158. X-Ray Crystal Structure of the 2-Phenyladamant-2-yl Cation

by **Thomas Laube*** and **Sandro Hollenstein**

Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

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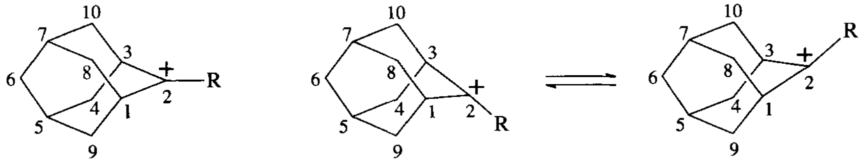
The crystal structure of the Sb_2F_{11} salt of the 2-phenyladamant-2-yl cation, **1** · Sb_2F_{11}, was determined at 183 K ($P2_1/c$, $R1 = 0.0652$, σ(C–C) = 0.02 Å), because earlier published results indicated a charge delocalization from the cationic C(2) into the σ framework (C–C hyperconjugation) and a bending of the C(2) bridge. In the structure of **1**, a displacement of the C(2) bridge by 7.8(12)° from the symmetrical position and C–C bond-length deviations from expectation values were found which are in agreement with preferential C–C hyperconjugation on one face of C(2). The interactions of **1** with two Sb_2F_{11} counterions nearest to C(2) also indicate different behaviour of the two faces of C(2). The benzylic resonance in **1** is confirmed.

The 2-phenyladamant-2-yl cation (**1**; *Scheme 1*) was investigated for the first time by *Olah et al.* [1] in 1974. The methyl-substituted cation **2** had already been prepared by *Whitlock* and *Siefken* [2] in 1968, and *Schleyer* and coworkers [3] examined several polymethyl-substituted adamant-2-yl cations. The parent ion **3** could not be prepared up to now due to its fast rearrangement to the adamant-1-yl cation.

Scheme 1



1 R = Ph
2 R = Me
3 R = H

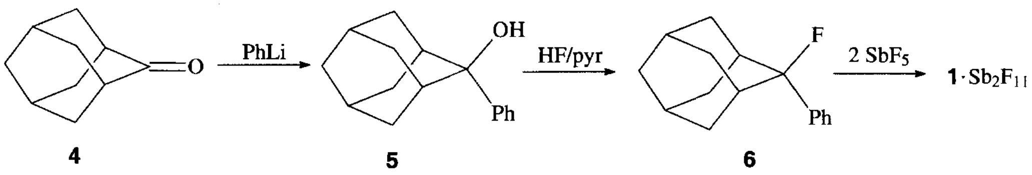
A

B

In recent years, adamant-2-yl cations and adamantanones attracted much attention (mainly by the groups of *Sorensen* [4] and *le Noble* [5]) due to their structural relationship to cyclohexyl cations and cyclohexanones, which were intensively investigated, because the nucleophilic attack on such substituted systems leads to diastereoisomeric products. *Sorensen* and coworkers concluded from NMR studies [4b] of **1**, **2**, and other adamant-2-yl cations and *ab initio* studies [4c] of **3** that the cationic C(2) is not planar, and that the C(2) bridge in adamant-2-yl cations is displaced from the symmetrical position and rapidly moves back and forth in a double-minimum potential (equilibration between **A** and **B**; see *Scheme 1*). Hyperconjugation with the C(1)–C(9) and C(3)–C(4) bonds (**A**) or with the C(1)–C(8) and C(3)–C(10) bonds (**B**) was considered as the reason for this behaviour. We wish to report here the results of the first crystal-structure analysis of an adamant-2-yl cation salt, **1**·Sb_2F_{11}, and compare them with the predictions mentioned above.

Results. – The synthesis of crystalline **1**·Sb_2F_{11} was carried out by addition of PhLi [6] to adamantanone (**4**), subsequent fluorination of **5** according to *Olah et al.* [7], and reaction of **6** with 2 equiv. of SbF_5 (see *Scheme 2*)[1].

Scheme 2



Crystallization of **1**·Sb_2F_{11} from CH_2Cl_2 yielded crystals suitable for the structure determination. The result is shown in *Figs. 1–3*. The structure has only mediocre *R* values ($R1 = 0.0652$, $wR2 = 0.1667$), and the rather large displacement ellipsoids (especially of the anion) indicate partial but unresolvable disorder. The closest contact between the cationic C(2) and a counterion is C(2)···F(25) = 3.37(2) Å (*i.e.* 0.2 Å greater than the sum of the *van der Waals* radii [8] of C and F: 1.70 Å + 1.47 Å = 3.17 Å). The symmetry-related anion below **1** in *Fig. 2* has no *van der Waals* contact to C(2) (C(2)···F(13′) = 4.11(2) Å). The most remarkable features of the cation **1** (*Fig. 3*) are the displacement of the C(2) bridge out of the plane[2] *P*(1,3,6) by 7.8(12)°, the additional

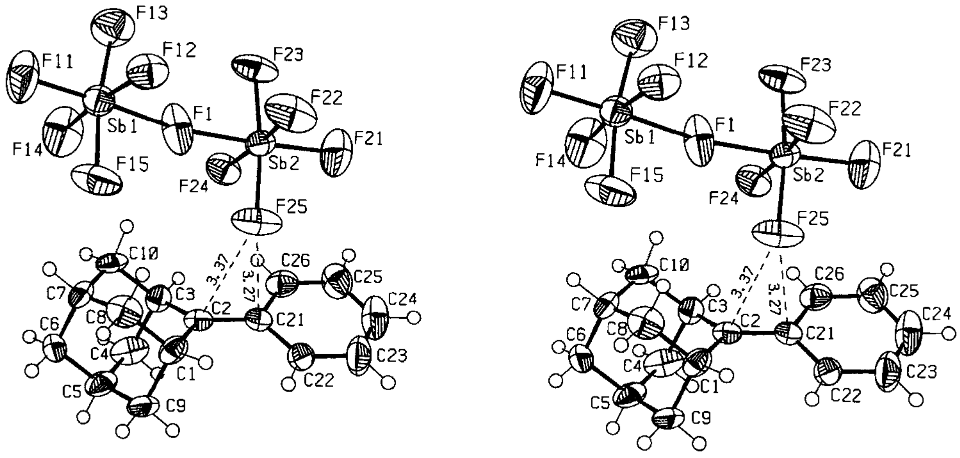


Fig. 1. *ORTEP Stereodrawing of the crystal structure of* **1**·Sb_2F_{11}. The displacement ellipsoids are drawn at the 50% probability level, the H-atoms are represented by spheres with a radius of 0.1 Å. Distances are given in Å.

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[1] We carried out many other crystallizations of adamant-2-yl salts with a variety of cations and anions (21 different ion pairs), but were successful only in the case of **1**·Sb_2F_{11}.

[2] $P(i_1, ..., i_n)$ is the (for $n > 3$: least-squares) plane defined by $C(i_1)$, ..., $C(i_n)$; $L(i_1, i_2)$ is the line through $C(i_1)$ and $C(i_2)$.

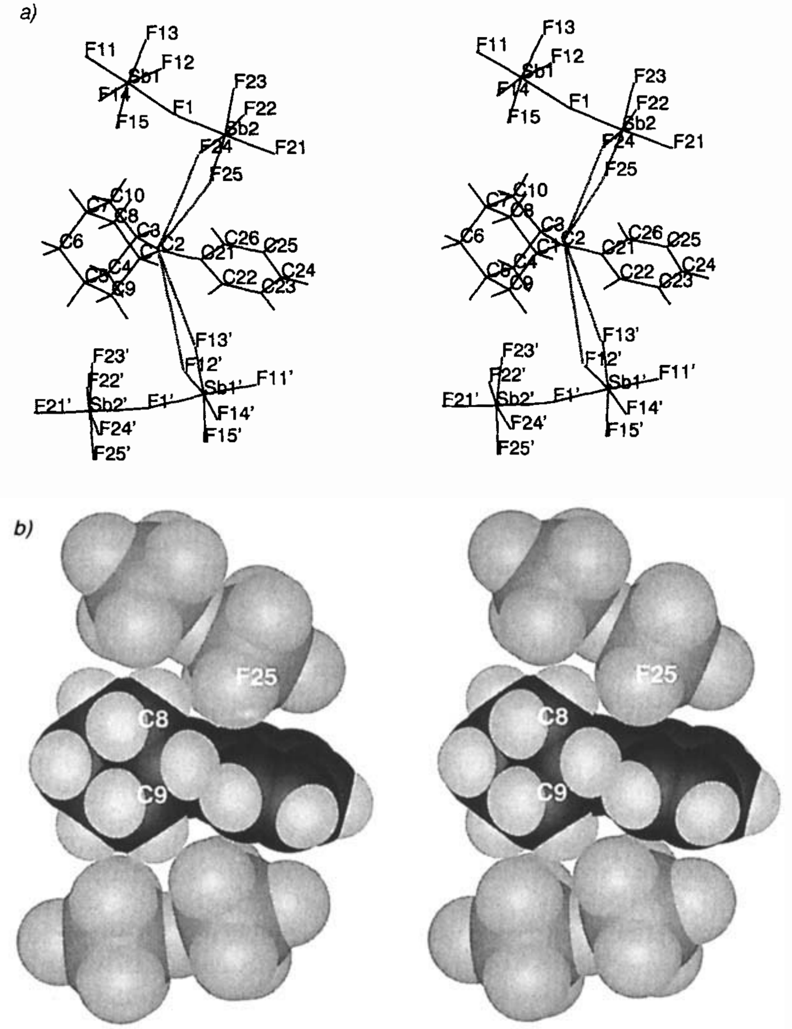

Fig. 2. *Stereodiagram of* **1** *and the two* $Sb_2F_{11}^-$ *ions nearest to C(2) in the crystal structure of* **1**·Sb_2F_{11} (the anion with the primed labels is generated by the symmetry operation $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$). a) *Wire-frame diagram* (the shortest C(2)···F distances are indicated by grey lines: C(2)···F(24) = 3.60(1), C(2)···F(25) = 3.37(2), C(2)···F(12′) = 4.15(1), C(2)···F(13′) = 4.11(2) Å). b) *Space-filling diagram of the approximate* Newman *projection along C(1)/C(3), C(8)/C(10), C(9)/C(4)* (*van der Waals* radii according to *Bondi* [8])

bending of the (planar) Ph ring out of the plane *P*(1,2,3) by 5.6(13)° leading to a slight pyramidalization of C(2) (C(2)-*P*(1,3,21) = 0.049(14) Å), and the elongated bonds C(1)–C(9) = 1.58(2) Å and C(3)–C(4) = 1.60(2) Å (reference value [9] for a $(C_{sp^3})_2HC{-}CH_2(C_{sp^3})$ bond: 1.531 Å). The Ph ring is slightly twisted by *ca.* 17° around C(2)–C(21) with regard to *P*(1,2,3), probably because of steric interactions between the H-atoms at C(1) and C(3) with the *ortho*-H-atoms (C(1)–*H*···*H*–C(22) = 2.01,

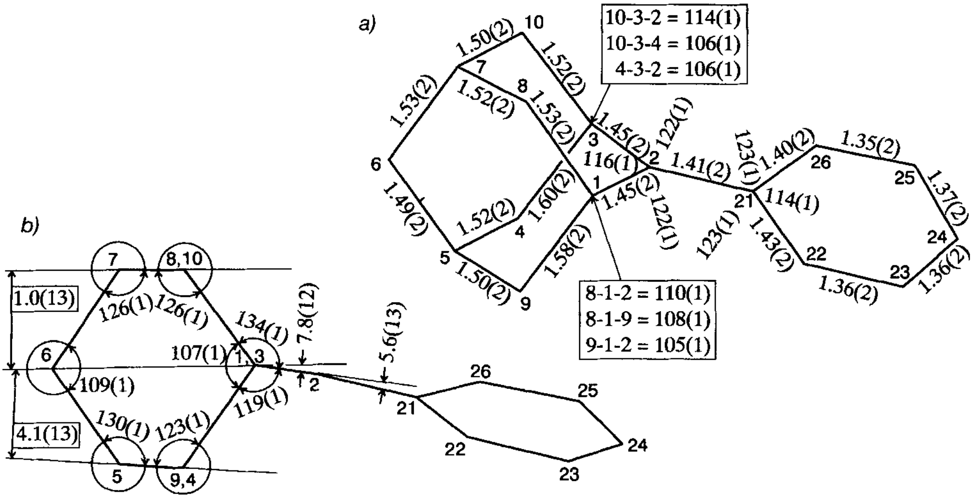

Fig. 3. *Selected structural parameters of the crystal structure of* **1** (distances in Å, angles in °; the C-atoms are labelled according to *Fig. 1*): a) *Bond lengths and bond angles.* b) *Approximate* Newman *projection along C(1)/C(3), C(8)/C(10), and C(9)/C(4) with the angles involving the planes*[2]) P*(1,3,6)*, P*(7,8,10)*, P*(1,3,8,10)*, P*(1,2,3)*, P*(1,3,4,9)*, *and* P*(4,5,9) and the lines*[2]) L*(2,21)*, L*(5,6)*, *and* L *(6,7)*

C(3)–$H\cdots H$–C(26) = 1.98 Å). All bonds emanating from C(2) are shortened by 0.06(2) Å if compared with reference values [9] from neutral molecules: C(2)–C(1) = C(2)–C(3) = 1.45(2) Å (average [9] $(C_{sp^3})_2HC-C_{sp^2}$ bond: 1.510 Å), C(2)–C(21) = 1.41(2) Å (average [9] $C_{sp^2}-C_{ar}$ bond with conjugation: 1.470 Å). The bond lengths in the Ph ring (see *Fig. 3*) resemble those in the unsubstituted trityl cation[3]).

Discussion. – Although most observed deviations of structural parameters of **1** from reference values are only just significant (3σ criterion) due to the large esd's (which were computed using the full covariance matrix wherever possible), the structural deformations of **1** are entirely consistent with the assumption of C–C hyperconjugation as predicted by *Sorensen* [4b] [4c] and as expected from the already known structures of the adamant-1-yl cation **7** [11] and the *tert*-butyl cation **8** [12], and with the effects observed in the norbornen-7-yl cation **9** [13], substituted cyclohexanones **10** [14] (which are in some cases activated by *Lewis* acids (LA)), and the activated adamantanone **11** [15] (see *Fig. 4*).

If compared with the *ab initio* results (basis set: 6-31G*) of *Rauk*, *Sorensen*, and coworkers [4c] about the secondary cation **3** (which must be described as equilibrating pair **3A** and **3B**, see *Scheme 1*), the displacements of the C(2) bridge and of the Ph ring in **1** are about half as large as the corresponding displacements in **3** (probably because **1** is less electron-deficient at C(2) than **3**), but the differences Δ(C–C) between the average C(1)–C(9)/C(3)–C(4) and C(1)–C(8)/C(3)–C(10) bonds[4]) are practically equal (**1**: 0.066(20) Å; **3**: 0.061 Å). The shortened C(1)–C(2) and C(2)–C(3) bonds in **1** indicate a partial double-bond character (comparable to the C^+-C bonds in **3** [4c], **7**, and **8**), and the

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[3]) The average ring bond lengths of Ph_3C^+ are: $C_{ipso}-C_{ortho}$ = 1.416(5), $C_{ortho}-C_{meta}$ = 1.384(6), $C_{meta}-C_{para}$ = 1.393(9) Å; they were computed from the structures in [10].

[4]) Δ(C–C) = [C(1)–C(9) + C(3)–C(4) – C(1)–C(8) – C(3)–C(10)]/2.

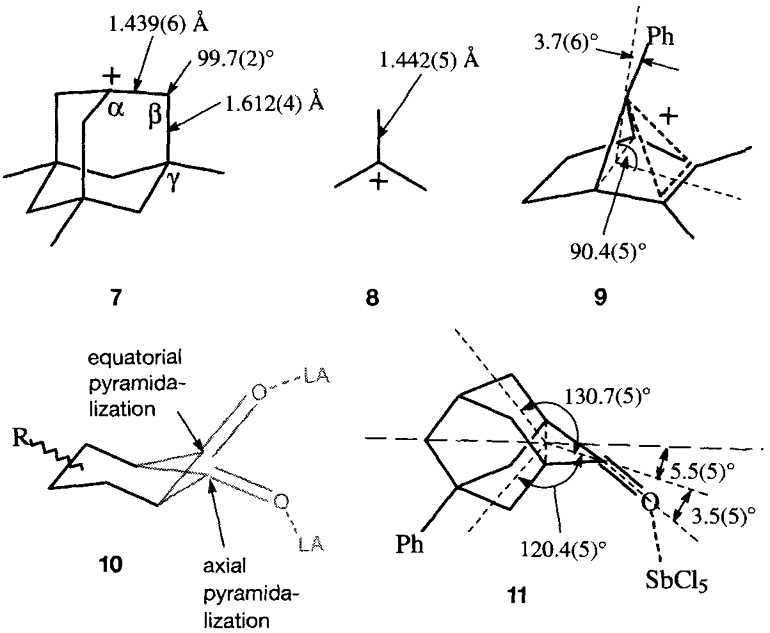

Fig. 4. *Important structural parameters of molecules related to* **1**. **7** [11] and **8** [12]: average values; **9** [13]: angles as defined in Fig. 6 in [13b]; **10** [14]: exaggerated deformation of the ring for the two possible pyramidalizations; **11** [15]: angles between planes and the line through the C=O bond defined as in *Fig. 3b*.

lengthened C(1)–C(9) and C(3)–C(4) bonds indicate weakened single bonds (*cf.* C(β)–C(γ) bonds in **7**). The short C(2)–C(21) bond points to a strong benzylic resonance as found by *Olah et al.* [1]. The displacement of the C(2) bridge in **1** is not as strong as that of the C(7) bridge in **9**, but the additional bending of the Ph ring in **1** is comparable to that in **9** (although **9** shows practically no benzylic resonance). One may assume, that the bendings of the C(2) bridge and of the Ph ring in **1** facilitate the overlap of the empty p orbital at C(2) ($p_{C(2)}$) with the filled $\sigma_{C(1)-C(9)}$ and $\sigma_{C(3)-C(4)}$ orbitals (at the cost of the overlap with $\sigma_{C(1)-C(8)}$ and $\sigma_{C(3)-C(10)}$) as shown in *Fig. 5*.

These bendings also facilitate the interaction of C(2) with a counterion from the top (see *Figs. 1–3*), which may be interpreted as a beginning axial nucleophilic attack on the axially pyramidalized [14] C(2) in the ring C(2)–C(3)–C(10)–C(7)–C(8)–C(1) and simultaneously as an equatorial nucleophilic attack on the equatorially pyramidalized [14] C(2) in the ring C(2)–C(3)–C(4)–C(5)–C(9)–C(1) (in agreement with the interpretation of structural deformations in **10** and non-activated cyclohexanones [14]). Consequently, the observed bendings obstruct the interaction of C(2) with a counterion from the bottom (see *Figs. 1–3*), and the observed packing (*Fig. 2*) agrees with this interpretation. The displacement of the C(2) bridge in the activated adamantanone **11** is similar to that in **1**, but weaker⁵) (*Fig. 4*), in agreement with the assumption, that the benzylic cation **1** is more electron-deficient at C(2) than the activated ketone **11**. Accordingly, no significant Δ(C–C) was observed in **11**.

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⁵) See also footnote 19 in [14] and footnotes 14 and 15 in [15].

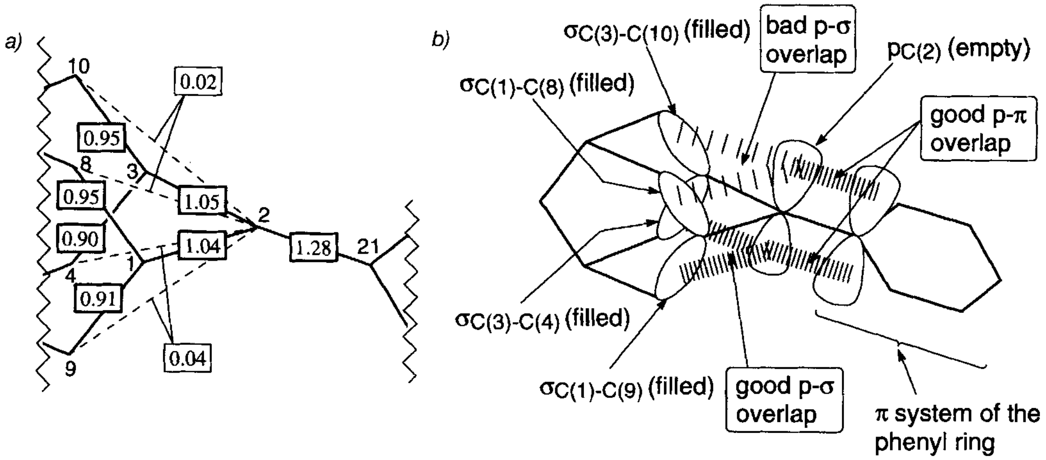

Fig. 5. *Bond orders and interpretation of the observed structural deformation of* **1** *in terms of C–C hyperconjugation and benzylic resonance. a)* AM1 Bond orders (framed) computed on the experimental geometry; *b)* assumed interactions between localized orbitals.

It is possible that the observed deformation of **1** represents only the lower limit of the deformation of the true structure of **1** in the crystal, because a superposition of **1A** and **1B** in the orientation shown in *Scheme 1* leads (due to the opposite displacement of the C(2) bridge) to a seeming reduction of this displacement (the disordered atoms could probably not be resolved in such a case, see Fig. S4 in the *Supplementary Material*). In the extreme case of equal population, a symmetrical averaged structure would result.

Conclusion. – The crystal structure of the 2-phenyl adamant-2-yl cation (**1**) shows that the C(2) bridge is displaced from the symmetrical position and that the cationic C(2) is slightly pyramidal. The shortening of the C(1)–C(2) and C(2)–C(3) bonds and the elongation of the C(1)–C(9) and C(3)–C(4) bonds may be explained by C–C hyperconjugation on one face of C(2) in agreement with the results obtained by other authors about several adamant-2-yl cations.

Experimental Part

2-Phenyladamantan-2-ol (= *2-Phenyltricyclo[3.3.1.1^{3,7}]decan-2-ol*; **5**). Starting from commercially available adamantanone (**4**; *Fluka*), **5** was synthesized by addition of PhLi [6]. The resulting yellowish solid was recrystallized from Et_2O/pentane 1:5: colourless crystals[6]).

2-Fluoro-2-phenyladamantane (= *2-Fluoro-2-phenyltricyclo[3.3.1.1^{3,7}]decane*; **6**). To an ice-cooled mixture of 5 ml of HF/pyridine (*Fluka*) and 5 ml of isopentane in a polyethylene bottle was slowly added a soln. of 1.00 g (4.38 mmol) of **5** in 15 ml of Et_2O [7]. The mixture was stirred for 2 h, and then additional 5 ml of HF/pyridine and 15 ml of isopentane were added. After another h of stirring, the mixture was poured on ice. The org. layer was separated in a poly(tetrafluoroethene) separating funnel, washed with half-sat. $NaHCO_3$ soln. and ice-H_2O, dried (Na_2SO_4), and evaporated. The resulting oil was purified by chromatography (Et_2O/pentane 1:20): 680 mg (67%) of **6**. Colourless solid. ^{1}H-NMR (300 MHz, $CDCl_3$; δ in ppm): 7.63–7.58 (*m*, 2 arom. H); 7.44–7.32 (*m*, 3 arom. H); 2.78 (br. *s*, 2 H); 2.43–2.32 (*m*, 2 H); 1.99–1.62 (*m*, 10 H). ^{19}F-NMR (282 MHz, $CDCl_3$; δ in ppm): −120.5 (br. *s*).

2-Phenyladamantan-2-ylium Undecafluorodiantimonate(V) (= *2-Phenyltricyclo[3.3.1.1^{3,7}]decan-2-ylium Undecafluorodiantimonate*; **1**·Sb_2F_{11}). The reaction was carried out in the special apparatus described earlier (see

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[6]) For the crystal structure of **5**, see [16].

Fig. 6 and Exper. Part in [17]). A soln. of 341 mg (1.48 mmol) of **6** in 40 ml of $CFCl_3$ was prepared at −80° in the reaction vessel. Through a septum at joint 3, 2 equiv. of SbF_5 (742 mg, 2.96 mmol; *Fluka*) in 10 ml of $CCl_2F\text{-}CClF_2$ were slowly added with a syringe. After 30 min, the yellow mixture was filtered at −80° and the solid raw product washed twice with 6 ml of $CFCl_3$ and dried under high vacuum at −60° for 3 h. The dry yellow filter cake was coarsely powdered under Ar in the reaction vessel, transferred into a 2-neck flask (with an Ar frit on its second neck) connected at joint 5 (instead of the 'filtration vessel'). At −78°, 7 ml of CH_2Cl_2 were slowly added, the soln. was rapidly filtered through the precooled Ar frit, and the clear yellow filtrate collected in a 2-neck flask (with a 3-way stopcock on the other neck) at −78° under Ar. The cooled flask was then disconnected from the Ar frit and stoppered. The solvent was slowly evaporated during 16 h at −78°/*ca.* 0.05 Torr through the 3-way stopcock. One obtains yellow thin plates (size up to 1.1 mm × 0.8 mm × 0.1 mm). Photographs of the crystals are shown in the *Supplementary Material* in Fig. S1.

X-Ray Crystal-Structure Analysis of **1**$\cdot Sb_2F_{11}$. A crystal of the size of 0.81 mm × 0.31 mm × 0.1 mm was mounted on a glass fiber under dry N_2 at −60° on a self-constructed cryostage (see Fig. 7 in [17]). The X-ray measurement was carried out on an *Enraf-Nonius-CAD4* diffractometer (MoK_α radiation with λ 0.71069 Å, graphite monochromator). The final data of the monoclinic unit cell (space group $P2_1/c$ (No. 14), $M_r(C_{16}H_{19}Sb_2F_{11})$ 663.81, $Z = 4$, $F_{000} = 1264$) at 183 K are $a = 7.352(3)$, $b = 17.365(6)$, $c = 16.201(6)$ Å, $\beta = 95.74(3)°$, $V = 2058(1)$ Å^3 (obtained from 25 reflections in the range $\theta = 8.36$ to $11.82°$); $\rho_x = 2.142$ g cm^{-3}; $\mu = 2.721$ mm^{-1}. A total of 3609 reflections (2224 with $I > 2\sigma_I$) up to $\theta = 25°$ were measured (ω-2θ scans; $-8 \leq h \leq 8$, $0 \leq k \leq 20$, $0 \leq l \leq 19$). The data reduction was carried out with DIFDAT [18] from the Xtal 3.2 system [19]. An empirical absorption correction with 36 scans of the reflection 416 which had $\chi_{Euler} = -82.2°$ was applied with ABSCAL [20] and a HKLF file for the SHELX programs [21] [22] was generated with LISTFC [23]. The 2 Sb-atoms and all other non-H-atoms were determined with the *Patterson* option of SHELXS-86 [21]. The structure was refined upon F^2 with SHELXL-93 [22]. After several cycles of isotropic and anisotropic refinement (full matrix), the H's could not be located in the difference-density maps. Therefore, all H positions were computed and refined riding on the corresponding C-atom with $U_{iso}(H) = 1.2U_{eq}(C)$. The final weights were $w = 1/[\sigma^2_{F_{obs}2} + (0.1351\ P)^2 + 12.6906\ P]$ with $P = (\max(F^2_{obs}, 0) + 2\ F^2_{calc})/3$. An attempt to refine an extinction parameter was not successful. The R values[7]) are for $I > 2\sigma_I$: $R1 = 0.0652$, $wR2 = 0.1667$; for all data: $R1 = 0.1006$, $wR2 = 0.2469$ (3609 data, 262 parameters). The highest difference-density maxima (up to 1.55 eÅ^{-3}) and minima (up to −2.81 eÅ^{-3}) occur around the Sb-atoms (root mean square deviation of the difference density from the mean: 0.26 eÅ^{-3}), see Fig. S5 in the *Supplementary Material*. The thermal motion analysis with THMA11 [24] shows that the displacement parameters of **1** are not well explained. Therefore, it is possible that **1** is not perfectly ordered. *Fig. 1* was generated with PIG [25], ORTEP [26], and PLOTX [27], *Figs. 2* and *3* with *SYBYL*® 6.0 [28] (besides *CorelDRAW* 4.0 [29] for *Fig. 3*). The geometry calculations and the preparation of most tables in the *Supplementary Material* were carried out with SHELXL-93 [22] and a modified version of PARST88 [30]. The bond orders of **1** (*Fig. 5*) were computed with MOPAC [31].

Supplementary Material. Available from the authors: Photographs of crystals, packing diagram, tables of positional and displacement parameters, bond distances, angles, torsion angles, interatomic distances, observed and calculated F^2 values for **1**$\cdot Sb_2F_{11}$ (46 pages). Atomic coordinates were also deposited with the *CCDC*.

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REFERENCES

[1] G. A. Olah, G. Liang, G. D. Mateescu, *J. Org. Chem.* **1974,** *39,* 3750.

[2] H. W. Whitlock, Jr., M. W. Siefken, *J. Am. Chem. Soc.* **1968,** *90,* 4929.

[3] D. Lenoir, P. Mison, E. Hyson, P. v. R. Schleyer, M. Saunders, P. Vogel, L. A. Telkowski, *J. Am. Chem. Soc.* **1974,** *96,* 2157.

[4] a) R. P. Kirchen, K. Ranganayakulu, T. S. Sorensen, *J. Am. Chem. Soc.* **1987,** *109,* 7811; b) E. S. Finne, J. R. Gunn, T. S. Sorensen, *ibid.* **1987,** *109,* 7816; c) R. Dutler, A. Rauk, T. S. Sorensen, S. M. Whitworth, *ibid.* **1989,** *111,* 9024.

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[7]) $R1 = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}|$, $wR2 = (\Sigma[w(F^2_{obs} - F^2_{calc})^2]/\Sigma[wF^4_{obs}])^{1/2}$.

[5] a) C.K. Cheung, L.T. Tseng, M.-H. Lin, S. Srivastava, W.J. le Noble, *J. Am. Chem. Soc.* **1986,** *108,* 1598; b) M.-H. Lin, M.K. Boyd, W.J. le Noble, *ibid.* **1989,** *111,* 8746.

[6] D. Seebach, H. Neumann, *Chem. Ber.* **1974,** *107,* 847.

[7] G.A. Olah, J.T. Welch, Y.D. Vankar, M. Nojima, I. Kerekes, J.A. Olah, *J. Org. Chem.* **1979,** *44,* 3872.

[8] A. Bondi, *J. Phys. Chem.* **1964,** *68,* 441.

[9] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, in 'International Tables for Crystallography, Volume C', Ed. A.J.C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, pp. 685–706.

[10] a) A.H. Gomes de Mesquita, C.H. MacGillavry, K. Eriks, *Acta Crystallogr.* **1965,** *18,* 437; b) B. Krebs, V. Paulat, *Z. Naturforsch., B* **1979,** *34,* 900; c) J. Krausse, G. Heublein, G. Rudakoff, P. Leibnitz, G. Reck, *J. Crystallogr. Spectrosc. Res.* **1991,** *21,* 45.

[11] a) T. Laube, *Angew. Chem.* **1986,** *98,* 368; *ibid. Int. Ed.* **1986,** *25,* 349; b) T. Laube, E. Schaller, submitted to *Acta Crystallogr., Sect. B.*

[12] S. Hollenstein, T. Laube, *J. Am. Chem. Soc.* **1993,** *115,* 7240.

[13] a) T. Laube, *J. Am. Chem. Soc.* **1989,** *11,* 9224; b) T. Laube, C. Lohse, *J. Am. Chem. Soc.* **1994,** *116,* in press.

[14] T. Laube, S. Hollenstein, *J. Am. Chem. Soc.* **1992,** *114,* 8812.

[15] T. Laube, H.U. Stilz, *J. Am. Chem. Soc.* **1987,** *109,* 5876.

[16] F.A.J. Singelenberg, B.P. van Eijck, *Acta Crystallogr., Sect. C* **1987,** *43,* 309.

[17] T. Laube, *Helv. Chim. Acta* **1994,** *77,* 943.

[18] J. Stewart, R. Merom, J. Holden, R. Doherty, S. Hall, T. Maslen, N. Spadaccini, in 'DIFDAT. Xtal 3.2 Reference Manual', Eds. S.R. Hall, H.D. Flack, and J.M. Stewart, Universities of Western Australia, Geneva, and Maryland, Lamb, Perth, Australia, 1992, pp. 104–110.

[19] 'Xtal 3.2 Reference Manual', Eds. S.R. Hall, H.D. Flack, and J.M. Stewart, Universities of Western Australia, Geneva, and Maryland, Lamb, Perth, Australia, 1992; the program version used here contains the August 1993 updates.

[20] K. Watenpaugh, J. Stewart, 'ABSCAL. Xtal 3.2 Reference Manual', Eds. S.R. Hall, H.D. Flack, and J.M. Stewart, Universities of Western Australia, Geneva, and Maryland, Lamb, Perth, Australia, 1992, pp. 41–43.

[21] G.M. Sheldrick, 'SHELXS-86', University of Göttingen, 1986; G.M. Sheldrick, *Acta Crystallogr., Sect. A* **1990,** *46,* 467.

[22] G.M. Sheldrick, 'SHELXL-93', University of Göttingen, 1993; G.M. Sheldrick, *J. Appl. Crystallogr.* **1994,** in preparation.

[23] S. Hall, 'LISTFC. Xtal 3.2 Reference Manual', Eds. S.R. Hall, H.D. Flack, and J.M. Stewart, Universities of Western Australia, Geneva, and Maryland, Lamb, Perth, Australia, 1992, pp. 153–155.

[24] K. Trueblood, 'THMA11, version of Oct. 21, 1988', University of California, Los Angeles, CA 90024.

[25] U. Bartsch, S. Hall, 'PIG. Xtal 3.2 Reference Manual', Eds. S.R. Hall, H.D. Flack, and J.M. Stewart, Universities of Western Australia, Geneva, and Maryland, Lamb, Perth, Australia, 1992, pp. 239–243.

[26] G. Davenport, S. Hall, W. Dreissig, 'ORTEP. Xtal 3.2 Reference Manual', Eds. S.R. Hall, H.D. Flack, and J.M. Stewart, Universities of Western Australia, Geneva, and Maryland, Lamb, Perth, Australia, 1992, pp. 219–224; original version: C.K. Johnson, 'ORTEP-II', Oak Ridge National Laboratory, TN 37830, 1976.

[27] S. Hall, R. Olthof-Hazekamp, H. Flack, J. Hester, U. Bartsch, 'PLOTX. Xtal 3.2 Reference Manual', Eds. S.R. Hall, H.D. Flack, and J.M. Stewart, Universities of Western Australia, Geneva, and Maryland, Lamb, Perth, Australia, 1992, pp. 244–246.

[28] '*SYBYL*® Version 6.0 for Sun Computers'[8]), November 1992, *Tripos Associates, Inc.* (a subsidiary of *Evans & Sutherland*), St. Louis, MO 63144-2913.

[29] '*CorelDRAW* Version 4.0', 1993, *Corel Corporation,* 1600 Carling Avenue, Ottawa, Ontario, Canada K1Z8R7.

[30] M. Nardelli, 'PARST88, Release April 1988', University of Parma, Italy; M. Nardelli, *Comp. Chem.* **1983,** *7,* 95.

[31] J.J.P. Stewart, 'MOPAC, Version 5.0' (integrated in *SYBYL*® 6.0 [28]); program # 455 from 'Quantum Chemistry Program Exchange', Indiana University, Bloomington, Indiana.

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[8]) The programs res2dat, dat2cry and cry2mol (*T. Laube*, ETH Zürich) were used for the conversion of coordinate files in various formats to files in the 'mol' format, which were read by *SYBYL*.