

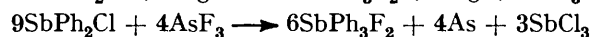
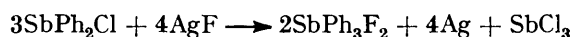
Diphenylantimony(III) Fluoride: Preparation and Crystal Structure

By Stephen P. Bone and D. Bryan Sowerby,* Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Attempts to prepare SbPh_2F by the modification of methods which give the corresponding chloride have not been successful, but this compound can be obtained by treating SbF_3 with $[\text{NH}_4]_2[\text{SiPhF}_5]$. Comparison of the mass spectra of SbPh_2F and SbPh_2Cl suggests the formation of strong fluorine bridges in the former, which has been confirmed by an X-ray analysis. Crystals of SbPh_2F are orthorhombic with $a = 8.18(1)$, $b = 11.04(1)$, $c = 12.02(1)$ Å, space group $P2_12_12_1$, and $Z = 4$. Atomic positions have been determined by Patterson and Fourier methods from X-ray diffractometer data and refined by least squares to R 0.042 for 1 170 reflections. The structure consists of infinite chains of SbPh_2F units, resulting from the formation of strong intermolecular fluorine bridges [$\text{Sb} \cdots \text{F}$ 2.221(5) Å]; the corresponding intramolecular Sb–F distance is 2.166(5) Å and the angle at the bridging fluorine is 140.2(3)°. The antimony lone pair of electrons is stereochemically active giving a structure based on a trigonal bipyramid with fluorines in axial positions and the phenyl groups occupying two of the equatorial positions. The mean Sb–C distance is 2.13 Å and angle between the phenyl groups [$\text{C}(1)\text{--Sb}(1)\text{--C}(7)$] is 99.9(4)°.

PHENYLANTIMONY(III) chlorides and bromides, *i.e.* SbPhX_2 and SbPh_2X where $\text{X} = \text{Cl}$ or Br , can be prepared by a number of methods including the partial arylation¹ of the appropriate trihalide with, among other things, $\text{MgPh}(\text{Br})$ or LiPh or the redistribution² of $\text{SbPh}_3\text{--SbX}_3$ mixtures in the appropriate ratio. Information on the corresponding fluorides on the other hand is sparse. Only one method is reported to give the monofluoride³ and attempts to obtain SbPhF_2 by an adaptation of this method were unsuccessful.

We have attempted to prepare SbPh_2F by a number of alternative methods including: (1) the fluorination of SbPh_2Cl with (a) KF in methanol, (b) AgF in acetonitrile, and (c) AsF_3 ; (2) the phenylation of SbF_3 with (a) SbPh_3 , (b) LiPh , and (c) $\text{MgPh}(\text{Br})$. In no case, however, was the required compound produced. With potassium fluoride there was no change even after long periods of reflux in methanol, while fluorination with both AgF and AsF_3 led to simultaneous oxidative fluorination and phenyl-group migration. In each case a black precipitate was obtained immediately on addition at room temperature, which was identified as elemental silver and arsenic respectively. It was also possible to isolate in good yield the compound SbPh_3F_2 ,⁴ identified by elemental analysis and by comparison of its m.p., mass spectrum, and i.r. spectrum with those of an authentic sample. The equations below can be written to represent the reactions:



Similar results were obtained when the starting material was SbPh_2Br .

Although SbCl_3 and SbBr_3 can be 'phenylated' by triphenylantimony, a similar reorganisation reaction with SbF_3 did not occur even after long periods of reflux of solutions in CH_2Cl_2 or MeOH . Nor was any change observed when the two components were melted and held at 150 °C for 40 h. With both phenyl-lithium and phenylmagnesium bromide, it was not possible to achieve partial arylation even when using the stoichiometric quantity of the reagent at temperatures as low as –90 °C.

In all cases the product isolated was triphenylantimony, of excellent purity and in good yield.

The method reported by Müller and Dathe,³ on the other hand, with minor modifications works well. In this approach SiPhCl_3 is fluorinated and converted into the salt $[\text{NH}_4]_2[\text{SiPhF}_5]$ which is used to phenylate SbF_3 in aqueous solution. Diphenylantimony fluoride is a white, air-stable, crystalline solid which dissolves in hot ethanol but is insoluble in non-polar organic solvents. It melts at 154 °C and sublimes in a vacuum. These general properties are in contrast to those of SbPh_2Cl and SbPh_2Br which, for example, have melting points of 69 and 82 °C respectively, and are soluble in a wide range of organic solvents. The difference between SbPh_2F on the one hand and the corresponding chloride and bromide on the other appears to be the same as that between SbF_3 , a fluorine-bridged polymer, and SbCl_3 or SbBr_3 which are molecular solids.

The presence of fluorine bridges in SbPh_2F is supported by mass spectrometric data (see Table 1), which shows $[\text{SbPh}_2\text{F}_2]^+$ as the highest *m/e* ion accounting for 22.4% of the total ion current compared with 9.1% for the molecular ion. Data for SbPh_2Cl are also included in Table 1; no species containing two chlorine atoms

TABLE I
Mass spectrometric data for SbPh_2Cl and SbPh_2F

Ion	% Total ion current	
	X = Cl	X = F
SbPh_3	0.1	
SbPh_2X_2		22.4
SbPh_2X	6.1	9.1
SbPh_2^*	2.0	0.6
SbPhX_2		0.1
SbPhX	4.5	14.2
SbPh^*	14.3	2.7
$\text{C}_4\text{H}_9\text{Sb}$	0.3	
SbX	1.2	0.3
Ph_2^*	33.2	21.7
Sb	3.8	0.2
PhX	0.3	0.2
$(\text{C}_4\text{H}_9)_2$	0.3	0.1
Ph^*	16.9	19.2
C_4H_9	13.3	9.3

* Value includes ions derived by addition or loss of one or more hydrogen atoms.

analogous to the $[\text{SbPh}_2\text{F}_2]^+$ ion was observed, and here even the molecular ion is of low intensity.

The i.r. spectrum (see Experimental section) shows the expected bands associated with C_6H_5 groups attached to antimony, and little comment is necessary beyond noting that the t mode⁵ is split, probably into asymmetric and symmetric components, to give bands at 290 and 269 cm^{-1} . There is no band that can be assigned unambiguously to the Sb-F mode, expected in the 500 cm^{-1} region. Terminal fluorine atoms give strong absorption in both antimony(III)⁶ and antimony(V)⁷ compounds but only weak bands apparently result from bridging fluorine atoms.⁷ In the present case the appropriate Sb-F band is presumed to be of low intensity. It was not possible to observe any ^{19}F n.m.r. signal, although whether this is a function of the low solubility of the compound or the influence of the quadrupole moment of the antimony is not known.

The general behaviour of SbPh_2F is thus consistent with a fluorine-bridged structure of the type known to be present in, for example, SbF_3 ⁸ and a number of derived fluoro-anions.⁷ Further interest in the present compound stems from the presence of a single fluorine atom which as a result of reduced competition for neighbouring antimony centres might be expected to lead to particularly short intermolecular antimony-fluorine distances. An X-ray analysis has therefore been carried out.

EXPERIMENTAL

Preparation of Diphenylantimony Fluoride.—Trichloro(phenyl)silane (21.2 g, 0.1 mol) was added dropwise under a blanket of nitrogen to antimony trifluoride (17.9 g, 0.1 mol) and the mixture warmed to initiate reaction. Subsequently the temperature was kept below 80 °C. After 30 min, the mixture was distilled, collecting the fraction boiling between 97 and 106 °C. The crude trifluoro(phenyl)silane was redistilled and the 101–102 °C fraction⁹ collected (yield: 15 g, 93%).

Trifluoro(phenyl)silane (9.7 g, 0.06 mol) was added dropwise with cooling to an aqueous solution (5 cm^3) of ammonium fluoride (4.4 g, 0.12 mol) and after reaction had ceased a 2% solution (30 cm^3) of ammonium fluoride was added to dissolve the precipitated $[\text{NH}_4]_2[\text{SiPhF}_5]$. A solution of antimony trifluoride (5.4 g, 0.03 mol) in water (15 cm^3) was then added and the solution filtered if necessary. During 2–3 d at room temperature the solution deposited a white solid which was filtered and dried over P_2O_5 . Pure diphenylantimony fluoride* was obtained by recrystallisation from a 1:1 mixture of ethanol and carbon tetrachloride (yield: 6.2 g, 70%), m.p. 154 °C, after sublimation (lit.³ 157–158 °C) (Found: C, 48.7; H, 3.4. Calc. for $\text{C}_{12}\text{H}_{10}\text{FSb}$: C, 48.8; H, 3.4%). Major bands below 800 cm^{-1} in the i.r. spectrum were found at 746(sh), 732vs, 700vs, 662w, 622vw, 460s, 290vs, and 269s cm^{-1} .

Crystals suitable for X-ray diffractometry were obtained by vacuum sublimation at 135 °C.

* **CAUTION:** This compound should be handled with care, particularly when dry, as it causes irritation of the eyes, nose, and throat.

Structure Determination.—*Crystal data.* $\text{C}_{12}\text{H}_{10}\text{SbF}$, $M = 294.8$, Orthorhombic, $a = 8.18(1)$, $b = 11.04(1)$, $c = 12.02(1)$ Å, $U = 1085.5$ Å³, $Z = 4$, $D_c = 1.80$ g cm^{-3} , $F(000) = 568$, space group $P2_12_12_1$ from systematic absences, Mo- K_α radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 25.4$ cm^{-1} , crystal size ca. $0.5 \times 0.3 \times 0.3$ mm, $\mu R = 0.38$.

The unit-cell parameters, initially determined from oscillation and Weissenberg photographs, were refined using a Hilger and Watts four-circle diffractometer on 15 strong reflections with Mo- K_α radiation. 1170 Reflections measured in the range $0 \leq \theta \leq 28^\circ$ had an intensity greater than $3\sigma(I)$ and were considered observed. Intensities were corrected for Lorentz and polarisation effects but not for absorption or secondary extinction. Data reduction and subsequent calculations used the CRYSTALS programs¹⁰ and atomic scattering factors were taken from ref. 11.

A three-dimensional Patterson synthesis gave a possible position for the antimony atom and, after a structure-factor calculation, a difference-Fourier synthesis revealed positions for the fluorine and 12 carbon atoms. Four cycles of full-matrix least-squares refinement gave convergence at R 0.099 with isotropic thermal parameters and after four further cycles of refinement with anisotropic thermal parameters R converged at 0.046. Hydrogen atoms were placed at the calculated positions but were not refined in subsequent cycles. After three cycles of refinement and application of a four-coefficient Chebyshev weighting scheme, final convergence occurred at R 0.042. A final difference Fourier showed that, except in the vicinity of the antimony atom, there were no peaks >0.4 e Å⁻³. Atomic co-ordinates are given in Table 2, while

TABLE 2

Atomic co-ordinates ($\times 10^3$) with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Sb(1)	703.82(5)	248.70(9)	-22.50(4)
F(1)	465.3(6)	201.8(6)	42.9(6)
C(1)	791.0(9)	154.7(8)	119.9(8)
C(2)	846(1)	211.9(9)	215(1)
C(3)	916(1)	146(1)	301(1)
C(4)	927(2)	22(1)	293(1)
C(5)	872(2)	-38(1)	199(1)
C(6)	805(1)	29(1)	113(1)
C(7)	674(1)	425(1)	47(1)
C(8)	744(1)	522(1)	-11(1)
C(9)	716(2)	641(1)	28(1)
C(10)	623(2)	662(1)	118(2)
C(11)	551(2)	568(1)	175(1)
C(12)	575(1)	448(1)	139(1)

observed and calculated structure factors, anisotropic thermal parameters, and the calculated hydrogen positions are listed in Supplementary Publication No. SUP 22559 (11 pp.).†

DISCUSSION OF THE STRUCTURE

Figure 1 shows the structure of the compound and also gives the atom-numbering scheme; bond-distance and -angle data are collected in Table 3. This structure determination confirms the presence of strong intermolecular fluorine bridges which leads to infinite chains of SbPh_2F units lying parallel to the a axis (see Figure 2); individual molecules in the chain are related by the two-fold screw axis down a .

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 3

Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

Sb(1)-F(1)	2.166(5)	F(1)-Sb(1)-C(1)	83.9(3)
Sb(1)-C(1)	2.124(9)	F(1)-Sb(1)-C(7)	88.5(3)
Sb(1)-C(7)	2.132(11)	C(1)-Sb(1)-C(7)	99.9(4)
C(1)-C(2)	1.39(1)	C(6)-C(1)-C(2)	118(1)
C(2)-C(3)	1.39(1)	C(1)-C(2)-C(3)	121(1)
C(3)-C(4)	1.38(2)	C(2)-C(3)-C(4)	120(1)
C(4)-C(5)	1.39(2)	C(3)-C(4)-C(5)	121(1)
C(5)-C(6)	1.38(2)	C(4)-C(5)-C(6)	119(1)
C(1)-C(6)	1.39(1)	C(5)-C(6)-C(1)	121(1)
C(7)-C(8)	1.39(1)	C(12)-C(7)-C(8)	119(1)
C(8)-C(9)	1.42(2)	C(7)-C(8)-C(9)	119(1)
C(9)-C(10)	1.35(1)	C(8)-C(9)-C(10)	121(1)
C(10)-C(11)	1.36(2)	C(9)-C(10)-C(11)	121(1)
C(11)-C(12)	1.41(2)	C(10)-C(11)-C(12)	120(1)
C(7)-C(12)	1.40(1)	C(11)-C(12)-C(7)	120(1)
Sb...F(1')*	2.221(5)	F(1')...Sb(1)-F(1)	165.0(1)
		F(1')...Sb(1)-C(1)	83.4(3)
		F(1')...Sb(1)-C(7)	85.9(3)
		Sb(1')-F(1')...Sb(1)	140.2(3)

* Atoms carrying a prime are related to unprimed atoms by the transformation $x, y, z \rightarrow x + \frac{1}{2}, \frac{1}{2} - y, z$.

The geometry about the antimony atom is based on a distorted trigonal bipyramid with the phenyl groups and the lone pair of electrons on antimony occupying the equatorial positions and two fluorine atoms in the axial positions. The intramolecular Sb-F distance, 2.166(5) Å, is longer than that found⁸ in SbF₃ (1.92 Å) and a number of anionic antimony(III) fluorides, e.g. 1.94–2.08 Å in Na[SbF₄]⁶ and 1.91–2.08 Å in K[Sb₂F₇],¹² a function presumably of the presence of two lower electron-withdrawing groups. An unusual feature of the structure, however, is the small difference between the intra- and inter-molecular Sb-F distances. The value for the latter in the present compound is 2.221 Å, much shorter than that found in the majority of other fluorine-bridged antimony(III) compounds (cf. values of 2.61 in SbF₃;⁸ 2.66–2.86 in Na[SbF₄]⁶ and 2.41–2.57 Å in K[Sb₂F₇]¹²). In Cs[Sb₂F₇] the Sb-F-Sb bridge is symmetrical and the Sb-F distances are both 2.24 Å.¹³

The presence of a very strong Sb-F...Sb bridge is thus substantiated; this is probably a consequence of the presence of only a single fluorine atom and reduced competition for the vacant site in the antimony co-

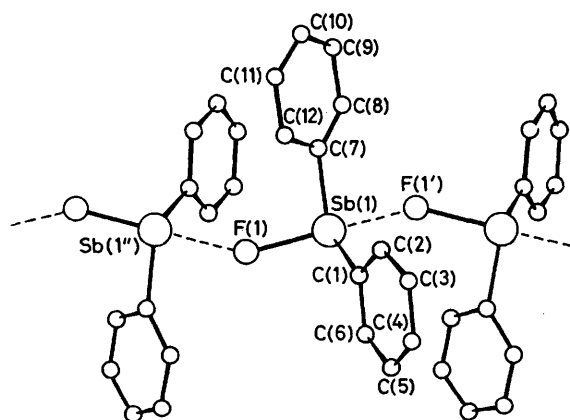


FIGURE 1 The structure of SbPh₂F showing the atom-numbering scheme

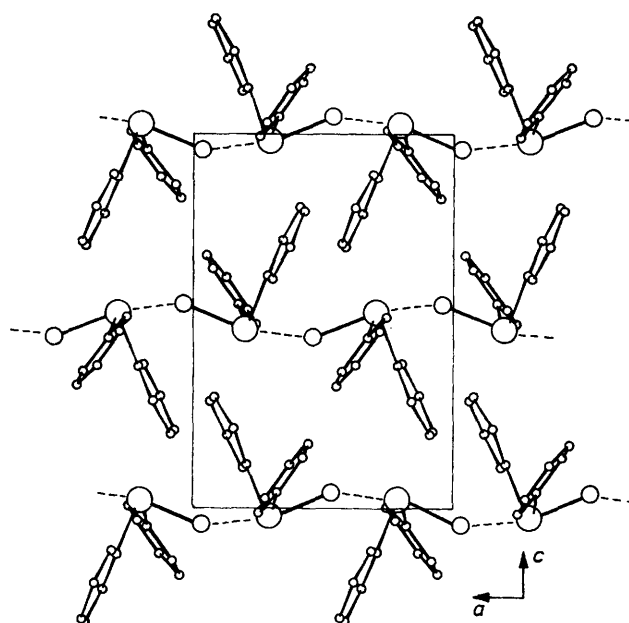


FIGURE 2 Projection of the unit-cell contents down the *b* axis

ordination sphere. The angle at the bridging fluorine atom is 140.2(3)°; for comparison purposes, values for this parameter are 154 and 163° in SbF₃⁸ and 130.9 and 148.2° in K[Sb₂F₇].¹² Again, Cs[Sb₂F₇] is different with the fluorine angle being 125.3°.¹³

The presence of the antimony lone pair leads to a reduction in (a) the angle between the phenyl groups from 120° in an ideal trigonal bipyramid to 99.9° and (b) the angles between the intra- and inter-molecular fluorine atoms and respectively C(1) and C(7) from 90° to a mean value of 85.4°.

TABLE 4

Selected torsion angles (°)	
F(1)-Sb(1)-C(1)-C(2)	-101.3
C(7)-Sb(1)-C(1)-C(2)	-13.8
F(1)-Sb(1)-C(7)-C(8)	-147.1
C(1)-Sb(1)-C(7)-C(8)	129.4
C(1)-Sb(1)-F(1)-Sb(1')	164.9
C(7)-Sb(1)-F(1)-Sb(1')	64.9
F(1')-Sb(1)-F(1)-Sb(1')	132.8

* Atoms carrying a double prime are related to unprimed atoms by the transformation $x, y, z \rightarrow \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z}$.

The phenyl groups are planar, with the maximum deviation of any atom from the appropriate best plane being 0.007 Å. A number of torsion angles are included in Table 4 showing among other things the relative orientation of the phenyl groups.

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