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Ab Initio Calculations of the ^{13}C NMR Spectrum of 2-Propyl Cations in Ion Pairs[1]

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NMR chemical shift calculations (DFT-GIAO-B3LYP) on the 2-propyl cation in ion pairs were conducted for the C_s conformation (**2**) found earlier to be the energy minimum of the cation in the ion pair, as well as for the C_2 conformation (**1**), which is the energy minimum of the isolated cation. The level of the agreement between the isotropic chemical shift calculated with the dzvp basis set and the experiment increased with the increase in the calculated negative charge of the anion in the series $HLiH^-$, H_3BF^-, BF_4^-, AsF_6^-, and SbF_6^-. The calculated charge and the agreeement with experiment also increased with the basis set to tzp for HBF_3^-, tzp and tz2p for BF_4^-, and to tzp, tz2p, qz2p, and pz3d for HF_2^-. The value calculated for the isolated ion was off by 20 ppm and did not improve from the dzvp to the pz3d level, which indicates that even in solution the cations are mostly ion-paired or, even more likely, move in aggegates of varying sizes. From the two conformations of the cation in the ion pair, **2·X**$^-$ gave a better agreement at all levels, but **1·X**$^-$ differed by less than the combined uncertainty of theory and experiment. Two of the three principal components, δ_{11} and δ_{33}, were significantly off at all levels. Better to describe the system, a fragment of the ionic crystal was employed, placing two anions on the two sides of the cation and two to six LiF pairs at the remaining corners of a cubic structure, after the model of the crystal of the *tert*-butyl cation homologue. It was concluded that a good agreement of all parameters could be achieved for a placement of the LiF pairs between 2.8 Å and 3.8 Å from the center, but lacking the information about the crystal structure of the salt of the 2-propyl cation itself, the perfect match was not sought.

Introduction

Ab initio calculations of chemical shifts[3] of the tricoordinated carbon atoms in carbocations[4] have been used to corroborate the structures predicted by the same type of calculations.[5] For example, MP2/6-311G** calculations of five conformations of the 2-propyl cation indicated that the only energy minimum has a C_2 symmetry with C1 and C3 staggered; that is, it is chiral (**1**, Figure 1). Even though the barrier to methyl rotation via a C_s conformation was only 0.5 kcal/mol (MP4(FC)/6-311G**//MP2/6-31G** + ZPE), the latter had one imaginary frequency and thus was the transition structure for the process.[5c] Recalculation at the MP2/6-311++G** level[6] gave essentially the same geometry for the energy minimum **1** as in the earlier report,[5c] showing that the diffuse functions are not important in carbocations. The chemical shift for C2 in **1** calculated at the HF level (the IGLO method[3]) fitted the experiment, whereas those for three alternative conformations did not.[5c] The chemical shift for the C_s rotational transition structure was not calculated.

Following the successful preparation of the 2-propyl cation in a solid matrix at low temperature, the principal components of the chemical shift tensor for the cation were measured.[6] The calculated ^{13}C spectrum for the isolated cation **1** at the RHF level did not match the experiment. The same observation had been made in the study of the benzenium cation, which required GIAO-MP2 calculations for satisfactory results.[7] For ion **1**, inclusion of electron correlation (GIAO-MP2[8] or DFT-GIAO-B3LYP[9]) gave marginal fitting for the isotropic chemical shift, but the principal components showed large differences. To describe better the cation in the solid matrix, the calculations were repeated for the structure **1** paired with an anion, F_2H^- for GIAO-MP2 and SbF_6^- for DFT calculations. The calculations for this model matched the experimental isotropic shift and improved two of the principal components. The third was not affected, however, and only one of the other two was within the accepted margin of error from the experimental values.[6]

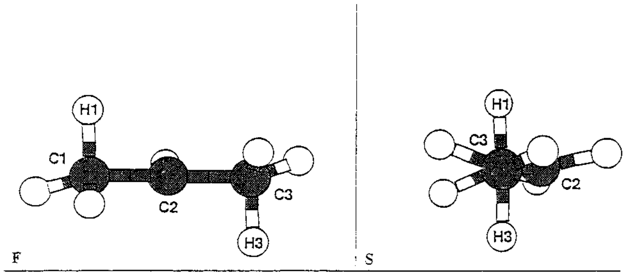

Figure 1. Chiral form of the 2-propyl cation: F, front view; S, side view.

As part of a more extensive study of structures of carbocations in ion pairs, it was shown that ion pairing changes the preferred conformation of the 2-propyl cation, such that the C_s form (C1, C3 eclipsed), **2**, is the energy minimum. The calculated geometry of the ion pair with trihydrofluoroborate as the anion is shown in three projections in Figure 2. Conformer **1** is about 3 kcal/mol [10] (MP2(FC)/6-31G*, MP2(FC)/6-31++G*, and MP2(FU)/ 6-311G**) higher in energy at an interionic distance (d) of 3.4 Å and relaxes into **2** upon optimization.[1] Both the conformation of the cation and the relative position of the cation

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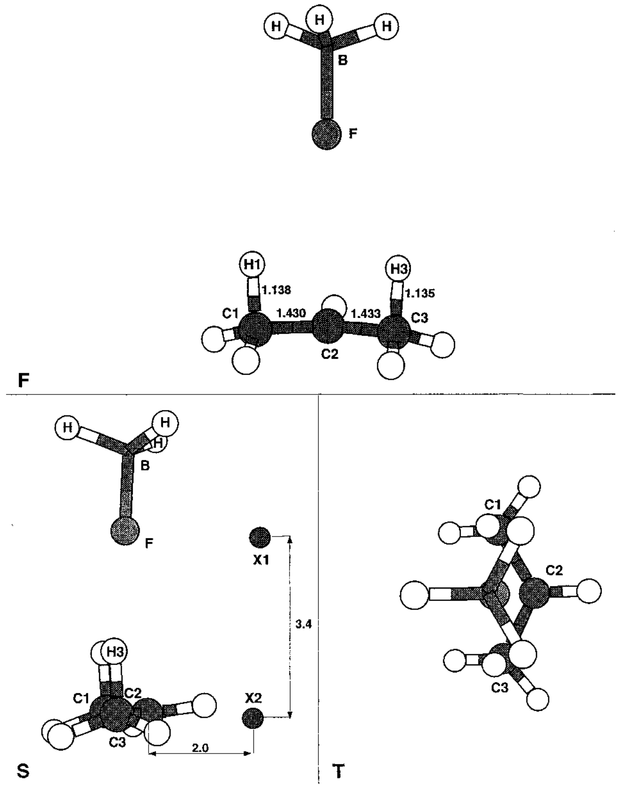

Figure 2. Minimum energy conformation (C_s symmetry) of the 2-propyl trihydrofluoroborate ion pair ($2{\cdot}FBH_3^-$) calculated at the MP2-(FU)/6-311G** level. (X1, X2: dummy atoms) F, S, as in Figure 1; T, top view.

and anion are determined more by the interionic electrostatic interactions than by the hyperconjugation in the carbocation. We decided, therefore, to repeat and expand the previous calculations of the chemical shift tensor, using the low-energy conformation, **2**, of the cation in the ion pair. Our calculations sought to examine the effect of several parameters upon the calculated chemical shift tensor: (1) the nature of the anion; (2) the basis set; (3) the cation conformation (**1** or **2**); and (4) the ionic environment in a simulated crystal. The goal of the study was to establish the level of model complexity at which the experimental values can be satisfactorily duplicated.

Computational Method

1. Principle. Considering that for more complex structures the RHF-level chemical shift calculations did not give satisfactory results,[6,7] we ran only calculations including electron correlation. As a matter of fact, HF calculations, even with large basis sets, can give erroneous predictions for structures as well.[11] Second, we chose to use the same basis set for all the atoms in the ion pair. The only exception was the tzp calculation of the assembly with six LiF added to simulate the field in the crystal, in which the Li cations were described by a "stripped" dzvp basis set (without d function).

2. Application. All NMR calculations were conducted with the GIAO (gauge-including atomic orbitals) approach at the B3LYP level,[3c,12] implemented in the Gaussian 94 series of programs.[13] All chemical shifts of C2 are deduced relative to methane calculated with the same basis set, using the MP2/6-311G** optimized geometry for methane in all cases. The values were then converted to the usual scale, with TMS as reference, by subtracting 2.3 ppm from each.[5c] The basis sets used in the calculations are described in Table 1.[14]

The interionic distance, *d*, defined as the distance between the fluorine atom of the anion and the C1C2C3 plane,[1] was varied between 2.6 and 3.0 Å (fixed in each run), on the basis of the value measured in the crystals of $Me_3C^+{\cdot}Sb_2F_{11}^-$ (2.93 Å).[15] Indeed, the "thickness" for stacking in the crystal of Me_2CH^+ and Me_3C^+ should be very similar. Most runs were conducted, however, with $d = 2.8$ Å, on the idea that the ion pair should be somewhat tighter for the smaller, secondary ion **2** than for its next homologue (tertiary).

The geometry of **2** was obtained by optimization at the MP2/6-311G** level of the ion pair with FBH_3^- as counterion at an interionic distance $d = 3.4$ Å This is the shortest distance that avoids complications due to the chemical reaction between ions in the ion pair (elimination). Examination of the cation geometries for values of *d* between 5 and 3.4 Å indicates that the geometry change to $d = 2.8$ Å should be unimportant. The position of the anion, in the bisector plane of the C1−C2−C3 angle and at a distance of 0.48 Å "inside" that angle from the line perpendicular to the C1C2C3 plane at C2, was obtained from the same optimization. The geometry of **1** was that of the isolated ion optimized with the MP2/6-311G** basis set; the anion was placed in the same position as for **2**.

The projections of the molecular geometry shown here were generated with the computer program XMOL.[16]

Results and Discussion

1. Effect of the Anion. In all the papers that reported preparation of the 2-propyl cation, the counterion was $Sb_nF_{5n+1}^-$. For the *tert*-butyl cation, however, there are enough data to conclude that the isotropic shift for C2 is not significantly influenced by the counterion or by the medium (solution or crystal), as shown in Table 2.[17] To test whether the calculations predict this feature, we employed six anions as counterions for **2**, with geometries (Table 3) obtained as indicated: LiH_2^- and FBH_3^- (optimization of the ion pairs with **2**),[1] BF_4^- (DFT-B3LYP/aug-cc-pVDZ optimization of the hydronium salt at an interionic distance of 2.5 Å),[18] HF_2^-, AsF_6^-, and SbF_6^- (literature geometries).[6,19]

The results of calculations at the dzvp level are shown in Table 4. It is immediately apparent that the values for the isotropic shift are all on the lower side of the experimental value, and they improve markedly with the increase in the size of the anion, the values for AsF_6^- and SbF_6^- being within the normal error range from the experiment and BF_4^- at the border of that range. The two anions containing negatively charged hydrogens, H_2Li^- and H_3BF^-, are not satisfactory at this level of calculation, although they might become adequate with a much larger basis set (see below). It is interesting to note that H_3BF^- was more suitable than H_2F^- for calculating the geometry and energy of carbocations in ion pairs; H_2F^- was more basic, interacting strongly with the cation, particularly with the positively charged hydrogens, capable of elimination.[1]

It can be noted, however, that the ordering of the anions is the same as that of the calculated values of their negative charge, shown in Table 5. Even though the absolute values calculated by the Mulliken method are rough approximations, the trend is real. For the same anion, the calculated anion charge increases with the basis set (also shown in Table 5); therefore the fit with the experiment for the ion pairs with lighter anions improves, as it will be shown below. The chemical shift depends, of course, upon the distribution of charges in the anion, its dipole, and quadrupole moments.

The calculated values for two of the principal components, δ_{11} and δ_{22}, follow the same trend as the isotropic shift (with

TABLE 1: Basis Sets

basis set	type of basis set	contraction		ref
		C, B, F	H	
dzvp	double-zeta, polarization	9s5p1d/3s2p1d[a]	5s/2s	14a
cc-pVDZ	correlation consistent polarized valence double zeta	9s4p1d/3s2p1d	4s1p/2s1p	14e
aug-cc-pVDZ	augmented cc-pVDZ	10s5p2d/4s3p2d	5s,2p/3s,2p	14e
tzp	triple-zeta, polarization	9s5p1d/5s3p1d	5s1p/3s1p	14b
tz2p	triple-zeta, double polarization[b]	11s6p3d/5s3p2d	5s3p/3s2p	14c
qz2p	quadruple-zeta, double polarization[c]	11s7p2d/6s4p2d	6s2p/3s2p	14d
pz3d	quadruple-zeta, double polarization[d]	13s8p3d/8s5p3d	8s3p/5s3p	14d[e]

[a] Other atoms: Li (in the anion LiH_2^-), 9s1p1d/3s1p1d (the d function was removed for the Li of LiF in the crystal model); As, 15s11p5d/5s4p2d; Sb, 18s14p9d/6s5p3d. [b] Polarization exponents (contraction coefficients) are C 1.3751 (0.357851), 0.4073 (0.75961); 0.34 (1.00); F 3.57 (0.357851), 1.0575 (0.759561); 0.7 (1.00); H 1.2203 (0.32564), 0.2839 (0.785386); 0.26 (1.00). [c] Polarization exponents are 1.39 and 0.46 for C, H; 2.42 and 0.81 for F. [d] Polarization exponents are 0.228, 0.649, 1.848 for C; 0.586, 1.725, 5.014 for F; 0.292, 0.838, 2.292 for H.[14e] [e] This is the basis set pz3d2f with the f functions removed.

TABLE 2: Experimental ^{13}C NMR Chemical Shifts for the *tert*-Butyl Cation

no.	anion[a]	system	chemical shifts		ref
			C^+	Me	
1	SbF_6^-	$R-Cl + SbF_5$ in SO_2FCl solution	330.0[b]	49.3[b]	17a
2	SbF_6^-	$R-Cl$ (0.93 M) $+ SbF_5$ (4.3 M) in SO_2FCl, at −78 °C	335.8[c]	47.8[c]	17b
3	SbF_6^-	$R-Cl + SbF_5 + SO_2FCl$ (1:4:20) at −78 °C	335.2[d]	47.5[d]	17c
4	TaF_6^-	$R-Cl + TaF_5 + HF$ (1:3:30), ≥0 °C	335.7[e]	46.5[e]	17d
5	SbF_6^-, $FSO_3SbF_5^-$(?)	ROH + (1:1) FSO_3H - SbF_5 in SO_2FCl (1 vol. per 1 vol. acid), −70 to −80 °C	335.7[f]	48.3[f]	17e
6	SbF_6-	$R-Cl + SbF_5$ (1:8.66) at −190 °C, solid	330[g]	48[g]	17f,g,h
7	$AlCl_4$-	RCl deposited on solid $AlCl_3$ (large excess), −40 °C, referenced from a previous scan of a standard sample	339	49	17i

[a] Dimeric or oligomeric structure likely. [b] $\delta(TMS) = 193.7 - \delta(CS_2)$. [c] $\delta(TMS) = 192.8 - \delta(CS_2)$. [d] Ext. TMS in $CFCl_3$ as standard. [e] Coaxial CD_2Cl_2 taken as 54.5 ppm, standard. [f] TMS in CD_2Cl_2 or AcMe-d_6 (coaxial) as standard. [g] CPMAS ^{13}C NMR, with decoupling of both ^{19}F and ^{1}H; TMS as standard.

TABLE 3: Geometrical Parameters of the Anions

anion	bond length	configuration	ref
LiH_2	Li−H = 1.755[a], 1.703[b]	linear	1
HF_2	H−F = 1.37	linear	6
BH_3F	B−H = 1.228; B−F = 1.505	tetrahedral	1
BF_4	B−F = 1.476[a], 1.403[b]	tetrahedral	*c*
AsF6	As−F = 1.71	octahedral	19
SbF6	Sb−F = 1.906	octahedral	6

[a] Proximal. [b] Distal. [c] See text.

TABLE 4: Influence of the Type of Anion for A^-·2 (d = 2.8 Å), at the dzvp Level[a]

anion	isotropic (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
LiH2	250	376	349	26
BH3F	270	450	335	26
HF2	290	497	346	27
BF4	307	515	381	24
AsF6	313	524	393	24
SbF6	317	531	396	22
experimental[b]	320	497	385	77

[a] Calculated from methane (the dzvp absolute shielding of methane is 187.26 ppm) and converted to the TMS scale by subtracting 2.3 ppm, ref 5c). [b] Ref 6.

TABLE 5: Calculated Mulliken Charges in Carbanions, MF_n^-, in $2{\cdot}MF_n^-$ Ion Pairs at d = 2.8 Å

anion	basis set	proximal F	equatorial F	distal F	M	total
H_3BF	dzvp	−0.15		0.01, 0.01, 0.03[a]	−0.49	−0.59
HF_2	dzvp	−0.43		−0.57	0.40	−0.60
BF_4	dzvp	−0.17		−0.24, −0.25, −0.25	0.17	−0.74
AsF_6	dzvp	−0.205	3(−0.305), −0.31	−0.30	0.94	−0.79
SbF_6	dzvp	−0.25	4(−0.34)	−0.33	1.11	−0.83
HF_2	tzp	−0.59		−0.62	0.39	−0.82
BF_4	tzp	−0.45		3(−0.36)	0.65	−0.88
BF_4	tz2p	−0.52		3(−0.45)	0.95	−0.92
HF_2	pz3d	−0.67		−0.66	0.46	−0.87

[a] Hydrogen atoms.

the exception of δ_{22} for LiH_2^-), but the numbers match the experiment for HF_2^- (δ_{11}) and for BF_4^- and AsF_6^- (δ_{22}); the calculations for pairs with heavier anions overshoot the mark. The values for δ_{33} are essentially unaffected by the anion; if anything, they might decrease slightly when the anion increases in size.

2. Effect of the Basis Set. It was reported that the DFT-NMR calculations were not better than the corresponding calculations at the HF level for the 6-31G* basis set, but they were definitely superior when larger basis sets were employed.[9a] In view of the poor match of the values for δ_{11} and, especially, δ_{33}, calculations with larger basis sets than dzvp were in order. It was also worthwhile checking the effect of the basis set change, in particular the convergence of numbers with the increase in basis set size. Because of the program limitations and unavailability of higher basis sets for As and Sb, we had to limit ourselves to an extensive study of $\mathbf{2}{\cdot}HF_2^-$ and a limited study of $\mathbf{2}{\cdot}BF_4^-$ and $\mathbf{2}{\cdot}FBH_3^-$ (Tables 6, 7, and 8, respectively). The isotropic shift value increased with the basis set and the level at which the experimental data are satisfactorily reproduced was lower for heavier anions. In line with the findings discussed in the previous subsection, these results indicate that the isotropic shift should not be a function of the anion, but matching results are secured when the calculated charge at the atom of the anion facing the cation reproduces the actual value. Thus, a well-performing model can be achieved with a smaller anion provided the basis set is large enough. Troublesome, however, is the observation that the values for the principal components δ_{11} and δ_{22} did not show a convergence toward the experimental value, but overshot it, whereas the third component, δ_{33}, was

TABLE 6: Calculated NMR Chemical Shift of 2 in $2{\cdot}HF_2^-$ Ion Pairs ($d = 2.8$ Å) as a Function of Basis Set[a]

basis set	isotropic (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
dzvp	290	497	346	27
tzp	306	514	372	33
tz2p	314	523	382	36
qz2p	317	530	386	34
pz3d	321	537	392	33
expt[b]	320	497	385	77

[a] See footnote *a* of Table 4; the absolute shieldings (in ppm) of methane are 191.56 (tzp), 194.82 (tz2p), 187.95 (qz2p), 187.43 (pz3d). [b] Ref 6.

TABLE 7: Calculated NMR Chemical Shift of 2 in $2{\cdot}BF_4^-$ Ion Pairs ($d = 2.8$ Å) as a Function of Basis Set[a]

basis set	isotropic (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
dzvp	307	515	381	24
tzp	315	524	389	32
tz2p	318	528	393	35
expt[b]	320	497	385	77

[a] See footnote *a* of Table 6. [b] See footnote *b* of Table 6.

TABLE 8: Calculated NMR Chemical Shift of 2 in $2{\cdot}FBH_3^-$ Ion Pairs ($d = 2.8$ Å) as a Function of Basis Set[a]

basis set	isotropic (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
dzvp	270	450	335	26
tzp	288	475	356	33
cc-pvdz[b]	266	441	329	29
aug-cc-pvdz[c]	274	452	341	30
expt[c]	320	497	385	77

[a] See footnote *a* of Table 6. [b] The absolute shielding of methane is 197.90 ppm. [c] The absolute shielding of methane is 198.60 ppm. [d] See footnote *b* of Table 6.

little affected by the basis set increase. These mismatches could come either from some deficiencies of the method of calculations or from an incorrect or incomplete modeling of the environment of the carbocation in the crystal; the latter possibility will be addressed in detail below.

Finally, introduction of diffuse functions (for $2{\cdot}FBH_3^-$) had no effect upon the principal components or the isotropic chemical shift of the carbocation (Table 8, entries 3 and 4). It was indicated that the split-valence basis sets are not satisfactory for the purpose at hand, anyway.[20]

3. Effect of the State of the Cation and Its Conformation. By state of the cation we understand here whether it is isolated or ion-paired. For the isolated cation, only conformation **1** was considered. The two conformations were considered in the ion pairs $\mathbf{1}{\cdot}HF_2^-$ and $\mathbf{2}{\cdot}HF_2^-$ (Table 9) and to a more limited extent, because of program limitations, in the pairs with a larger anion, $\mathbf{1}{\cdot}BF_4^-$ and $\mathbf{2}{\cdot}BF_4^-$ (Table 10).

It is seen from the data listed in Table 9 that the calculated values for the isolated cation **1** do not match the experimental results (isotropic shift in solution, isotropic shift and principal components in the solid), and they do not change systematically or significantly with the basis set (from tzp to pz3d). These findings indicate that even in the superacid solution the 2-propyl cations are ion-paired, in agreement with the representation offered before.[1] On the other hand, the values calculated for the conformers **1** and **2** ion-paired with either anion (Tables 9 and 10) do not differ from each other by more than the combined margin of error at any basis set level. Both conformations satisfactorily reproduce the experimental value of the isotropic shift, meaning that we cannot distinguish between them on the basis of these calculations (even though in each case the value for **2** was closer to the experimental number than the value for **1**). This good correlation results, however, from the compensation of the downfield deviation of δ_{11} with the upfield deviation of δ_{33}. The values for δ_{22} in the ion pairs calculated with basis sets larger than tzp are reasonably close to the experimental values for both conformations.

Effect of Other Ions in the Crystal on the Carbocation in the Ion Pair. It is clear from the results discussed above and it was indicated before[6] that for a better agreement between theory and experiment it is necessary to consider the full tridimensional environment of the carbocation. This environment is not known for the 2-propyl cation salt;[6] therefore we modeled it after the crystal structure of the *tert*-butyl fluoroantimonate (anion: $Sb_2F_{11}^-$). The latter, elucidated by single-crystal X-ray diffraction, "looks like a distorted CsCl lattice".[15] The cationic carbon is faced by two anions, the closest C⋯F distances being 2.93 and 3.11 Å, respectively. In addition, this "sandwich" structure is surrounded by six anions located at the other six apexes of a distorted cube with the sp^2 carbon at the center, such that the smallest F⋯H distances (one for each surrounding anion) vary between 2.29 and 2.45 Å.[15]

In our model of the crystal, two HF_2^- anions are placed on the diagonal of a cube, which is perpendicular to the plane of the cation **2**. The sp^2 carbon is off-diagonal, in agreement with the calculated geometry of the 2-propyl cation ion pairs.[1] The nominal counterion is at 2.8 Å and the other anion is at 3.0 Å from the plane of the cation. The distances from the anions to C2 are slightly longer, but still somewhat shorter than the distances in the tertiary homologue, which should be less tightly packed. Six LiF "molecules" (ion pairs) are placed in the other corners of the cube, oriented toward the center of the cube, with the fluoride ions toward the central cation. The "proto-crystal" thus obtained is represented in three projections in Figures 3 (front), 4 (side), and 5 (top). The distances from the fluoride anions of the equatorial LiF pairs to the center of the aggregate shown in the figures were chosen such as to ensure that the shortest F⋯H distance for each of them is around 2.5 Å, but these distances were varied in the calculations.

To determine the influence of various components of the field on the chemical shift tensor for C2, we ran calculations in which two LiF (four equatorial positions empty), three LiF (three

TABLE 9: Effect of the State of the Cation (Isolated or Ion-paired) and Its Conformation ($\mathbf{1}{\cdot}HF_2^-$ or $\mathbf{2}{\cdot}HF_2^-$ at $d = 2.8$ Å) on the Calculated ^{13}C NMR Spectrum[a]

	cation											
	1				$\mathbf{2}^+{\cdot}HF_2^-$				$\mathbf{1}^+{\cdot}HF_2^-$			
basis set	iso.	δ_{11}	δ_{22}	δ_{33}	iso.	δ_{11}	δ_{22}	δ_{33}	iso.	δ_{11}	δ_{22}	δ_{33}
tzp	342	552	439	34	306	514	372	33	294	487	360	35
tz2p	333	546	417	37	314	523	382	36	304	502	372	38
qz2p	336	552	422	34	317	530	386	34	308	510	378	35
pz3d	340	560	427	34	321	537	392	33	313	519	384	34
expt[b]	320	497	385	77	320	497	385	77	320	497	385	77

[a] See footnote *a* of Table 6. [b] See footnote *b* of Table 6.

TABLE 10: Effect of the State of the Cation (Isolated or Ion-Paired) and Its Conformation ($1\cdot BF_4^-$ or $2\cdot BF_4^-$ at $d = 2.8$ Å) on the Calculated ^{13}C NMR Spectrum[a]

	cation											
	1				$2^+\cdot BF_2^-$				$1^+\cdot BF_2^-$			
basis set	iso.	δ_{11}	δ_{22}	δ_{33}	iso.	δ_{11}	δ_{22}	δ_{33}	iso.	δ_{11}	δ_{22}	δ_{33}
tzp	342	552	439	34	315	524	389	32	329	538	416	34
tz2p	333	546	417	37	318	528	393	35	324	535	401	37
expt[a]	320	497	385	77	320	497	385	77	320	497	385	77

[a] See footnote *a* of Table 6. [b] See footnote *b* of Table 6.

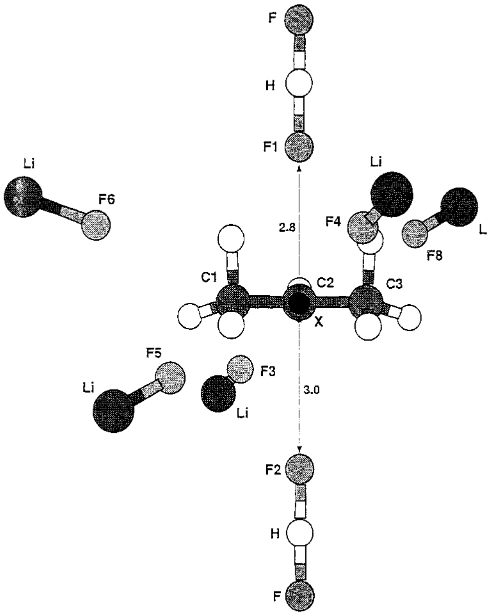

Figure 3. Front view of the aggregate of the $[HF_2^-\cdot \mathbf{2}\cdot HF_2^-]$ triple ion with six LiF in a cubic arrangement.

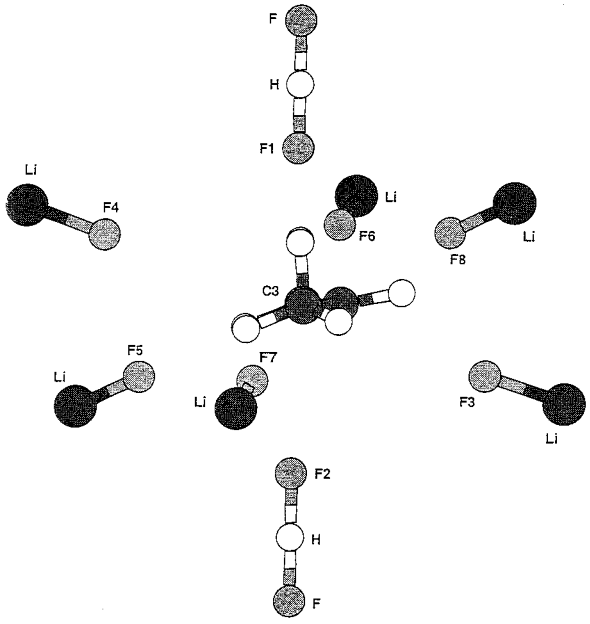

Figure 4. Side view of the aggregate of the $[HF_2^-\cdot \mathbf{2}\cdot F_2^-]$ triple ion with six LiF in a cubic arrangement.

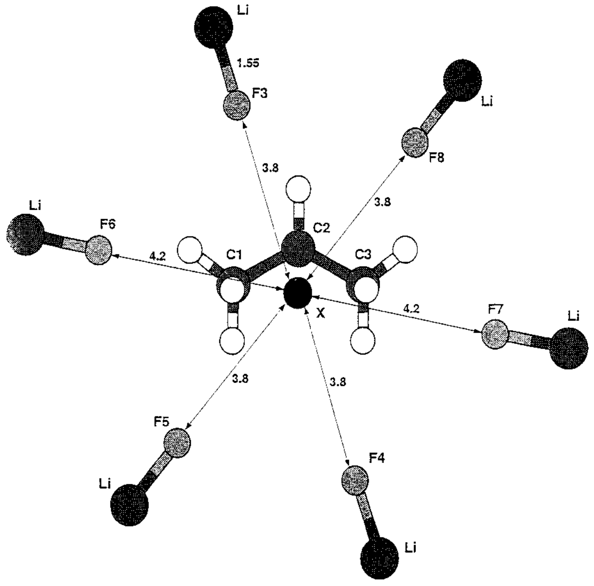

Figure 5. Top view of the aggregate of the $[HF_2^-\cdot \mathbf{2}\cdot HF_2^-]$ triple ion with six LiF in a cubic arrangement.

equatorial positions empty), and six LiF surrounded the central triple ion. It was particularly interesting to see what component of the electrical field in the crystal influences the value of the principal component normal to the plane of the carbon atoms, δ_{33}, shown above to be rather insensitive to the counterion and basis set. Finally, another Li cation was placed on the other side of the HF_2^- ion farthest from the carbocation, in two runs. With one exception, all the calculations in this cycle were conducted with the dzvp basis set. The results are presented in Table 11; for easier comparison, the values for the ion pair from Table 6 and the experimental values are given here again (entries 1 and 14, respectively).

We undertook first the NMR calculation for the cation in the triple ion $\mathbf{2}\cdot(HF_2^-)_2$. As shown in entry 2 of Table 11, the second anion caused an upfield correction of δ_{11} and δ_{22}, but had no influence on δ_{33}. Addition of a Li cation at 2.8 Å on the other side of the farthest HF_2^- (entry 3) restored δ_{11} and δ_{22} close to the original values in the ion pair (perhaps slightly beyond), but δ_{33} stayed unchanged.

Next, we considered the case of the triple ion together with two LiF pairs at close distance from the cations (2.8 Å from the center). The first set included LiF3 and LiF8, which are closest to the H bonded to C2. These two LiF increase δ_{11} and δ_{22} and do not affect δ_{33} (entry 4 compared with entry 2). When the included pairs were LiF5 and LiF8 (one close to H−C2, the other in the opposite corner of the cube, entry 5 in Table 11), δ_{11} was slightly more affected and δ_{22} significantly less than in the previous case. If the effects are independent and additive, one can conclude that δ_{22} is significantly affected by LiF3 and LiF8, but not at all by LiF4 and LiF5, δ_{11} is moderately affected by all these, and δ_{33} not at all.

When the included pairs were LiF6 and LiF7 (entry 6, compared with entry 2), δ_{33} shifted downfield by 30 ppm, identifying, at last, a crystal parameter that has an effect on this principal component. In addition, δ_{11} showed a small to moderate shift downfield and δ_{22} moved significantly *upfield*. Increasing the distances of F6 and F7 from the center of the

TABLE 11: Influence of the Medium on the Chemical Shift of 2 (C_s Configuration of the 2-Propyl Cation) at the dzvp Level[a]

no.	anion	isotropic (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)
1	HF_2 (2.8 Å)[b]	290	497	346	27
2	2 HF_2 (2.8 and 3.0 Å)	277	470	332	29
3	2 HF_2 (2.8 Å and 3.0 Å) + Li^+ (2.8 Å from the farthest HF_2)	295	504	355	28
	2 LiF + 2HF_2 (2.8 and 3.0 Å)				
4	2 HF_2 + 2 LiF F3, F8 (2.8 Å)	297	485	379	26
5	2 HF_2 + 2 LiF F5, F8 (2.8 Å)	293	491	358	30
6	2 HF_2 + 2 LiF F6, F7 (2.8 Å)	279	489	289	59
7	2 HF_2 + 2 LiF F6, F7 (3.8 Å)	289	498	337	31
	3LiF + 2HF_2 (2.8 and 3.0 Å)				
8	2 HF_2 + 3 LiF F4, F7, F8 (2.8 Å)	307	514	339	70
9	2 HF_2 + 3 LiF F4 (3.2 Å), F7 (3.0 Å), F8 (3.5 Å)	300	522	341	38
	6LiF + 2HF_2 (2.8 and 3.0 Å)				
10	2 HF_2 + 6 LiF (2.8 Å)	327	448	379	154
11	2 HF_2 + 6LiF (3.5 Å)[c]	315	521	390	35
12	2 HF_2 + 6 LiF (3.8 Å)[d]	310	517	382	31
13	2 HF_2 + 6LiF (3.8 Å)[d] + Li^+ (2.9 Å from the farthest HF_2)	316	528	396	23
14	2 HF_2 + 6 LiF (3.8 Å)[e]	316	521	388	37
15	expt[f]	320	497	385	77

[a] See footnote *a* of Table 4. [b] All distances are measured from the center of the cube, X, cf. Figures 3 and 5. [c] $d(X-F_i) = 3.5$, $i \neq 6, 7$; $d(X-F_i) = 3.8$, $i = 6, 7$. [d] $d(X-F_i) = 3.8$, $i \neq 6, 7$; $d(X-F_i) = 4.2$, $i = 6, 7$. [e] Calculation conducted at the tzp level (see footnote *a* of Table 6); $d(X-F_i) = 3.8$, $i \neq 6, 7$; $d(X-F_i) = 4.2$, $i = 6, 7$. [f] See footnote *b* of Table 6.

aggregate, from 2.8 Å to a more realistic 3.8 Å, eliminated, however, the effects upon δ_{22} and δ_{33}. This finding was unsettling, at first, until we realized that the charges in the LiF dipole are underestimated at this level of calculation, as already established in the study of the counterion discussed above (Table 5). Mulliken analysis gives the average charge at F of the LiF pairs as −0.31, to be contrasted with a value of −0.84 determined experimentally in the LiF crystal.[21] Even though Mulliken atomic charges are only crude approximations, it seems clear that the calculations underestimated the charges. Crowding the LiF pairs at only 2.8 Å from the center is a rough way to compensate for this underestimation.

Inclusion of three LiF at 2.8 Å from the center, one of each orientation (LiF4, LiF7, and LiF8) at one side of the cation, in the calculation gave the results listed in Table 11, entry 8, which match satisfactorily the experimental values for two out of three principal components, δ_{11} and δ_{33} (the uncertainty in the experimental values is 6 ppm).[6] If the effects of the LiF pairs were independent and additive, we could predict from entries 4−6 values of 503 and 338 for δ_{11} and δ_{22}, both in agreement with the numbers in entry 8, but only 45 for δ_{33}, much less than the value in entry 8. Therefore the additivity is, at best, limited. How difficult it is to model the right environment for the ion pair is shown by entry 9, in which the distances of the three LiF pairs have been increased to 3.2 Å (LiF4), 3.0 Å (LiF7), and 3.5 Å (LiF8). As a result, δ_{11} increased somewhat, δ_{22} was not affected, and δ_{33} decreased markedly (Table 11, entry 9 compared with entry 8).

When all the six available corners of the cube were filled with six LiF pairs at 2.8 Å, the changes in the principal components, shown by entry 10 compared with entry 2, were dramatic: δ_{11} deviated from the experiment by 49 ppm *upfield* and δ_{33} by 77 ppm *downfield*. Both δ_{22} and the average, δ_{iso}, were in agreement with the experiment. Moving away the LiF pairs, first to 3.5 Å (LiF3, LiF4, LiF5, and LiF8) and 3.8 Å (LiF6 and LiF7), as in entry 11, then to 3.8 Å (LiF3, LiF4, LiF5, and LiF8) and 4.2 Å (LiF6 and LiF7), as in entry 12, moved both δ_{11} and δ_{33} in the opposite direction, on the other side of the correct values. Adding a lithium cation in the same position as in entry 3, to the aggregate of entry 12, made things slightly worse (entry 13). The values for δ_{22} and δ_{iso} stayed correct in entries 10−13. Finally, repeating the calculation of entry 12 at the tzp basis set (Table 11, entry 14) improved somewhat the result for δ_{33}, but not for δ_{11}, whereas the values for δ_{22} and δ_{iso} stayed within the correct range.

It thus appears that there is a placement of the LiF pairs between 2.8 and 3.5 Å from the center (not necessarily all at the same distance) for which the calculated values of all three principal components and their average will be within the combined error of calculation and experiment. Also, increasing the basis set beyond the level of entry 14 might have the same effect. We did not go farther, however, because the final comparison of theory and experiment requires an exact description, rather than an approximation, of the environment of the ion pair of **2** in the crystal. We can reach, however, some valid conclusions from our study.

First, the sensitivity of the isotropic shift, δ_{iso}, to the ion pairing (Table 9) and its relative insensitivity to the surrounding charges and dipoles in the crystal (Table 11, entries 10−14) suggest that the ion pair moves in solution surrounded by a variable aggregate of other ion pairs. Calculations on the isolated ion at the highest level attempted (pz3d, apparently converged) did not match the experimental result. Next, the necessary requirement for the theoretical evaluation of the principal components is the right description of the charges of the surrounding ions and dipoles. The cubic crystal symmetry is most likely correct, but experimental verification of it should be most useful in checking the calculations. Each principal component of the chemical shift tensor seems to be less influenced by the dipoles (of ion pairs) nearly parallel to itself than by the dipoles at a wider angle.

The isotropic chemical shift appears to converge toward the experimental value with the increase in basis set, irrespective of the anion taken in the ion pair, but the values for the principal components overshoot the mark in some cases (Tables 6−8). It is not clear whether this nonconvergence represents a problem of the method of calculation or it should be ascribed to the approximate description of the ionic environment of the ion pair. As discussed, it is likely that on average the cation is present in solution in an aggregate of ions larger than the ion pair. Also, only the isotropic shift is available for solution, anyway.

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