427. *The Crystal and Molecular Structure of Antimony Tribromide: β-Antimony Tribromide.*

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There are two forms of antimony tribromide. The crystal structure of β-$SbBr_3$, m. p. 96°, has been determined. The crystal is orthorhombic, space group, *Pbnm*, and contains discrete pyramidal molecules of antimony tribromide. The mean Sb–Br distance, determined from projections having an overall reliability factor of 12%, is 2·49 ± 0·03 Å, and the mean Br–Sb–Br angle is 95·1° ± 2·4°.

DURING other work,[1] it was observed that antimony tribromide could apparently be obtained in one or other of two crystal " habits," acicular and bipyramidal. Various morphological measurements on antimony tribromide have been reported,[2-4] but they are in no way reconcilable with one another. To clarify the issue and to obtain an accurate estimate of the antimony–bromine distance in the solid state, as distinct from the vapour,[5,6] the crystal structure of antimony tribromide has been determined.

It soon became clear that the two " habits " were, in fact, derived from two quite different antimony tribromide structures, which we shall call the α- and the β-structure. The present paper is concerned only with the structure of β-antimony tribromide.

EXPERIMENTAL

Preparation of the Crystals.—When a warm carbon disulphide solution of antimony tribromide is cooled, needle-like crystals of α-antimony tribromide are obtained as the main product, contaminated with a few rather irregular bipyramidal crystals of the β-form. High yields of β-crystals were occasionally obtained by seeding solutions of antimony tribromide in carbon disulphide with freshly crushed bipyramidal crystals, although the α-form appeared more often, there being no clear correlation with the conditions of crystallisation. Reported values for the m. p. of antimony tribromide [7] range from 90·0° to 96·6°. We find the m. p. of β-antimony tribromide to be 96·0° ± 0·5°.

Because of the very hygroscopic nature of the crystals and their irregular appearance, no other optical properties were established except straight extinction. Crystals of diameter ∼0·2 mm. were sealed into Lindemann glass tubing. Once sealed they were stable indefinitely.

X-Ray Data.—β-$SbBr_3$, $M = 361·5$, orthorhombic bipyramidal with *a* as the bipyramidal axis. $a = 6·68 ± 0·01$, $b = 8·25 ± 0·01$, $c = 9·96 ± 0·01$ Å, $U = 549$ Å³, as determined from Cu-$K_α$ single-crystal oscillation and zero-, first-, and second-layer Weissenberg photographs about each of the three principal axes. $D_m = 4·27$ (by displacement). Groth [8] gives 4·15 g./c.c. Despite this difference we deduce that there are four molecules in the unit cell, $D_c = 4·38$, so that $F(000) = 624$.

The only systematically absent reflections are $0kl$ with k odd and $h0l$ when $h + l$ is odd. There are thus two possibilities for the space group, *Pbnm* (D_{2h}^{16} No. 62) and *Pbn2₁* (C_{2v}^9 No. 33). Statistical $N(z)$ plots [9] for the $0kl$ and $h0l$ zones indicate that the corresponding projections have centres of symmetry. This is possible only for the space group *Pbnm*, in agreement with Lindqvist and Niggli's conclusion [10] for the similar antimony trichloride structure.

[1] Hulme and Szymanski, *Acta Cryst.*, 1960, **13**, 1024.
[2] Nicklès, *J. prakt. Chem.*, 1860, **79**, 15; *Compt. rend.*, 1861, **52**, 396; *J. Pharm. Chim.*, 1862, **41**, 145.
[3] Cooke, *Proc. Amer. Acad.*, 1877, **13**, 1, 72; *Amer. J. Sci.*, 1880, **19**, 469; *Chem. News*, 1880, **44**, 221, 233, 245, 255.
[4] Slawson, *Amer. Min.*, 1922, **7**, 173.
[5] Hassel and Sandbo, *Z. phys. Chem.*, 1938, B, **41**, 75.
[6] Gregg, Hampson, Jenkins, Jones, and Sutton, *Trans. Faraday Soc.*, 1937, **33**, 852.
[7] Mellor, " Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1929, Vol. IX, p. 494.
[8] Groth, *Chem. Kryst.*, 1906, **1**, 227; Kaye and Laby, " Tables of Physical and Chemical Constants," Longmans, Green & Co., London, 10th edn., 1948, p. 141.
[9] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.
[10] Lindqvist and Niggli, *J. Inorg. Nuclear Chem.*, 1956, **2**, 345.

Zero-layer integrated Weissenberg photographs about the b- and the c-axis were obtained with Mo-K_α radiation to minimise absorption errors ($\mu_{Cu} = 690$, $\mu_{Mo} = 290$ cm.$^{-1}$). The intensity of each reflection, recorded by the multiple-film technique, was estimated visually. No allowance was made for absorption or extinction. This procedure was subsequently justified in that there was no significant change in the final R factor for the c-axis data when absorption and extinction corrections were applied; these effects were thus adequately minimised by the use of small crystals and molybdenum radiation. The intensities, after Lorentz-polarisation correction, gave the sets of structure amplitudes recorded in Tables 2a and b. For the corresponding Cu-K_α data about the a-axis, absorption and extinction corrections became very important. By using a small, almost spherical crystal, the appropriate transmission factors for a spherical sample at $\mu R = 7$ could be applied to correct for absorption.[11] A correction for extinction was made by the method of Pinnock, Taylor, and Lipson.[12] The Cu-K_α data recorded in Table 2c are corrected for both these effects.
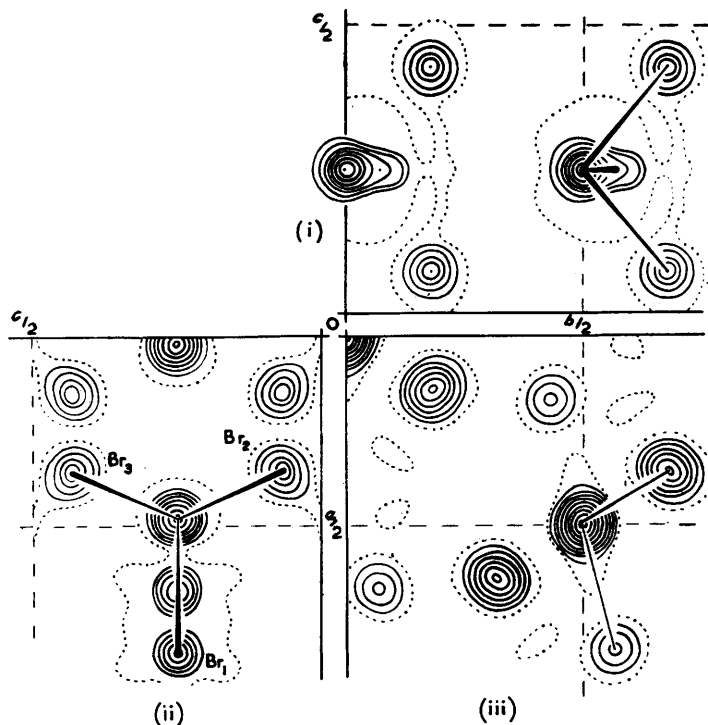

FIG. 1. Electron density projections. Zero contour (broken) at 1 e/Å². Thereafter contours are at intervals of 2 e/Å². (i) From Cu data, projected on to (100), symmetry *pgm*. (ii) From Mo data, projected on to (010), symmetry *cmm*. (iii) From Mo data, projected on to (001), symmetry *pgg*.

Structure Determination.—Patterson vector maps for the b- and the c-axis were obtained from the molybdenum data. No immediate interpretation was apparent and recourse was made to the sign product method,[13] there being a dozen sizable unitary F values about the c-axis. The cell dimensions of β-antimony tribromide were closely proportional to those obtained by Lindquist *et al.*[10] for antimony trichloride. These molecules might be expected to pack in a similar manner, so that the fractional co-ordinates quoted by them for antimony trichloride were applied to β-antimony tribromide. The observed structure amplitudes for β-antimony tribromide were scaled to give the best agreement possible with the structure

[11] Buerger, " Crystal Structure Analysis," Wiley, New York, 1960, Table 9, p. 215.
[12] Pinnock, Taylor, and Lipson, *Acta Cryst.*, 1956, **9**, 175.
[13] Cochran, *Acta Cryst.*, 1952, **5**, 65.

factors calculated on the basis of antimony and bromine atoms in the positions found by Lindquist *et al.* for antimony and chlorine atoms. An error synthesis then confirmed these positions and led to an R factor of 27·5%. Four stages of refinement by difference synthesis reduced R to a final value of 13·4%, corresponding to the electron density projection shown in Fig. 1(iii). These R factors, $\sum(F_o \sim F_c)/\sum F_o$, were calculated with the inclusion of unobserved reflections in the following manner. When F_c exceeded the locally observed minimum F_o ($_mF_o$), a term ($_mF_o \sim F_c$) was included in the numerator without any corresponding addition to the denominator. When F_c was less than $_mF_o$, no terms were included in either the numerator or the denominator.

It was then possible, by using the x co-ordinates obtained from the c-axis refinement, to interpret the b-axis Patterson map, and obtain an approximate set of z-co-ordinates. Two stages of refinement by least squares and one difference synthesis resulted in a final value of 10·4% for R, calculated as above. The corresponding electron-density projection is shown in Fig. 1(ii). The final co-ordinates obtained from the two projections are listed in Table 1.

TABLE 1.

Final fractional atomic co-ordinates and corresponding co-ordinates
(with e.s.d. values in parentheses), in Å.

Atom	x	y	z	
Sb	0·0267, 0·178 (0·008)	0·9950, 8·213 (0·008)	$\frac{1}{4}$	2·490 —
Br$_1$	0·6710, 4·482 (0·011)	0·0750, 0·619 (0·014)	$\frac{1}{4}$	2·490 —
Br$_2$	0·1420, 0·949 (0·013)	0·1840, 1·518 (0·013)	0·0670,	0·667 (0·008)
Br$_3$	0·1420, 0·949 (0·013)	0·1840, 1·518 (0·013)	0·4330,	4·313 (0·008)

TABLE 2.

Observed structure amplitudes, $|F_o|$, and calculated structure factors, F_c, for planes of index hkl. (Details of the atomic scattering factors used are given in the text.)

(a) $hk0$ integrated Mo data, with $B = 2\cdot8$, $R = 13\cdot4\%$.

h k 0	$|F_o|$	F_c	h k 0	$|F_o|$	F_c	h k 0	$|F_o|$	F_c	h k 0	$|F_o|$	F_c	h k 0	$|F_o|$	F_c	h k 0	$|F_o|$	F_c
2 0 0	43	51	0 2 0'	109	88	3	224	225	5	106	−101	1	<24	−33	4	>28	26
4	69	−65	1	66	−46	4	53	41	6	<28	14	2	85	81	5	44	44
6	137	118	2	129	135	5	62	64	7	<28	23	3	<24	−19	0 8 0	<28	−48
1 1 0	163	185	3	38	−53	6	<28	−19	1 5 0	209	192	4	<28	7	1	<28	−24
2	200	−223	4	141	140	7	<28	−33	2	<24	25	5	<28	33	2	70	72
3	120	128	5	34	42	0 4 0	102	88	3	34	−45	6	<28	20	3	<28	2
4	73	79	6	38	24	1	199	189	4	<24	17	1 7 0	91	72	4	62	80
5	<24	17	7	<28	25	2	143	120	5	40	37	2	38	−65	1 9 0	<28	28
6	38	55	1 3 0	23	24	3	54	54	6	<28	−14	3	<28	29	2	44	61
7	30	32	2	<16	−13	4	59	76	0 6 0	137	119						

(b) $h0l$ integrated Mo data, with $B = 2\cdot5$, $R = 10\cdot4\%$.

h 0 l	$|F_o|$	F_c	h 0 l	$|F_o|$	F_c	h 0 l	$|F_o|$	F_c	h 0 l	$|F_o|$	F_c	h 0 l	$|F_o|$	F_c	h 0 l	$|F_o|$	F_c
0 2	142	−141	5	70	−56	8	79	62	11	<36	41	5 0 1	72	−64	4	64	61
4	197	218	7	46	−52	10	<34	69	4 0 0	66	−66	3	193	187	6	90	−84
6	264	−290	9	81	63	3 0 1	94	−104	2	123	−135	5	<28	−13	8	<34	16
8	28	33	11	<34	26	3	<24	−1	4	64	60	7	73	78	7 0 1	<32	−16
10	125	−123	2 0 0	43	52	5	116	−100	6	29	28	9	72	−78	3	<34	18
12	83	76	2	110	−118	7	<28	32	8	91	91	6 0 0	137	121	5	<34	−13
1 0 1	<14	−1	4	98	80	9	<32	−11	10	<34	−1	2	52	−42	8 0 0	<34	24
3	190	−216	6	26	−38												

(c) $0kl$ Cu data corrected for absorption and extinction, with $B = 3\cdot4$, $R = 17\cdot2\%$.

0 k l	$|F_o|$	F_c	0 k l	$|F_o|$	F_c	0 k l	$|F_o|$	F_c	0 k l	$|F_o|$	F_c	0 k l	$|F_o|$	F_c	0 k	$|F_o|$	F_c
0 0 2	180	−142	4	150	187	0 4 0	98	85	9	50	−52	6	59	−62	4	27	25
4	204	212	5	134	−138	1	33	4	10	21	−27	7	<20	−6	5	11	15
6	228	−270	6	73	−63	2	113	−102	11	33	−20	8	<20	−28	6	<20	16
8	16	28	7	28	21	3	140	180	0 6 0	135	110	9	<20	13	7	<20	−18
10	87	−99	8	126	140	4	80	79	1	20	−26	10	<20	−22	0 10 0	36	44
12	47	56	9	<24	6	5	56	50	2	20	19	0 8 0	<20	−36	1	35	35
0 2 0	107	86	10	49	−40	6	55	−52	3	42	−50	1	28	24	2	22	−14
1	156	−148	11	44	44	7	41	45	4	27	19	2	52	−59	3	<20	2
2	282	−312	12	<20	29	8	58	47	5	24	−39	3	32	−35	4	15	20
3	93	−64															

The Sb and Br$_1$ atoms lie in the plane of symmetry at $z = \frac{1}{4}$, while Br$_2$ and Br$_3$ are reflections of each other in this same plane. Table 1 also records the standard deviations calculated by Cruickshank's method.[14] We estimated the standard deviations by using a curvature obtained from the observed peaks in projection, the electron density around the peak being fitted to an

[14] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

equation of the type $\rho = Ae^{-pr^2}$. The recent method of Ehrlich [15] appears in our case to underestimate the standard deviations by a factor of about two.

These co-ordinates lead to a satisfactory electron-density projection down the *a*-axis [Fig. 1(i)] although *R*, calculated as before, is somewhat higher (17·2%). We believe that this reflects the considerably lower accuracy of the copper data used for this axis, so that no attempt was made at refinement.

From the final co-ordinates the structure factors listed in Table 2 were obtained. The atomic scattering factors used for antimony and bromine were those recorded in Appendix IV of " The Crystalline State." [16] Because the wavelength of Mo-K_α is close to the *K* absorption edge of bromine, a small correction [17] (-0.65 electron) was applied to the scattering factor of that atom when molybdenum radiation was used to obtain the *F* data. A single isotropic temperature factor was used with $B = 2.8$ for the *hk*0 molybdenum data, $B = 2.5$ for the *h0l* molybdenum data, and $B = 3.4$ for the *0kl* copper data.

DISCUSSION

Cell Dimensions and Morphology.—From the cell dimensions determined above, the axial ratios $a : b : c$ are $0.81 : 1 : 1.21$. These are close to the axial ratios, $0.781 : 1 : 1.165$, determined goniometrically by Slawson [4] for crystals belonging to the orthorhombic bipyramidal class. We believe Nicklès's preparations [2] also gave these crystals, whereas Cooke's morphological data [3] refer to the acicular α-form.

Molecular Dimensions.—The structure of antimony tribromide contains discrete pyramidal molecules. The observed bond distances and angles are listed in Table 3, together with their estimated standard deviations. For reference, the only other reported

TABLE 3.

Sb–Br Bond distances and angles at Sb.

Compound	Sb–Br (Å)		∠Br–Sb–Br
Sum of radii: [1] ionic	2·57		
tetrahedral covalent	2·47		
normal covalent ...	2·55		
$(NH_4)_2SbBr_6$, *X*-ray [2]	2·60		
Rb_2SbBr_6, *X*-ray [2]	2·59		
$SbBr_3$, *E*-diffraction [5]	2·47 ± 0·04		98° ± 2°
E-diffraction [3]	2·52 ± 0·03		96° ± 2°
E-diffraction [4]	2·51 ± 0·02		97° ± 2°
Present *X*-ray *			
Sb–Br_1	2·46₅ (e.s.d. 0·015)	$Br_1Br_{2,3}$	97·5° (e.s.d. 1·3)
Sb–$Br_{2,3}$	2·51₇ (e.s.d. 0·016)	Br_2Br_3	92·8° (e.s.d. 1·1)
Mean	2·49 ± 0·03		95·15° ± 2·4°

* For numbering of bromine atoms, see Fig. 1.

[1] Wells, " Structural Inorganic Chemistry," Oxford, 1945.
[2] Jensen, *Z. anorg. Chem.*, 1937, **232**, 193.
[3] Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 393.
[4] Allen and Sutton quoting Swingle (unpublished), *Acta Cryst.*, 1950, **3**, 46.
[5] Hassel and Sandbo, *Z. phys. Chem.*, 1938, *B*, **41**, 75.

values of the antimony–bromine distance are included. Our mean distance agrees well with the sum of the tetrahedral covalent radii and with the results of electron-diffraction investigations, although the mean bond angle appears a little smaller. The difference, amounting to 0.05_2 Å, between the two independent antimony–bromine distances is rather more than twice the estimated standard deviation for the two bonds. In itself this would not be significant, but, in that Lindqvist and Niggli [10] report a rather similar difference in the same sense for the corresponding antimony trichloride structure, we consider that the difference probably has meaning in terms of molecular packing in the crystalline state. The molecular packing is illustrated in Figs. 2a and b, which show that the bromine atoms

[15] Ehrlich, *Acta Cryst.*, 1960, **13**, 960.
[16] Bragg, " The Crystalline State," Bell, London, 1955, Vol. I, Table XV, p. 332.
[17] Henry, Lipson, and Wooster, " The Interpretation of *X*-Ray Diffraction Photographs," Macmillan, London, 1960, p. 208.

are approximately close packed within slightly corrugated layers parallel to (100). The vertical separation of these layers of bromine atoms, which are held together by the antimony atoms, is about 3·34 Å. Each antimony atom is attached singly to one layer, by the short Sb–Br distance, and doubly to another layer, by the longer Sb–Br distance.
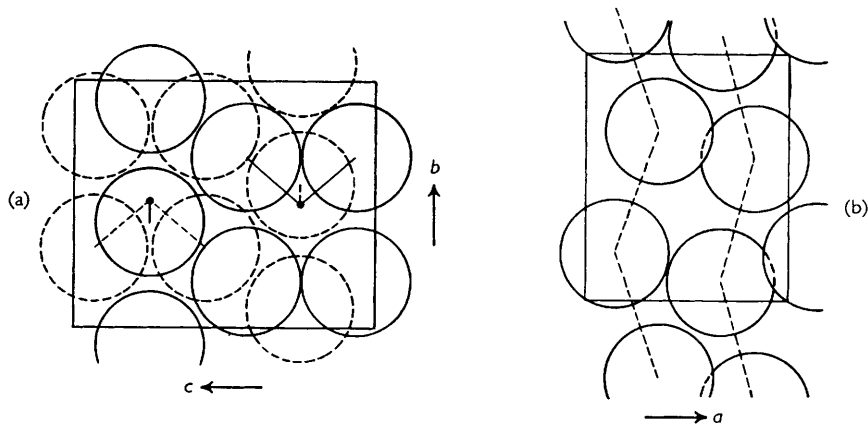

FIG. 2. (a) Packing of bromine atoms in central slice through cell parallel to (100). The two layers of bromine atoms occur close to $\frac{1}{4}a$ (full lines), and $\frac{3}{4}a$ (broken lines). Antimony atoms between these layers are represented by ●.
(b) Packing perpendicular to the *c*-axis, illustrated by a slice through the structure between $z = 0$ and $\frac{1}{2}$.

The layers themselves only approximately fit together as for close packing, probably because the antimony atoms, being larger than bromine atoms, can only fit into distorted octahedral holes. This is clear from the values of the six Sb–Br distances, three of which correspond to bonds and are about 2·49 Å, whereas the other three are 3·6 Å or greater.

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