Crystal Structures of Diphenylantimony(v) Tribromide, Dibromide Chloride, and Bromide Dichloride

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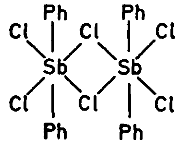
The crystal structures of $SbBr_3Ph_2$ (1), $SbBr_2Ph_2Cl$ (2), and $SbBrPh_2Cl_2$ (3) have been determined by Patterson and Fourier methods from *X*-ray diffractometer data and refined by least squares to *R* 0.080 (1) (997 reflections), 0.046 (2) (917), and 0.058 (3) (979) respectively. Crystals of all the compounds are orthorhombic, space group $Cmc2_1$, $Z = 4$, with unit-cell dimensions: (1) $a = 15.49(1)$, $b = 10.96(1)$, $c = 8.07(1)$; (2) $a = 15.44(1)$, $b = 10.97(1)$, $c = 7.93(1)$; (3) $a = 15.25(1)$, $b = 11.00(1)$, $c = 7.83(1)$ Å. In all cases the heavy atoms lie on a mirror plane and the structure contains antimony in distorted trigonal-bipyramidal co-ordination, with a bromine atom and two phenyl groups (related by the mirror plane) in the equatorial positions. Antimony–bromine equatorial distances decrease from 2.478(3) to 2.446(4) Å with increasing chlorine content; the Sb–C distances show a similar but smaller variation and are close to 2.14 Å. The two bonds from antimony to the axial halogen atoms have different lengths in all three compounds, with the halogen at the greater distance being involved in weak intermolecular bonding to a neighbouring antimony atom. The intermolecular bonds vary between 3.433(3) and 3.363(5) Å. Problems arise in the case of (2) since there is disorder in the bromine–chlorine occupancy of the two axial positions. A major consequence of the intermolecular interaction is an increase in the C–Sb–C angle from the expected value of 120 to *ca.* 154°.

DIPHENYLANTIMONY(V) trichloride can be recrystallized from dilute hydrochloric acid as, probably, an octahedrally co-ordinated monohydrate,[1] and converted by heating *in vacuo* into the anhydrous compound. Recently the structure of the latter has been determined [2] showing the presence of dimeric units (see below) in which the antimony atom is again in octahedral co-ordination.



This behaviour raises again the problem of the solid-state structures of Group 5 compounds which from their stoicheiometry would be expected to be five-co-ordinate. Many examples are, of course, known where trigonal-bipyramidal geometry is found and there is also the unusual square-pyramidal arrangement about antimony in the pentaphenyl derivative. Equally, there are a number of examples where the expected five-co-ordination is not found and structures based on tetrahedral and/or octahedral units appear.

This paper describes a structural investigation of the recently prepared [3] organoantimony trihalides $SbBr_3Ph_2$, $SbBr_2Ph_2Cl$, and $SbBrPh_2Cl_2$ which was carried out in an attempt to define more closely the relationship between structural type and formal stoicheiometry.

EXPERIMENTAL

The compounds $SbBr_3Ph_2$ (1), $SbBr_2Ph_2Cl$ (2), and $SbBrPh_2Cl_2$ (3) were prepared as described previously;[3] suitable crystals were obtained from chloroform solutions and sealed in capillaries.

Crystal Structure of $SbBr_3Ph_2$ (1).—*Crystal data.* $C_{12}H_{10}Br_3Sb$, $M = 515.5$, Orthorhombic, $a = 15.49(1)$, $b = 10.96(1)$, $c = 8.07(1)$ Å, $U = 1\,378.9$ Å^3, $Z = 4$, $D_c = 2.482$ g cm^{-3}, $F(000) = 952$, space group $Cmc2_1$, from systematic absences and subsequent refinement, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 112.1 cm^{-1}, crystal size *ca.* $0.6 \times 0.3 \times 0.3$ mm, $\mu R = 1.7$.

The unit-cell dimensions originally obtained from oscillation and Weissenberg photographs were refined by a least-squares procedure on the positions of 18 strong reflections, accurately measured on a Hilger and Watts four-circle diffractometer. Intensity data were collected on the diffractometer by use of an ω—2θ scan in the range $0 \leqslant \theta \leqslant 30°$ using Mo-K_α radiation. The intensities were corrected for Lorentz and polarization effects and an absorption correction appropriate for a cylinder was applied. A total of 1 849 reflections was measured, but after averaging the equivalent pairs and considering only reflections with $I \geqslant 4.0\sigma(I)$ a total of 997 reflections remained. Data reduction and subsequent calculations used the CRYSTALS programs:[4] atomic scattering factors were taken from ref. 5.

The initial ambiguity concerning the space group, *i.e.* $Cmc2_1$, *Cmcm*, or *C2cm* (standard setting *Ama*2), was resolved by successful refinement of the structure in $Cmc2_1$ with the antimony atom lying on a mirror plane. Attempts at refinement in the alternative space groups were unsuccessful.

A three-dimensional Patterson synthesis gave a possible position for the antimony at 0, 0.18, 0. After a structure-factor calculation a difference-Fourier synthesis phased on this atom showed possible positions for the three bromine atoms. These also lay on the mirror plane and were loaded with a site occupancy factor of 0.5. After two cycles of full-matrix least-squares refinement with isotropic thermal parameters a second difference-Fourier synthesis gave positions for the six carbon atoms in the independent phenyl group. Two further cycles of refinement gave convergence at *R* 0.162, and at *R* 0.090 after three cycles of refinement with anisotropic thermal parameters. The hydrogen positions were then calculated but were not refined in subsequent cycles. Application of a four-coefficient (41 371.6, 65 051.9, 30 846.0, and 7 453.7) Chebyshev weighting scheme gave final convergence at *R* 0.080 after three further cycles of full-matrix refinement. A final difference-Fourier synthesis showed no peaks >0.4 e Å^{-3}

except in the vicinity of the heavy atoms. Application of an anomalous-dispersion correction, even when the complete unaveraged reflection file was used, led to no improvement in the state of the refinement.

Crystal Structure of $SbBr_2Ph_2Cl$ (2).—*Crystal data.* $C_{12}H_{10}Br_2ClSb$, $M = 471.2$, $a = 15.44(1)$, $b = 10.97(1)$, $c = 7.93(1)$ Å, $U = 1\,343.2$ Å^3, $D_c = 2.332$ g cm^{-3}, $F(000) = 880$, μ(Mo-K_α) = 85.5 cm^{-1}, crystal size *ca.* 0.6 × 0.15 × 0.15 mm, $\mu R = 0.65$. Other details as for (1).

Oscillation and Weissenberg photographs showed this compound to be isostructural with (1). Intensities were collected for 917 reflections in the range $0 \leqslant \theta \leqslant 30°$ for which $I \geqslant 3.0\sigma(I)$ and an appropriate absorption correction was applied. The solution and refinement of the structure followed that outlined above and positions for all atoms were found. After two cycles of full-matrix least-squares refinement however, even though R was reduced to 0.171, the isotropic thermal parameter of the atom designated as an axial chlorine atom was low (0.015) and the distance from antimony was 2.60 Å. The second bromine atom was expected to occupy the other axial position but the Sb–Br distance was 2.48 Å and the bromine had a high (0.077) thermal parameter. These data were taken as indication of disorder in the occupancy of the axial positions and subsequent calculations therefore involved the site-occupancy factors of the axial atoms as variables. Two cases were considered, *i.e.* where both atoms were chlorine or both were bromine. Since both approaches gave the same results the following discussion is in terms of the former approach.

After five cycles of full-matrix refinement with anisotropic thermal parameters the hydrogen atoms were placed at the calculated positions and the R value converged at 0.048. The site-occupation factors however had refined to values of 0.763 (11) for Cl(1) and 0.830 (10) for Cl(2) giving the total electron count in the two axial positions as 27.1. Since the compound contains a chlorine and a bromine atom in these positions the total electron count should be 26.0, *i.e.* $(17 + 35)/2$, and in subsequent refinement the total electron count in the two axial positions was constrained to this value. Under these conditions, convergence was reached at R 0.046 after application of a Chebyshev weighting scheme and four cycles of full-matrix refinement. The site-occupation factors for Cl(1) and Cl(2) were now 0.714(6) and 0.815(6) respectively. A final difference map showed no peaks with an intensity >0.4 e Å^{-3} except those close to the heavy atoms.

Crystal Structure of $SbBrPh_2Cl_2$ (3).—*Crystal data.* $C_{12}H_{10}BrCl_2Sb$, $M = 426.8$, $a = 15.25(1)$, $b = 11.00(1)$, $c = 7.83(1)$ Å, $U = 1\,313.5$ Å^3, $D_c = 2.158$ g cm^{-3}, $F(000) = 808$, μ(Mo-K_α) = 57.2 cm^{-1}, crystal size *ca.* 0.4 × 0.2 × 0.2 mm, $\mu R = 0.6$. Other details as for (1).

Oscillation and Weissenberg photographs clearly indicated that this compound was isostructural with (1) and (2) and the solution closely followed those described above. Intensity data were measured for 979 reflections which had $I \geqslant 3.0\sigma(I)$ and an appropriate absorption correction was applied. The antimony position was obtained from a Patterson map and difference-Fourier syntheses phased on this atom gave positions for the other non-hydrogen atoms. Three cycles of full-matrix least-squares refinement with isotropic thermal parameters gave convergence at R 0.121 and at R 0.064 after four cycles with anisotropic thermal parameters. Placing the hydrogen atoms at their calculated positions and application of a Chebyshev weighting scheme gave final convergence at R 0.058 after two further cycles of refinement. Except in the vicinity of the heavy atoms, a final difference map showed no peaks >0.4 e Å^{-3}.

Atomic co-ordinates for compounds (1), (2), and (3) are given in Tables 1, 2, and 3 respectively. Observed and calculated structure factors and anisotropic thermal parameters for all the compounds are listed in Supplementary Publication No. SUP 22421 (37 pp.).* The numbering of the atoms is shown in Figure 1.

TABLE 1

Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses, for (1)

Atom	x/a	y/b	z/c
Sb(1)	0	1 861(1)	0
Br(1)	0	3 946(2)	1 191(5)
Br(2)	0	2 637(3)	−2 989(3)
Br(3)	0	983(3)	3 090(3)
C(1)	−1 350(8)	1 435(11)	−203(18)
C(2)	−1 672(10)	392(11)	567(23)
C(3)	−2 569(10)	220(15)	497(24)
C(4)	−3 086(9)	1 075(16)	−277(25)
C(5)	−2 742(9)	2 108(16)	−995(31)
C(6)	−1 864(8)	2 262(14)	−973(25)
H(2)	−1 246	−203	1 160
H(3)	−2 859	−512	982
H(4)	−3 743	910	−434
H(5)	−3 151	2 729	−1 429
H(6)	−1 587	3 013	−1 562

TABLE 2

Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses, for (2)

Atom	x/a	y/b	z/c
Sb(1)	0	1 836(1)	0
Br(1)	0	3 914(2)	1 176(3)
Cl(1) [a]	0	2 605(3)	−3 000(4)
Cl(2) [b]	0	966(2)	3 067(3)
C(1)	−1 353(5)	1 422(8)	−141(7)
C(2)	−1 691(6)	385(9)	584(14)
C(3)	−2 582(6)	204(10)	542(15)
C(4)	−3 117(6)	1 061(11)	−224(18)
C(5)	−2 735(7)	2 118(11)	−956(20)
C(6)	−1 853(7)	2 270(10)	−931(15)
H(2)	−1 290	−217	1 150
H(3)	−2 839	−550	1 055
H(4)	−3 762	934	−263
H(5)	−3 138	2 760	−1 386
H(6)	−1 595	2 990	−1 502

[a] Site occupancy 0.714(6). [b] Site occupancy 0.815(6).

TABLE 3

Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses, for (3)

Atom	x/a	y/b	z/c
Sb(1)	0	1 786(1)	0
Br(1)	0	3 822(3)	1 250(6)
Cl(1)	0	2 543(7)	−2 921(8)
Cl(2)	0	928(4)	3 024(6)
C(1)	−1 364(6)	1 390(9)	−141(19)
C(2)	−1 728(8)	345(9)	577(18)
C(3)	−2 588(9)	186(10)	587(19)
C(4)	−3 166(8)	1 060(13)	−218(22)
C(5)	−2 775(9)	2 118(12)	−948(20)
C(6)	−1 878(8)	2 243(10)	−956(16)
H(2)	−1 330	−292	1 085
H(3)	−2 846	−556	1 172
H(4)	−3 818	929	−277
H(5)	−3 150	2 777	−1 452
H(6)	−1 597	2 946	−1 553

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

RESULTS AND DISCUSSION

Bond distances and angles are summarized in Tables 4, 5, and 6 respectively for compounds (1), (2), and (3). The major features in the structures of the three compounds are as follows. (*a*) Distorted trigonal-bipyramidal co-ordination about antimony with a bromine atom and the two phenyl groups occupying the equatorial positions; the chlorine atoms in $SbBr_2Ph_2Cl$ and $SbBrPh_2Cl_2$, as expected from established correlations,[6] are found in axial positions. (*b*) The presence of weak intermolecular interactions between an axial halogen atom and a neighbouring antimony atom. A consequence of this is an increase in the angle between the two phenyl groups from the expected value of 120° to *ca.* 154°.

TABLE 4

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for (1)

Sb(1)–Br(1)	2.478(3)	Br(1)–Sb(1)–Br(2)	93.4(1)
Sb(1)–Br(2)	2.557(3)	Br(1)–Sb(1)–Br(3)	88.3(1)
Sb(1)–Br(3)	2.673(3)	Br(1)–Sb(1)–C(1)	103.3(3)
Sb(1)–C(1)	2.149(12)	Br(2)–Sb(1)–Br(3)	178.3(1)
		Br(2)–Sb(1)–C(1)	90.0(4)
C(1)–C(2)	1.39(2)	Br(3)–Sb(1)–C(1)	89.6(4)
C(2)–C(3)	1.40(2)	C(1)–Sb(1)–C(1′) [a]	153.4(7)
C(3)–C(4)	1.38(3)		
C(4)–C(5)	1.38(3)	Sb(1)–C(1)–C(2)	119.5(10)
C(5)–C(6)	1.37(2)	Sb(1)–C(1)–C(6)	117.5(10)
C(1)–C(6)	1.36(2)		
C(2)–C(1)–C(6)	122.8(12)	C(3)–C(4)–C(5)	121.5(12)
C(1)–C(2)–C(3)	116.6(14)	C(4)–C(5)–C(6)	118.7(15)
C(2)–C(3)–C(4)	120.1(14)	C(5)–C(6)–C(1)	120.4(14)

Sb(1) · · · Br(3″) [b]	3.477(3)
Sb(1)–Br(3) · · · Sb(1″)	137.4(1)
Br(1)–Sb(1) · · · Br(3″)	176.5(2)
Br(2)–Sb(1) · · · Br(3″)	83.1(4)
Br(3)–Sb(1) · · · Br(3″)	95.2(1)
C(1)–Sb(1) · · · Br(3″)	76.8(3)

[a] Atoms carrying a prime are related to unprimed atoms by the transformation $x, y, z \rightarrow \bar{x}, y, z$. [b] Atoms carrying two primes are related to unprimed atoms by the transformation $x, y, z \rightarrow \bar{x}, \bar{y}, \frac{3}{2} + z$.

TABLE 5

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for (2)

Sb(1)–Br(1)	2.462(2)	Br(1)–Sb(1)–Cl(1)	92.7(1)
Sb(1)–Cl(1) [a]	2.522(3)	Br(1)–Sb(1)–Cl(2)	89.2(1)
Sb(1)–Cl(2) [b]	2.611(3)	Br(1)–Sb(1)–C(1)	102.5(3)
Sb(1)–C(1)	2.141(8)	Cl(1)–Sb(1)–Cl(2)	178.1(1)
		Cl(1)–Sb(1)–C(1)	91.2(4)
C(1)–C(2)	1.38(1)	Cl(2)–Sb(1)–C(1)	88.3(4)
C(2)–C(3)	1.39(1)	C(1)–Sb(1)–C(1′) [c]	154.8(5)
C(3)–C(4)	1.39(2)		
C(4)–C(5)	1.42(2)	Sb(1)–C(1)–C(2)	121.6(7)
C(5)–C(6)	1.37(2)	Sb(1)–C(1)–C(6)	115.6(7)
C(1)–C(6)	1.36(2)		
C(2)–C(1)–C(6)	122.8(8)	C(3)–C(4)–C(5)	118.9(9)
C(1)–C(2)–C(3)	118.9(9)	C(4)–C(5)–C(6)	120.2(10)
C(2)–C(3)–C(4)	120.1(10)	C(5)–C(6)–C(1)	119.2(10)

Sb(1) · · · Cl(2″) [c]	3.433(3)
Sb(1)–Cl(2) · · · Sb(1″)	138.0(1)
Br(1)–Sb(1) · · · Cl(2″)	175.7(1)
Cl(1)–Sb(1) · · · Cl(2″)	83.0(1)
Cl(2)–Sb(1) · · · Cl(2″)	95.1(1)
C(1)–Sb(1) · · · Cl(2″)	77.7(3)

[a] Site occupancy 0.714(6). [b] Site occupancy 0.815(6). [c] See footnotes to Table 4.

TABLE 6

Bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for (3)

Sb(1)–Br(1)	2.446(4)	Br(1)–Sb(1)–Cl(1)	93.5(2)
Sb(1)–Cl(1)	2.433(5)	Br(1)–Sb(1)–Cl(2)	88.2(2)
Sb(1)–Cl(2)	2.548(4)	Br(1)–Sb(1)–C(1)	102.0(3)
Sb(1)–C(1)	2.128(10)	Cl(1)–Sb(1)–Cl(2)	178.3(2)
		Cl(1)–Sb(1)–C(1)	91.2(4)
C(1)–C(2)	1.40(2)	Cl(2)–Sb(1)–C(1)	88.4(4)
C(2)–C(3)	1.38(2)	C(1)–Sb(1)–C(1′) *	155.7(5)
C(3)–C(4)	1.45(2)		
C(4)–C(5)	1.43(2)	Sb(1)–C(1)–C(2)	122.4(8)
C(5)–C(6)	1.38(2)	Sb(1)–C(1)–C(6)	116.3(8)
C(1)–C(6)	1.38(2)		
C(2)–C(1)–C(6)	121.5(10)	C(3)–C(4)–C(5)	117.6(11)
C(1)–C(2)–C(3)	120.4(11)	C(4)–C(5)–C(6)	119.8(12)
C(2)–C(3)–C(4)	120.2(12)	C(5)–C(6)–C(1)	120.1(11)

Sb(1) · · · Cl(2″) *	3.363(5)
Sb(1)–Cl(2) · · · Sb(1″)	139.1(1)
Br(1)–Sb(1) · · · Cl(2″)	176.2(1)
Cl(1)–Sb(1) · · · Cl(2″)	82.7(2)
Cl(2)–Sb(1) · · · Cl(2″)	95.6(1)
C(1)–Sb(1) · · · Cl(2″)	78.2(3)

* See footnotes to Table 4.

In all three structures there is a mirror plane passing through the antimony and halogen atoms, and in addition the atoms Sb(1), Br(1), C(1), and C(1′) are also closely planar. The carbon atoms of the phenyl rings are coplanar, the maximum deviation of any atom from the appropriate best plane being *ca.* 0.01 Å.

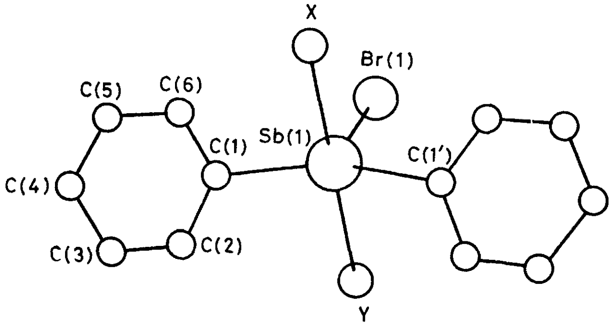

FIGURE 1 View of the molecule and numbering of the atoms in: (*a*) $SbBr_3Ph_2$ (1) [X = Br(2), Y = Br(3)]; (*b*) $SbBr_2Ph_2Cl$ (2) [X = Cl(1) ($\equiv Br_{0.4}Cl_{0.6}$), Y = Cl(2) ($\equiv Br_{0.6}Cl_{0.4}$)]; (*c*) $SbBrPh_2Cl_2$ (3) [X = Cl(1), Y = Cl(2)]

Bond Distances.—The present compounds are the first to be investigated structurally in which antimony(V)–bromine bonds are present in a trigonal-bipyramidal environment. In this arrangement, bonds to atoms in equatorial positions are invariably shorter than those to the same atom in the axial positions; this general correlation is borne out by the present data. The data also show the structural consequences of minor changes in constitution. For example, the antimony–bromine (equatorial) distances decrease from 2.478(3) in $SbBr_3Ph_2$ to 2.462(2) for the dibromide to 2.446(4) Å for the monobromide. The mean value (2.462 Å), is considerably shorter than any previously quoted Sb–Br bond distance [7] and, within the limits of the quoted estimated standard deviations, the progressive bond shortening of 0.016 Å as the bromine atoms in the axial positions are replaced successively by chlorine is significant. A similar shortening is suggested for the Sb–C bond but the effect is less pronounced and, since the estimated standard deviations are higher with the lighter carbon atom, cannot be shown to be statistically significant. The shortening of both bonds would appear to be a direct consequence of the increased electronegativity of the atoms in the axial positions.

In compounds (1) and (3) there is a striking difference (*ca.* 0.11 Å) in the bond distances to the axial atoms. This is clearly a consequence of the weak intermolecular interaction, mentioned earlier, resulting from electron donation from an axial halogen atom to a neighbouring antimony atom. The effect is to weaken the bond between the donor halogen and the central antimony atom. The difference in the axial bond lengths with compound (2) is smaller (0.09 Å) and is influenced by disorder in the structure.

During refinement of the structure of $SbBr_2Ph_2Cl$ it became clear at an early stage that the halogen occupancy of the axial positions was disordered. In some respects this is a surprise since in terms of donor ability, which should have a large bearing on the formation of intermolecular bonds, an axial chlorine atom would be preferred over bromine. If this had been the case, fixing the chlorine in the bridging position would have removed any cause for disorder. The structure, however, was disordered and, although the bromine and chlorine atoms might have been equally distributed over the axial positions, refinement of the occupation factors led to significantly different values at Cl(1) and Cl(2). These values lead to electron counts of 12.14 and 13.86 respectively and are equivalent to the Cl(1) position being occupied by 0.60 Cl and 0.40 Br and the Cl(2) position by 0.40 Cl and 0.60 Br. An unexpected consequence of the disorder is that the bridging halogen atom [Cl(2)] has in fact a greater bromine occupancy.

The non-bridging axial halogen distances, *i.e.* 2.557(3) for (1) and 2.433(5) Å for (3), are expected to be greater than those for the same type of atom in an equatorial position. The present data confirm this statement for the tribromide but the only experimental value for the distance between antimony and a chlorine atom in an equatorial position (2.29 Å) comes from a structural study of $SbCl_5$ at –30 °C.[8] Since no standard deviations are quoted it is difficult to know if this equatorial distance is significantly shorter than the quoted axial distances (2.34 Å).* However, the Sb–Cl(axial) distance observed here is comparable with the values found for $SbMe_3Cl_2$ (2.49 Å)[9] and $SbPh_3Cl_2$ [2.458(4) and 2.509(4) Å],[10] but the actual length is probably influenced by the nature of the other attached groups.

The weak intermolecular interaction which is present in all three compounds leads to zigzag chains of molecules at $x = 0$ and $x = 0.5$ running parallel to c (see Figure 2). The antimony–halogen distance, which decreases from 3.477 in compound (1) to 3.363 Å in (3), is significantly shorter than the sum of the appropriate van der Waals radii, *i.e.* 4.2 and 4.0 Å respectively. The value in compound (2), 3.433 Å, is closer to that for $SbBr_3Ph_2$ and reflects the greater bromine content of the bridging axial position.

Bond Angles.—There is little deviation from the 180° angle which is expected for the axial atoms in all three compounds, but the angle between the equatorial bromine and the non-bridging axial atom is invariably $>90°$ while the corresponding angle with the bridging halogen is $<90°$. There is a similar difference in angles at antimony between the axial halogens and the carbon atom in the independent phenyl group, although in compound (1) the difference is too small to be considered significant.

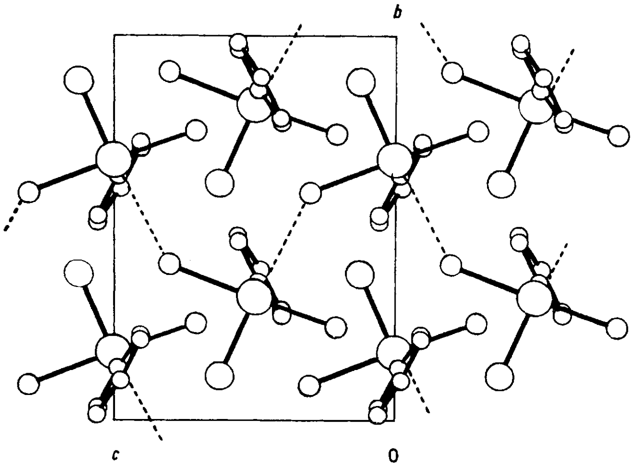

FIGURE 2 Projection of the unit-cell contents down *a* showing the intermolecular interaction between an axial halogen and antimony. The symmetry-related phenyl group has been omitted for clarity

The orientation of the independent phenyl group is best described by the torsion angle of the Sb(1)–C(1) bond; values of –125.7 and 140.3° for Br(1)–Sb(1)–C(1)–C(2) and Cl(1)–Sb(1)–C(1)–C(2) have been found for compound (3) and these are typical.

The major distortion from trigonal-bipyramidal geometry in all three structures is shown by a value of *ca.* 154° for the C(1)–Sb(1)–C(1') angle; there is also a decrease in the other two 'equatorial' angles to *ca.* 102°. In all three cases, however, the equatorial angles at antimony sum to 360°, indicating planarity.

This large distortion of the angle between the phenyl groups is directly attributed to the intermolecular interaction between the central antimony and the appropriate axial halogen atom. This is itself a consequence of the co-ordinative unsaturation of the antimony atom and the presence of available lone-pair electron density on the axial halogen atoms. In the tribromide the donor halogen atom is necessarily a bromine atom while in $SbBrPh_2Cl_2$ it is clear that the single bromine atom preferentially occupies the equatorial site as a consequence

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* *Note added at proof:* A recalculation using the data in ref. 8 gave convergence at R 0.108 with isotropic thermal parameters and Sb–Cl distances of 2.28(4) and 2.34(4) Å. The difference between the axial and equatorial distances is thus not significant.

of its smaller electronegativity, and the bridging atom is therefore chlorine. As mentioned above it is surprising that in the disordered compound, $SbBrPh_2Cl_2$, the bridging halogen has a higher bromine content.

There is, on the surface, little similarity between the solid-state structures adopted by $SbPh_2Cl_3$ on the one hand and the compounds in the series $SbBr_nPh_2Cl_{3-n}$ on the other. In the first the acceptor power of the antimony is sufficiently enhanced by the presence of three chlorine atoms to promote the formation of two relatively strong chlorine bridges [Sb $\cdots$ Cl(bridge) 2.839(4) Å] in a dimer. On substitution of one chlorine by bromine the new structure appears with an increase in the Sb $\cdots$ Cl(bridge) distance to 3.363 Å. This is a surprising change and shows again the structural consequences of minor changes in constitution.

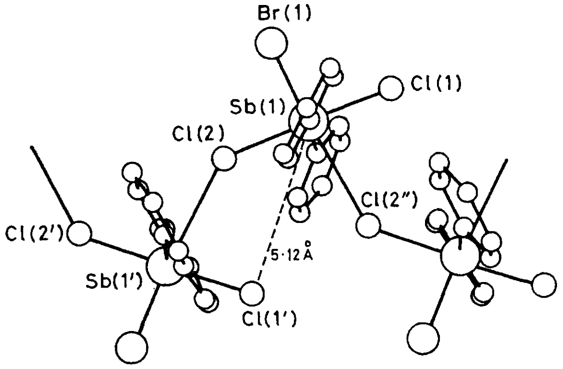

FIGURE 3 Section of the $SbBr_nPh_2Cl_{3-n}$ structure showing its relationship to the $(SbPh_2Cl_3)_2$ structure

The relationship between the structures of $SbBr_nPh_2Cl_{3-n}$ and $SbPh_2Cl_3$ can be shown by considering a section of the chain structure of the former (see Figure 3). Conversion into the $(SbPh_2Cl_3)_2$ structure has the following requirements. (*a*) Distortion of the Ph–Sb–Ph angle from *ca.* 154 to 180°. The other bond angles are already close to 90° as required for octahedral coordination about antimony. (*b*) Breaking of one intermolecular antimony–halogen bond, *i.e.* Sb(1) $\cdots$ Cl(2'') and formation of a second intermolecular bridge with the other axial halogen atom, *i.e.* Sb(1) $\cdots$ Cl(1'). The latter distance is *ca.* 5.12 Å for compound (2). (*c*) Rotation of one molecule to reduce both the Sb(1)–Cl(1') distance and simultaneously the Sb(1)–Cl(2) $\cdots$ Sb(1') angle to *ca.* 99° as found in $(SbPh_2Cl_3)_2$.

We thank Professor T. J. King for obtaining the data and for help in the solution, and Dr. M. J. Begley for helpful discussions.

[8/1114 *Received, 14th June*, 1978]

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