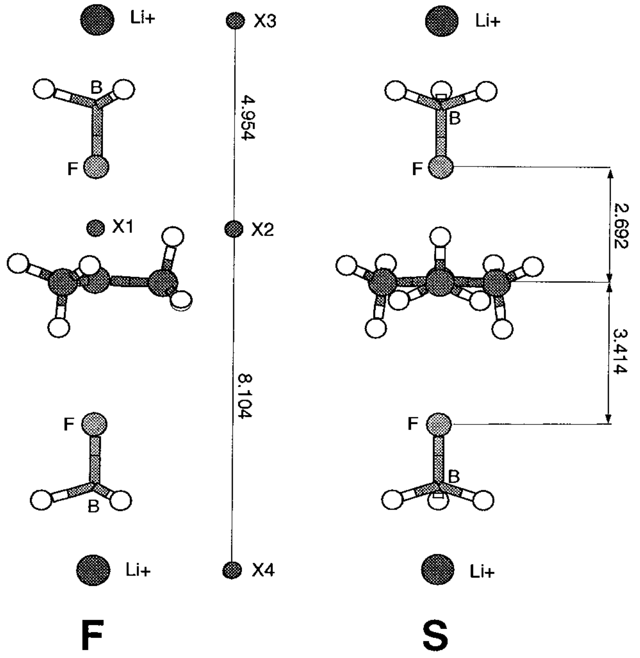

Figure 2. Geometry of the ionic aggregate with the C_s cation in the perpendicular orientation **3(p.o.)** for an aggregate size (L) of 13.06 Å, optimized at the MP2/6-3 1G** level. **F**: front view; **S**: side view; X1,X2,X3,X4: "dummy" atoms.

In the second step, optimization of the aggregate **2A** allowing the carbocation to tilt and flip freely (free cation orientation, **f.c.o.**, Figure 1b), starting from the C_{3h} conformation, led again to the C_s conformation, **3(f.c.o.)**, by methyl group rotation, after which the cation continued to rock around and across the axis of the aggregate, changing the direction of tilt in each optimization step. At L = 13.458 Å, the cation settled in a position with d_{eq} and d'_{eq} (3.14 and 3.50 Å, respectively) less different from each other than in **3(p.o.)** at the same overall cluster size (L). Two methyl groups were pointing a hydrogen toward the closest anion. Upon the expenditure of an enormous (by our standard) amount of supercomputer time at L = 12.92 Å, the optimization was completed at the structure shown in Figure 4, in which the carbocation is tilted such that the angle between the axis of the cluster and the C^+−C(up) bond, where C(up) points to the closest anion (in all the figures), is 72.12°. The other two methyl groups pointed a hydrogen each toward the farthest anion. The closest anion ("up" from the cation) is negligibly off the axis of the cluster, but the farthest anion has moved somewhat "inside" the Me(down)−C^+−Me′(down) angle, as shown by the F(down)...C^+−C(up) angle of 111.82°, instead of 180 − 72.12° = 107.88° (Figure 4). A similar position of the anion was calculated for the ion pair of the 2-propyl cation.[6] The C^+−C bond for the methyl group facing the closest anion was shortened, the C−H bond of the hydrogen facing the same anion (proximal hydrogen, Hp) was lengthened, and the bond angle θ(C^+−C−Hp) was reduced in **3(f.c.o.)** from the values in **3(p.o.)**; as shown in Table 1, other geometric parameters were little affected.

The values for d_{eq} and d'_{eq} (3.00 and 3.06 A) were quite close to those found in the crystal.[14a,b] The tilt, defined as the angle between the normal to the plane of the cation and the F....F

TABLE 1: Main Geometrical Parameters and Atomic Charges for the *tert*-Butyl Cation in the Aggregate 2A, from the Geometry Optimization at the MP2/6-31G Level[a]**

geometrical parameter	**3(p.o.)** $L = 13.058^b$	**3(f.c.o.)**, **3(r.r.)** $L = 12.918^b$	**3(u.o.)** $L = 12.918^b$		**4(p.o.)**, **4(f.c.o.)** $L = 12.658^b$	**4(r.r.)** $L = 12.658^b$
			A	B		
d_{eq}	2.69	3.00	3.00	2.99	2.20	1.66
d'_{eq}	3.41	3.06	3.06	3.09	3.45	4.97
d(C1−C2)	1.456	1.447	1.447	1.449	1.466	1.496
d(C2−C3)	1.457	1.459	1.459	1.459	1.466	1.496
d(C2−C4)	1.457	1.459	1.459	1.458	1.466	1.497
θ(C1,C2,C3)	119.55	120.26	120.26	120.16	118.82	116.20
θ(C1,C2,C4)	119.55	120.26	120.27	120.16	118.82	115.89
θ(C3,C2,C4)	120.54	119.39	119.37	119.57	118.82	115.87
φ(C1,C2,C3,C4)	186.96	183.64	183.68	183.87	201.45	218.79
d(C1-Hp)^c	1.103	1.113	1.113	1.110	1.101	1.091
d(C1−Hd)^d	1.086	1.085	1.085	1.086	1.085	1.087
θ(C2,C1,Hp)	99.85	97.62	97.64	98.35	102.20	106.83
θ(C2,Cl,Hd)	113.20	114.02	114.01	113.85	112.56	111.18; 111.82^f
d(C3−Hp)^c	1.105	1.104	1.104	1.104	1.101	1.091; 1.094^f
d(C3−Hd,i)^{d,e}	1.084	1.086	1.086	1.086	1.085	1.086
d(C3-Hd,o)^{d,e}	1.085	1.085	1.085	1.085	1.085	1.087
θ(C2,C3,Hp)^c	100.87	100.70	100.71	100.86	102.20	107.07; 108.72^f
θ(C2,C3,Hd,i)^{d,e}	113.47	112.83	112.82	112.93	112.57	111.64; 111.01^f
θ(C2,C3,Hd.o)^{d,e}	112.54	113.34	113.35	113.30	112.56	111.05; 110.80^f

[a] See descriptions of the structures in Figures 1−3; distances (L, d) in Å, angles (θ, φ) in degrees; (p.o.) = perpendicular orientation, (f.c.o.) = free cation orientation, (r.r.) = reduced restrictions on anion orientation, (u.o.) = unrestricted orientation (cation and anion). [b] The size of the aggregate, L, is the distance between the two parallel planes within which the two Li^+ ions are allowed to move. The Li^+... Li^+ distance after optimization is essentially equal to L. [c]Hydrogen facing the fluorine (proximal). [d] Hydrogen away from fluorine (distal). [e] i = inward, o = outward. [f] The second value pertains to C4 instead of C3.

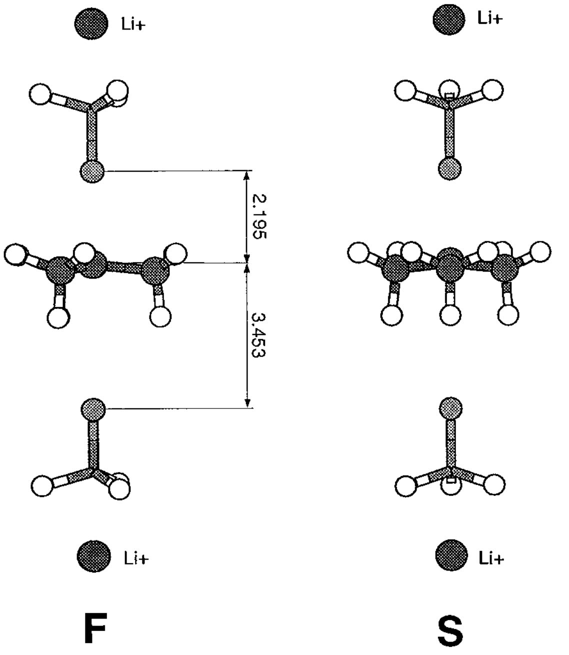

Figure 3. Geometry of the ionic aggregate with the C_{3v} cation in the perpendicular **4(p.o.)** or free cation orientation **4(f.c.o.)** for an aggregate size (L) of 12.66 Å, optimized at the MP2/6-31G** level. **F**: front view; **S**: side view (dummy atoms not represented).

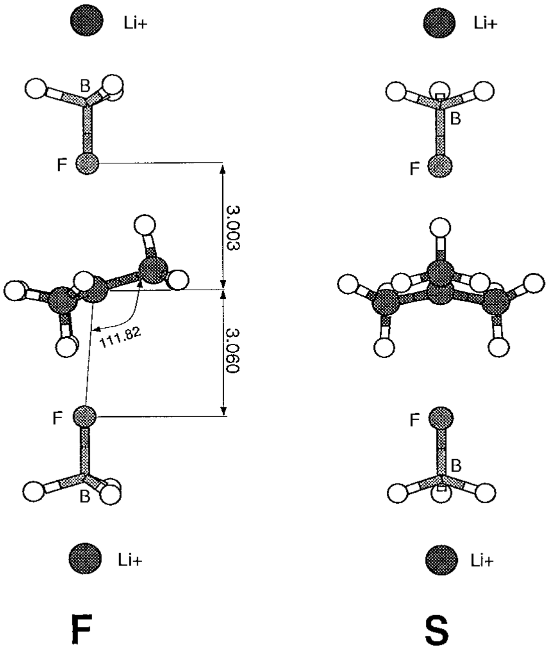

Figure 4. Geometry of the ionic aggregate with the C_s cation in the free cation orientation **3(f.c.o.)** for an aggregate size (L) = 12.92 Å, optimized at the MP2/6-31G** level. The same overall geometry of the aggregate (cation and anion) is retained in **3(r.r.)** and in **3(u.o.)** (see text). **F**: front view; **S**: side view (dummy atoms not represented).

axis is 5.47° in the crystal,[14c] as opposed to the value of 17.88° (90° − 72.12°) calculated for **3(f.c.o.)**. The orientation of the cation in the crystal (perpendicular or tilted) is also influenced by the other anions surrounding it. A significant influence of "lateral" anions in the crystal upon the principal components of the chemical shift tensor of the sp^2 carbon of the 2-propyl cation was evidenced in the calculations on that system.[1] The hydrogen bonding of methyl hydrogens with the "lateral" anions,[14b] together with the tendency toward efficient packing in the crystal, reduce the angle of tilting to that determined by X-ray diffraction.[14c]

Optimization of the C_{3v} conformation of **2A** at L = 12 658 Å with the carbocation free to reorient itself, gave the aggregate **4(f.c.o.)** with the same geometry as **4(p.o.)** (Figure 3 and Table 1).

In the third stage of calculations, with reduced level of orientation restriction **(r.r.)**, the orientation of the anion was also allowed to vary by optimizing the angle between each Li...B axis and the plane in which the Li cation moves, as discussed in the Methods section and shown in Figure 1c. The aggregate

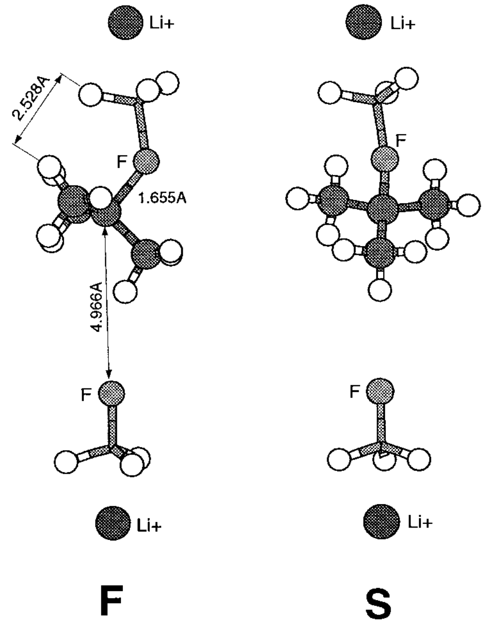

Figure 5. Geometry of the ionic aggregate with the C_{3v} cation in the **4(r.r.)** arrangement (see text) for an aggregate size (L) of 12.66 Å, optimized at the MP2/6-31G** level. **F**: front view; **S**: side view (dummy atoms not represented).

with the cation in the C_s conformation, **3(r.r.)**, optimized quickly and had the same geometry as **3(f.c.o.)** (Table 1 and Figure 3). In the C_{3v} conformation **4**, however, optimization tilted the closest anion, after which location of a minimum was very sluggish, the cation moving for many cycles among regions located between 1.60 Å and 2.80 Å from the fluorine of the closest anion, F(up), with concomitant changes of the degree of tilting of the proximal anion and of the degree of planarity of the carbocation, pyramidalization being observed at short distances from the proximal anion because of bonding interaction with it and at 2.7−2.8 Å because of attraction between methyl hydrogens and the distal anion. At 1.75−1.8 Å from the proximal anion, the cation was planar. Trying to locate a minimum, we relaxed slightly one of the optimization criteria (see the Methods section) and after many optimization cycles the geometry shown in Figure 5 and in the last column of Table 1 [**4(r.r.)**, C^+...F(up) = 1.655 Å], in which the cation is at coordinating distance from the anion, was obtained. A reduction in the size of the aggregate, L, from 12.658 Å to 12.258 Å also led to the movement of the cation toward one of the anions. After 50 cycles, the C^+...F(up) distance was 1.67 Å and the C^+...F(down) distance was 4.01 Å, therefore the optimization was terminated.

In the fourth stage of the calculations, starting with **3(f.c.o.)**, the Li...B...F angles were also allowed to vary (Figure ld), thus giving an aggregate with totally unrestricted orientation of the cation and anions between the planes containing the Li cations, **3(u.o.)**. Again, the optimization steps produced very small jumps of the anions in opposite directions, without any change in the geometry of the carbocation and negligible changes in energy. When optimization was completed (85 cycles, about 160 h) the cluster was about where it had started: the nearest anion ("up") was negligibly tilted (the Li...B axis at 88.68° to the Li plane from 90°, θ(Li...B−F) at 180.25° from 180.00°) and the farthest anion even less (90.05° and 179.84°, respectively). The angle between the C^+−C(up) bond and the axis of the cluster was 71.96°, the F(down)...C^+−C(up) angle was 112.04°, whereas d_{eq} and d'_{eq} were unchanged. The main geometrical parameters for the cation are shown in the fourth column of Table 1 [**3(u.o.)**, A]. They were the same as for **3(f.c.o.)** (the previous column of Table 1). An optimization of the **4(u.o.)** system was not attempted.

Finally, all the constraints in the cation *and* anion were removed, in three steps: (a) The optimization of the B−H bonds in the anion was performed by freezing the geometry of the cation in **3(u.o.)** and freeing all other parameters of the aggregate. (b) The new values for the B−H bond lengths and angles were next frozen and the five-ion system optimized. Some minor changes in the relative orientation of the ions in the aggregate resulted. Thus, for the nearest anion ("up"), the Li...B axis was at 89.67° from the Li plane and θ(Li...B−F) was 174.81°; for the farthest anion ("down"), the values were 91.06° and 174.54°. The level of tilting of the cation was slightly lower: the angle between the C^+−C(up) bond and the axis of the cluster was 73.44° and the angle F(down)...C^+−C(up) was 110.79°. The interionic distances, d_{eq} and d'_{eq}, were 2.99 and 3.10 Å, respectively. (c) All the geometric parameters in the aggregate (except, of course, for the distance between the planes containing the Li^+ ions) were allowed to optimize (several weeks were necessary). The geometry of the cation, shown in the fifth column of Table 1 (**3(u.o.)**, B) was the same as in the previous case. The ions moved slightly toward the perpendicular orientation: the Li^+(up)...B axis was at 88.42° from the Li plane and θ(Li...B−F) was 179.73°; for the farthest anion ("down"), the values were 90.05° and 179.80°. The angle between the C^+−C(up) bond and the axis of the cluster was 73.89° and the angle F(down)...C^+−C(up) was 110.34°. The interionic distances, d_{eq} and d'_{eq}, were 2.99 and 3.09 Å, respectively. The B−H bonds of both anions and the C^+−C bonds of the cation were nearly perfectly staggered ($\varphi = 60 \pm 0.25°$). Overall, the changes in the aggregate from the structure shown in Figure 4 were not discernible upon the examination of the perspective drawing or of the projections of the aggregate, therefore no new figure was generated.

Before closing, it is worthwhile to note that the calculations of the IR spectrum of the isolated *tert*-butyl cation for comparison with experimental spectra in solid matrices were conducted on the C_s conformation, even though the energy minimum was an asymmetric conformation close to the C_{3h} form.[10] Our calculations provide a justification for that choice.

Conclusion

The *tert*-butyl cation in an ionic aggregate mimicking the interactions in the crystal along the axis normal to the carbon plane adopts a conformation of the C_s type. The orientation of the cation is tilted relative to the line connecting the anions bracketing it. The degree of tilt is expected to be influenced, however, by the ions interacting laterally with the cation. The geometry of the cation shows little sensitivity to the degree of freedom of movement of ions within the aggregate. The calculations also indicate that at the interionic distances (d_{eq}, d'_{eq}) observed in the crystal of *tert*-butyl fluoroantimonate[14a] a conformation of the C_{3v} type is also stable.

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