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Crystal Structure of the *tert*-Butyl Cation

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Abstract: The structure of the *tert*-butyl cation (**1**) could be determined by an X-ray crystal structure analysis of its $Sb_2F_{11}^-$ salt at −80 °C ($P2_1$, $a = 6.123(2)$ Å, $b = 13.758(4)$ Å, $c = 7.614(4)$ Å, $\beta = 100.67(3)°$; $R = 0.029$, $R_w = 0.029$). Suitable crystals of $\mathbf{1}\cdot Sb_2F_{11}$ were obtained only from a methylene chloride solution of the corresponding *tert*-pentyl salt by slow decomposition. The cation is planar within our limits of accuracy, the C^+–C bonds have an average length of 1.442(5) Å, and the C–C^+–C bond angles are 120(1)°. These results agree with the nutation NMR results of Yannoni, Myhre, et al. and recent ab initio results of Schleyer et al. In the crystal, the cation is surrounded by fluorine atoms from a total of eight counterions. The packing motif of cations and anions is similar to that of CsCl. Several other simple tertiary alkyl salts gave no suitable crystals for an X-ray structure determination.

The simple alkyl cations have been the subject of many structural investigations, especially of Olah[1–5] (NMR spectroscopy in solution). Saunders studied the *sec*-butyl cation by dynamic NMR techniques.[6] Recently, the molecular geometry parameters of the simplest tertiary alkyl cation, the *tert*-butyl cation (**1**), were determined by Yannoni, Myhre, et al. with nutation NMR spectroscopy of multiply labeled isotopomers of **1** in SbF_5 matrices.[7] (See Chart I.) They found a C–C bond length of about 1.46 Å and C–C–C angles of 120°. Schleyer et al. carried out ab initio calculations and confirmed these results.[8] Although the preparation of crystalline tertiary alkyl salts was already described by Olah et al.[1,2] in 1967, attempts to determine the crystal structure of alkyl salts have failed up to now. This is very remarkable because the crystal structures of less stable carbocations like substituted norbornyl[9] and norbornenyl[10] cations could be obtained already some years ago. We describe in the present report the difficulties of growing suitable crystals of alkyl salts and how they could be overcome, leading to the crystal structure of $\mathbf{1}\cdot Sb_2F_{11}$.

Results

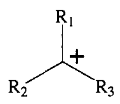
The most suitable counterions for our purposes are SbF_6^- and $Sb_2F_{11}^-$ because of their low nucleophilicity and their simple preparation. The corresponding salts were obtained in our studies by reaction of an alkyl fluoride (prepared according to reaction 1 from commercially available alcohols) with 1 or 2 equiv of SbF_5 (reactions 2 and 3) or by reaction of an alkyl chloride (prepared according to reaction 4) with $HSbF_6$ (reaction 5; all methods were often applied by Olah et al.[11]). (Scheme I). Another possibility is the reaction with $SbCl_5$ according to reaction 6. We tried to crystallize a wide variety of *tert*-alkyl salts (see Table I), but finally, only the *tert*-butyl cation (**1**) gave suitable crystals.

Table I. Crystallinity of Some Alkyl Fluoroantimonates(V) Obtained by Recrystallization from Methylene Chloride

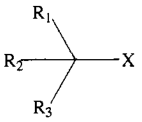
precursor		salt obtained by reaction	
alcohol	fluoride[a]	(2)	(3)
2-OH	**2**-F	very thin and twinned plates[b]	stacks of thin plates with roundish shape[b]
3-OH	**3**-F	dendritic growth	oil
4-OH	**4**-F	intergrown bunches	powder
5-OH	**5**-F	intergrown bunches and thin plates	plates[b,c]
6-OH	**6**-F + **7**-F (1:1 mixture)	powder	very small crystals

[a] Synthesized from the corresponding alcohol according to reaction 1. [b] Photographs of the crystals in the supplementary material. [c] A crystal has been measured, but the structure is disordered (see Table II).

Chart I



n



n-X

n =	**1**	**2**	**3**	**4**	**5**	**6**	**7**
R_1 =	Me	Et	Et	Et	Me	Me	Me
R_2 =	Me	Me	Et	Et	Me	Et	Me
R_3 =	Me	Me	Me	Et	*i*-Pr	*i*-Pr	*sec*-Bu

Scheme I

$$\text{R-OH} \xrightarrow{\text{HF/pyridine}} \text{R-F} \qquad (1)$$

$$\text{R-F} + SbF_5 \longrightarrow R^+\ SbF_6^- \qquad (2)$$

$$\text{R-F} + 2\,SbF_5 \longrightarrow R^+\ Sb_2F_{11}^- \qquad (3)$$

$$\text{R-OH} \xrightarrow{\text{HCl}} \text{R-Cl} \qquad (4)$$

$$\text{R-Cl} + HSbF_6 \longrightarrow R^+\ SbF_6^- \qquad (5)$$

$$\text{R-Cl} + SbCl_5 \longrightarrow R^+\ SbCl_6^- \qquad (6)$$

$$\mathbf{2}\text{-F} + 2\,SbF_5 \longrightarrow \mathbf{2}\cdot Sb_2F_{11} \rightleftarrows \mathbf{1}\cdot Sb_2F_{11} \qquad (7)$$

$$\mathbf{1}\text{-Cl} + HSbF_6 + SbF_5 \longrightarrow \mathbf{1}\cdot Sb_2F_{11} \qquad (8)$$

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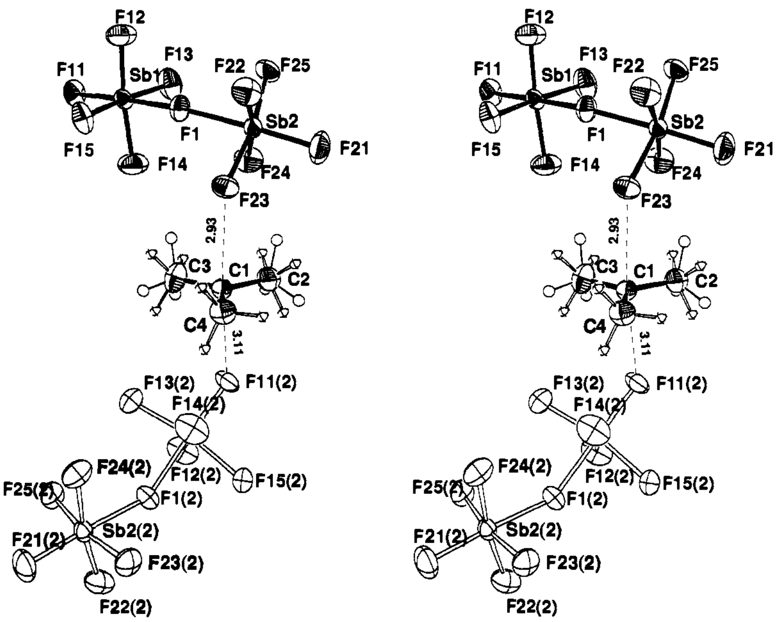


Figure 1. ORTEP stereo drawing of the crystal structure of **1**·Sb_2F_{11}. The atoms of the symmetry-related anion are drawn as white ellipsoids, and their labels are followed by the symmetry operation number (see caption for Figure 2). The displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are represented by spheres with a radius of 0.1 Å. For C2 and C3, two partially populated sets of methyl hydrogens were refined (populations: 0.75/0.25 and 0.5/0.5). Distances are given in angstroms.

They were obtained from *tert*-pentyl fluoride by reaction with 2 equiv of SbF_5 and subsequent (in our first experiments accidental) thermal decomposition of the initially formed *tert*-pentyl cation (**2**) to **1** during the preparation of the raw salt and its recrystallization from methylene chloride (reaction 7). Although the crystals obtained in our studies were generally of poor quality, this reaction gave some good-looking crystals. Probably the crystals from this reaction were a mixture of different alkyl salts; the low-temperature ^1H NMR spectrum of a SO_2 solution obtained by dissolving these crystals shows a strong singlet from **1** at δ = 4.24 ppm as well as other unidentified signals (see supplementary material, Figure S12a). All suitable-looking crystals were twinned, but the twin composition plane could be found in most cases by slow turning of the crystals under polarized light at −25 °C due to their optical anisotropy. A crystal fragment, which did not contain such a plane, was obtained by cutting a twin. The mounting, measurement, and crystal structure determination are described in the Experimental Section; the final results are shown in Figure 1 and in Table II. The *tert*-butyl cation is planar within the limits of accuracy (distance of C1 from the plane through C2, C3, C4: 0.007(5) Å); its C–C bonds have an average length of 1.442(5) Å, and the C–C–C bond angles are 120(1)°, i.e. the C skeleton has D_{3h} symmetry. The individual C–C bonds have the lengths C1–C2 = 1.445(9) Å, C1–C3 = 1.44(1) Å, and C1–C4 = 1.442(8) Å, and the angles are C2–C1–C3 = 121.2(6)°, C2–C1–C4 = 117.9(5)°, and C3–C1–C4 = 120.9(5)°, but we do not consider the angle differences as significant despite the relatively good R values (R = 0.029, R_w = 0.029) because of the presence of two heavy atoms in the asymmetric unit. The hydrogen atoms were difficult to localize experimentally. For C2 and C3, two partially populated, internally rigid sets of hydrogen atoms (each set is twisted by 60° against the second set) were refined with the torsion angle as the only variable. For C4, one set of hydrogen atoms was refined.

Table II. Data of the Measured Crystals

	1·Sb_2F_{11}	prod. of reactn 5, R–C*l* = **1**-C*l*	prod. of reactn 3, R–F = **5**-F
space group (no.)	$P2_1$ (4)	$I23$ (197) or $I2_13$ (199) or $Im\bar{3}$ (204)	$P2_1/c$ (14)
a (Å)	6.123(2)	10.092(2)	7.753(2)
b (Å)	13.758(4)	10.092(2)	9.038(3)
c (Å)	7.614(4)	10.092(2)	10.318(3)
α (deg)	90	90	90
β (deg)	100.67(3)	90	107.93(2)
γ (deg)	90	90	90
V (Å^3)	630.3(4)	1027.9(3)	687.8(3)
measuring temp (°C)	−80	−80	−110
d_x (g·cm^{-3})	2.685	1.892^a	2.596^b
θ_{max} (deg)	35	40	25
no. of measd rflns	4256	1847	1453
no. of unique rflns with $I > n\sigma_I$; n	2677; 3	386; 3	739; 2
no. of params	154		
w	$1/\sigma_F^2$		
R	0.029		
R_w	0.029		
μ (cm^{-1})	44.3	27.3^a	40.6^b

^{a} Assuming that the product is **1**·SbF_6 and Z = 4. ^{b} Assuming that the product is **5**·Sb_2F_{11} and Z = 2.

The final difference density shows that the highest residual peak in the neighborhood of the cation, which could indicate an additional atomic position, has a maximal density of 0.489 e/Å^3 (located at a distance of 1.60 Å from C4, the angle peak–C4–C1 is 128°). The Sb atoms are surrounded by pairs of difference density peaks and holes of up to 1.67 and −1.82 e/Å^3, but these peaks must be considered as the result of the inadequacy of the Gaussian probability density functions for the heavy atoms.[10] Stereodiagrams of the location of the extremal values of the final difference density show no unusual features (the plots are found in the supplementary material in Figure S11). An estimation of the atomic charges from the difference density yielded for the cation a charge of +2.0(5) and for the anion −2.0(6); these values are not significantly different from the expected values of +1 and −1, and because there is no experimental or theoretical evidence for the presence of doubly charged ions, we consider these values as too high.

In the crystal, the cationic carbon atom C1 is surrounded by two fluorine atoms (F23 and F11(2), see Figure 1) from counterions. Both contacts are shorter than the sum of the van der Waals radii[12] of C and F (3.17 Å; C1···F23 = 2.928(6) Å, C1···F11(2) = 3.113(7) Å). Beside these C^+···F contacts, the cation is rather closely packed between F atoms from its eight nearest counterions (see Figure 2). Referring to C1 as the center of the cation and to F1 as the approximate center of the anion,

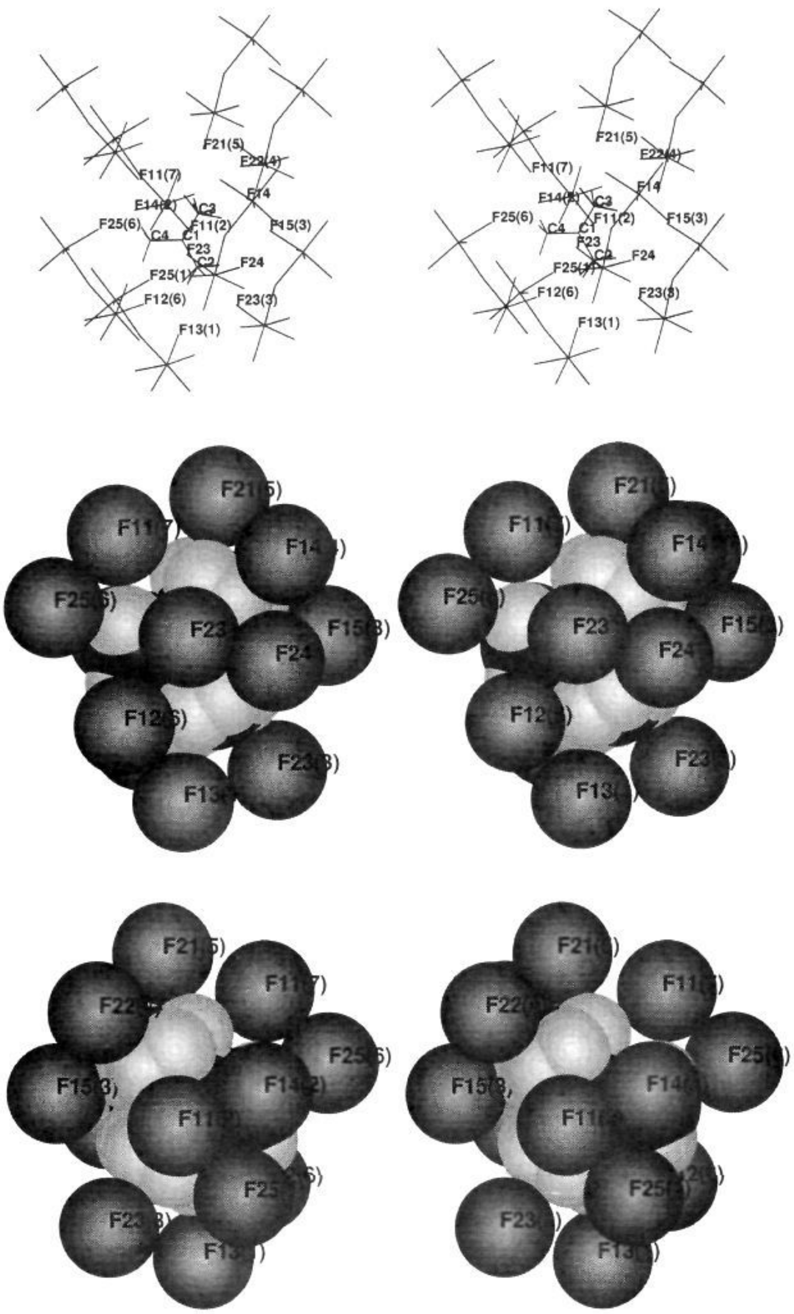


Figure 2. Stereo diagram of the surrounding of **1** in the crystal structure of **1**·Sb_2F_{11}. The symmetry operations (given in parentheses) are as follows: (1) $-x + 1, y + 1/2, -z + 1$; (2) $-x + 1, y + 1/2, -z + 2$; (3) $x + 1, y, z$; (4) $x + 1, y, z + 1$; (5) $x, y, z + 1$; (6) $-x, y + 1/2, -z + 1$; (7) $-x, y + 1/2, -z + 2$. Top: wire frame diagram of the cation **1** with its eight nearest counterions (the fluorine atoms with van der Waals contact to **1** are labeled). Middle: space-filling representation of the cation **1** and the fluorine atoms of the nearest counterions with van der Waals contacts (view direction as above). Bottom: the atom cluster shown in the middle diagram rotated by 180° around a vertical axis. H···F distances less than 2.47 Å (= sum of the van der Waals radii minus 0.2 Å) after normalization of the C–H bonds to 1.08 Å: H25···F24 = 2.43, H35···F14 = 2.45, H26···F13(1) = 2.44, H43···F14(2) = 2.29, H31···F15(3) = 2.37, H42···F25(6) = 2.40 Å.

the packing pattern of **1**·Sb_2F_{11} looks like a distorted CsCl lattice (see Figure 3).

We tried also to obtain suitable crystals of **1**·Sb_2F_{11} by using **1**-Cl as the direct precursor according to reaction 8, but the thus grown crystals were, in our hands, hopelessly twinned or suffering from other defects. Although these crystals had shapes comparable to those obtained by reaction 7 and although they also showed the characteristic twin composition planes, we never obtained a unit cell from them (photographs of crystals from both reactions are shown in the supplementary material in Figure S1). We also attempted to prepare crystalline **1**·SbF_6 from **1**-Cl according to reaction 5 and obtained optically isotropic cubes by recrystallization of the raw product from SO_2, but the solution of the crystal structure was not successful in any of the three space groups compatible with the systematic extinctions perhaps due to orientational disorder of cations and anions, although the crystal diffracted very well (up to 40° with Mo Kα radiation, see Table II). All solutions led to eight heavy atom positions in the unit cell (all reflections of the type $h = 2n$ and $k = 2n$ and $l = 2n$ were very strong, which indicates that the electron density can be approximately described by a primitive cubic cell with a unit cell edge length of $a/2$). Because the unit cell can contain only four ion pairs ($Z = 8$ leads to a density of 3.8 g·cm^{-3}), we assume on the basis of packing simulations that the solutions describe an average of several shifted and rotated unit cells.

The decomposition of the higher alkyl cations to **1** has already been observed by Olah,[2] but under his conditions, this reaction took place at higher temperatures than in our experiments.

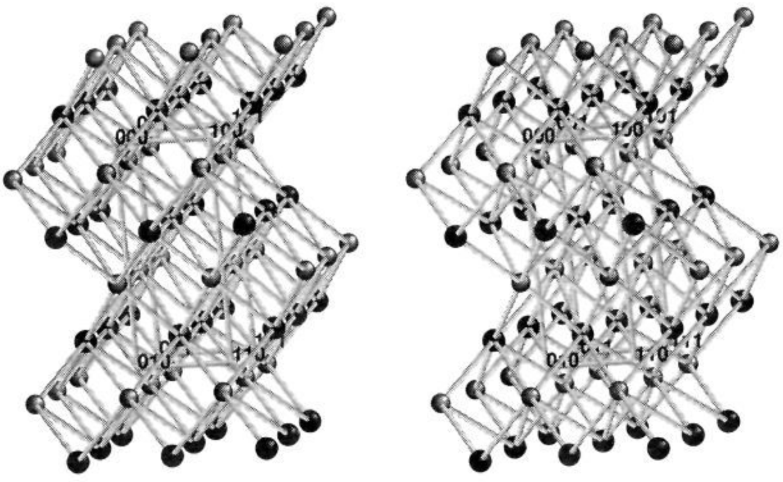
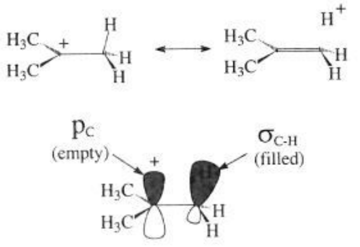


Figure 3. Stereo diagram of the spatial arrangement of C1 (center of the cation; dark spheres) and F1 (approximate center of the anion; light spheres) in the crystal structure of $\mathbf{1}\cdot Sb_2F_{11}$. Each ion (represented by its central atom) is connected to its eight nearest counterions by rods. The corners of the unit cell are labeled with their crystal coordinates.

Chart II. C–H Hyperconjugation in the VB (Top) and MO (Bottom) Descriptions



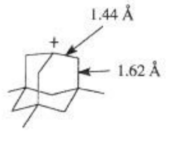
Therefore, we tried to grow crystals containing the undecomposed *tert*-pentyl cation ($\mathbf{2}\cdot SbF_6$; reaction 2) by keeping the temperature as low as possible during the syntheses and crystallization. We obtained thin and twinned plates, but a ^1H NMR spectrum recorded at low temperature after dissolving these crystals in CD_2Cl_2 shows the presence of **1**, **2**, and other alkyl cations (see supplementary material, Figure S12b). Obviously, the decomposition of **2** had already taken place to a considerable extent even under these gentle conditions.

Finally, we synthesized $\mathbf{5}\cdot Sb_2F_{11}$ according to reaction 3, but the resulting crystals did not diffract very well (see Table II), and a satisfactory solution could not be obtained probably due to disorder. Alkyl hexachloroantimonates like $\mathbf{2}\cdot SbCl_6$ were not stable under our crystallization conditions and led only to crystalline $SbCl_3$.[13]

Discussion

The experimental structure of **1** shows a 3-fold C–C shortening of about 0.061(5) Å (a normal C_{sp^2}–CH_3 bond has a length of 1.503 Å;[14] for **1**, the average C–C length is 1.442(5) Å) and thus agrees with the expectation for a charge delocalization from Cl into the C–H σ bonds (C–H hyperconjugation;[8,15] see Chart II), which leads to partial C–C π bonds. We have no experimental information about a corresponding C–H lengthening, because all hydrogens could only be refined with constraints and were probably disordered. For the same reason, we cannot make any statement about the conformation of the methyl groups. The same C^+–C shortening as in **1** was also observed in the crystal structure of the 3,5,7-trimethyl-1-adamantyl cation[16] (**8**) and to a reduced amount in the C2–C21 bond of the norbornyl cation[9] **9** (see Chart III).

Chart III



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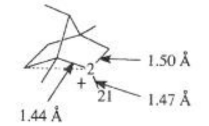

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The packing of **1** in the crystal reflects its chemical reactivity: the two close $C^+\cdots F$ contacts (see Figure 1) may be seen as partial electrophile–nucleophile interactions as in many other carbocation structures,[10] and the H···F contacts may be seen as acid–base interactions (hydrogen bonds).[17] Both seem to stabilize the crystal and are also favored for purely electrostatic reasons. The $C^+\cdots F$ contacts observed here (2.928(6) and 3.113(7) Å) are somewhat larger than in the related $\mathbf{8}\cdot Sb_2F_{11}$ (2.88(2) Å), but **8** may only interact with one counterion due to its cage structure. Because the crystal structure of $\mathbf{1}\cdot Sb_2F_{11}$ shows that **1** is completely "solvated" by anions, its structure may be very similar to that in solution, where a cation may be surrounded by counterions or solvent molecules.

We can only speculate about the reasons that the crystals obtained by reaction 7 were better than those obtained by reaction 8, although reaction 7 must lead to a mixture of cations. We assume that the growth of the crystals of $\mathbf{1}\cdot Sb_2F_{11}$ is influenced by other ions present in the mother liquor, as it was often observed by Addadi, Berkovich-Yellin, Lahav, Leiserowitz, et al.[18] Perhaps these impurities hinder the crystal growth in some directions by being bound preferentially on just those planes, which are also prone to false binding of new $\mathbf{1}\cdot Sb_2F_{11}$ ion pairs from the solution. The main kind of twinning, which could be circumvented by cutting and which is documented in the photographs in the supplementary material, however, seems to occur in crystals from both reactions. Thus, it may be possible that the measured crystal contains a few percent of another ion (like **2**) or any other molecule. The residual difference density peak near **1** may indicate a small amount of an incorporated impurity (we estimate from the

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difference density that not more than 5% was present in the measured crystal). Such an amount has no influence on the structure at our level of accuracy.

Conclusion

The crystal structure of the *tert*-butyl cation shows that this ion is planar and its C–C bonds are significantly shortened to 1.442(5) Å, i.e. the cationic carbon atom is sp^2-hybridized. Thus, the structure is in agreement with the assumption of a hyperconjugative interaction between the filled σ_{C-H} bond orbitals and the empty p orbital on the central carbon atom. The crystal packing may be interpreted in terms of electrophile–nucleophile and acid–base interactions, which lead to an arrangement of eight anions around each cation similar to the packing of CsCl.

Experimental Section

Preparation of the Alkyl Fluorides.[19,20] **General Procedure for Reaction 1 with 2-OH–6-OH (See Also Chart I).** For 3-OH–6-OH, the alcohol ***n*-OH** (50 mmol) dissolved in 40 mL of isopentane was added to 20 mL of HF/pyridine (FLUKA) in a polyethylene bottle at 0 °C. The reaction mixture was stirred for 2 h. In a Teflon separating funnel, the organic layer was separated and washed with ice water with half-saturated $NaHCO_3$ solution (ice cooled), and once again with ice water. After drying over Na_2SO_4, the isopentane was distilled off in a high-vacuum (HV) line at −80 °C, and the product (see also Table I) was distilled into a cold trap. The alcohol **2-OH** was dissolved in isooctane, and the product **2-F** was distilled off from the isooctane at −65 °C (yields: 59–73%).

Synthesis and Crystallization of Alkyl Fluoroantimonates(V). General Procedure for Reactions 2 and 3 (See Chart I and Scheme I). To a solution of 3.5–6.3 mmol of ***n*-F** in 40 mL of $CFCl_3$ was added a solution of 1 (reaction 2) or 2 equiv (reaction 3) of SbF_5 (FLUKA or Aldrich) in 10 mL of CCl_2FCClF_2 at −80 °C under argon. After 30 min, the solvents were filtered off at about −80 °C, and the colorless solid was washed with 8 mL of $CFCl_3$ and dried at −60 °C for 2 h in the HV. The salt was dissolved in 5–40 mL of CH_2Cl_2 at −60 °C, and after filtration, the solution was cooled to −90 °C within 18–100 h. After removal of the mother liquor with a syringe, the resulting crystals (see Table I) were dried for 1 h at −60 °C in the HV.

Synthesis of 1·Sb_2F_{11} According to Reaction 7 and Crystallization. To a solution of 352 mg of **2-F** (3.90 mmol) in 13 mL of CCl_2FCClF_2 was slowly added a solution of 1691 mg of SbF_5 (7.80 mmol) in 13 mL of CCl_2FCClF_2 at −30 °C under argon. After stirring for 20 min, the solvent was distilled off in the HV, and the pale yellow oil was dissolved in 17 mL of CH_2Cl_2 at −20 °C. After filtration, the solution was cooled from −20 to −60 °C within 100 h. The resulting colorless crystals were dried for 20 min at −30 °C in the HV after removal of the mother liquor with a syringe. The crystals were cut along the twin composition plane (photographs of the crystals are shown in the supplementary material, Figure S1a; ^1H NMR spectrum of the dissolved crystals is shown in Figure S12a).

Synthesis of 1·Sb_2F_{11} According to Reaction 8[4] **and Crystallization.** To a solution of 391 mg of **1-Cl** (4.22 mmol) in 15 mL of CH_2Cl_2 was slowly added 1.00 g of $HSbF_6$ (4.22 mmol; Aldrich) at −80 °C under argon. The reaction mixture was allowed to warm up to −40 °C, and a solution of 915 mg of SbF_5 (4.22 mmol) in 10 mL of CCl_2FCClF_2 was slowly added. After 30 min, the solvent was distilled off in the HV at −20 °C, and 13 mL of CH_2Cl_2 was added to the yellow precipitate at −50 °C. After being stirred at −20 °C for 30 min, the solution was filtered and cooled to −60 °C within 20 h (lower cooling rates cause decomposition). The resulting colorless crystals were dried for 20 min in the HV after removal of the mother liquor. No suitable crystals for a crystal structure determination were found (photographs of the crystals are shown in the supplementary material in Figure S1b).

Synthesis of 1·SbF_6 According to Reaction 5[4] **and Crystallization.** To a solution of 2.00 g of $HSbF_6$ (8.45 mmol) in 10 mL of CH_2Cl_2 was added a solution of 782 mg of **1-Cl** (8.45 mmol) in 10 mL of CH_2Cl_2 at −80 °C under argon. The reaction mixture was allowed to warm up to −30 °C, and the solvent was distilled off in the HV. The salt was dissolved in 4 mL of SO_2 (distilled off from P_2O_5) at −40 °C. After filtration, the solution was cooled from −40 to −72 °C within 65 h. The mother liquor was removed by filtration, and the resulting colorless crystals (cubes) were dried for 10 min in the HV (photographs of the crystals are shown in the supplementary material in Figure S13).

Crystal Selection and Mounting and X-ray Measurements. The dried crystals were examined and mounted under dry nitrogen on a self-constructed cryostage. After cooling the stage to −25 or −55 °C, the crystals were placed on a slide with a depression filled with decane or octane. Suitable crystals were selected and cut (if necessary) under a binocular microscope using polarized light and mounted on a glass fiber with a perfluorinated polyether with a suitable pour point as adhesive.[21] The crystals were kept at low temperature and under inert gas during all operations. The X-ray measurements were carried out on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation, graphite monochromator; for the crystal data see Table II).

X-ray Crystal Structure Determination of 1·Sb_2F_{11} (Synthesized According to Reaction 7). An empirical absorption correction (with $03\bar{3}$, which had $\chi \approx 90°$) was applied with ABSCAL[22] from the Xtal 3.0[23] system. The heavy atoms and all fluorine atoms of **1·Sb_2F_{11}** were determined with the Patterson option of SHELXS-86.[24] The remaining C atoms were located by a difference Fourier synthesis with SHELX-76.[25] After several cycles of isotropic and anisotropic refinement (full matrix; $w = 1/\sigma_F{}^2$), the H's could not be located safely in the difference density maps. Refinement of the methyl hydrogens in the riding mode yielded residual difference density peaks, indicating other methyl conformations. The H's at C2 and C3 were finally treated and refined as two rotationally disordered methyl groups: H21 to H23 with $p = 0.75$, H24 to H26 with $p = 0.25$, and H31 to H36 with $p = 0.5$. The best convergence was obtained with the following constraints: all *U*'s of the H's fixed at 0.08 Å^2, all H–C bond distances fixed at 1.08 Å, all H–C–C and H–C–H bond angles fixed at 109.5°, and all H···H distances between two neighboring disordered H's fixed at 1.0181 Å. The refinement (based on *F*) was completed with CRYLSQ,[26] where the obtained hydrogen parameters were kept invariant. An extinction correction according to Becker and Coppens[27] (Gaussian distribution) was applied and refined in the last cycles of the refinement with CRYLSQ ($\rho = 0.43(4)$). A correction for dispersion was applied, but not refined. A distinction between the enantiomorphic structures was not possible. The charges of the cation and the anion were obtained as the sum of the charges associated with the corresponding atoms, calculated from the difference density with CHARGE[28] (according to the Hirshfeld method[29]), and the esd's were obtained by error propagation. The electron and difference density contour maps for 21 planes (see supplementary material, Figures S4–S10) were generated with the program sequence FOURR,[30] SLANT,[31] CONTRS,[32] PLOTX;[33] the density functions were analyzed with

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PEKPIK.[34] Figure 1 was generated with ORTEP,[35] Figures 2 and 3 with SYBYL 6.0.[36] Most geometry calculations and the preparation of most tables in the supplementary material were carried out with a modified version of PARST88.[37] A thermal motion analysis of **1** with THMA11[38] gave unreliable results, because **1** delivers only 24 displacement parameters.

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Supplementary Material Available: Photographs of crystals, packing diagram, tables of positional and thermal parameters, bond distances, angles, torsion angles, interatomic distances; electron and difference density maps, and NMR spectra (33 pages); table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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