

### 798. *The Crystal and Molecular Structure of Antimony Tribromide: $\alpha$ -Antimony Tribromide.*

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There are two forms of antimony tribromide. The crystal structure of  $\alpha$ -SbBr<sub>3</sub>, m. p. 96°, has been determined. The crystal is orthorhombic, space group  $P2_12_12_1$ , and contains discrete pyramidal molecules of antimony tribromide. The mean Sb-Br distance, determined from three-dimensional data, is  $2.50 \pm 0.05$  Å, and the mean Br-Sb-Br angle is  $95.5 \pm 1.9^\circ$ .

PREVIOUSLY<sup>1</sup> we reported the existence of two forms of antimony tribromide and discussed the structure of the  $\beta$ -form. The present Paper is concerned with the structure of the acicular  $\alpha$ -form, which we believe must correspond to the morphological data of Cooke<sup>2</sup> and to the preliminary X-ray data of Braekken.<sup>3</sup> Apart from interpreting the morphological data, it is of interest to know whether or not the molecule which gives rise to the  $\alpha$ -modification differs from that found in the  $\beta$ -structure.

#### EXPERIMENTAL

*Preparation of Crystals.*— $\alpha$ -Antimony tribromide may be obtained as needle-like crystals upon cooling a warm solution of antimony tribromide in carbon disulphide. The yield may be contaminated to some extent by a few irregular bipyramidal crystals of the  $\beta$ -form. Reported values<sup>4</sup> for the m. p. of antimony tribromide range from 90.0 to 96.6°. We find the m. p. of  $\alpha$ -SbBr<sub>3</sub> to be  $96.0 \pm 0.5^\circ$ , a value which is identical with that of  $\beta$ -SbBr<sub>3</sub>. The crystals, which extinguish straight, are hygroscopic, and crystallisation was performed in a closed vessel inside a dry-box. A built-in polarising microscope facilitated the examination and selection of

<sup>1</sup> Cushen and Hulme, *J.*, 1962, 2218.

<sup>2</sup> Cooke, *Proc. Amer. Acad.*, 1877, **13**, 1, 72; *Amer. J. Sci.*, 1880, **19**, 469; *Chem. News*, 1880, **44**, 221, 233, 245, 255.

<sup>3</sup> Braekken, *Kgl. norske Videnskab Selskabs Forh.*, 1935, **8**, Nr. 10; *Ind. Eng. Chem., Analyt.*, 1938, **10**, 475.

<sup>4</sup> Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1929, Vol. IX, p. 494.

suitable crystals for X-ray analysis, the ones actually used being almost cylindrical and of diameter 0.05 mm. and length up to 2.0 mm. While still in the dry-box the crystals were sealed in suitable Lindeman glass tubing.

**X-Ray Data.**— $\alpha$ -SbBr<sub>3</sub>,  $M$  361.5, orthorhombic with needle axis  $c$ ;  $a = 10.12 \pm 0.01$ ,  $b = 12.30 \pm 0.01$ ,  $c = 4.42 \pm 0.01$  Å,  $U = 550$  Å<sup>3</sup>, as determined from Cu- $K_\alpha$  single-crystal oscillation and zero-, first-, and second-layer Weissenberg photographs about the  $c$  axis, together with oscillation and one zero-layer photograph about the  $a$  axis.  $D_m = 4.35$  (by displacement). Groth<sup>5</sup> gives 4.15 g./c.c. Despite this difference we infer that there are four molecules of SbBr<sub>3</sub> in the unit cell,  $D_c = 4.37$ , so that  $F(000) = 624$ .

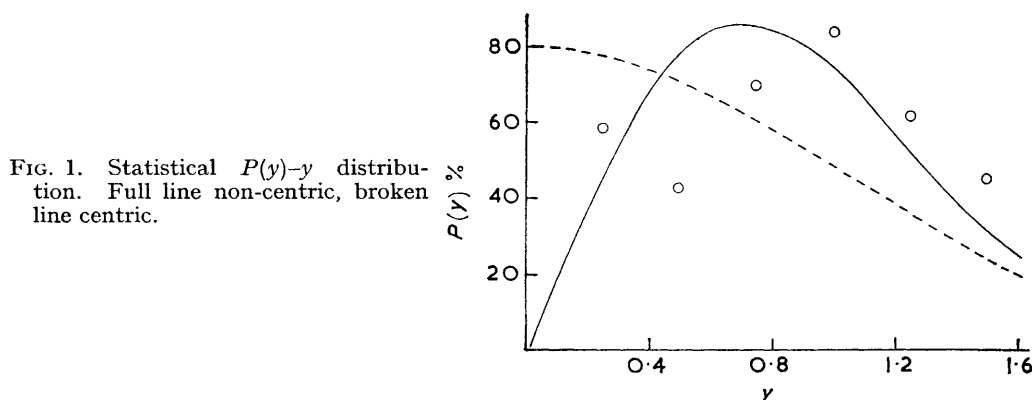


FIG. 1. Statistical  $P(y)$ - $y$  distribution. Full line non-centric, broken line centric.

The only systematically absent reflections are  $h00$  when  $h$  is odd,  $0k0$  when  $k$  is odd, and  $00l$  when  $l$  is odd. This leads to the space group  $P2_12_12_1$  ( $V^4$ ,  $D_2^4$ , No. 19). Because of the relatively few orders of  $00l$  observable, confirmation of this space group was sought from the statistical distribution of intensities. The experimental points, obtained by use of one of our

TABLE 1.

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

Atom	$x$	$y$	$z$
Sb .....	0.4492, 4.546 (0.011)	-0.0359, -0.442 (0.011)	0.2660, 1.176 (0.019)
Br <sub>1</sub> .....	0.4540, 4.594 (0.016)	0.1351, 1.662 (0.014)	-0.0221, -0.977 (0.026)
Br <sub>2</sub> .....	0.2612, 2.643 (0.015)	-0.1174, -1.444 (0.016)	-0.0207, -0.915 (0.035)
Br <sub>3</sub> .....	0.6233, 6.308 (0.016)	-0.1365, -1.679 (0.017)	-0.0394, -1.741 (0.024)

(b) Anisotropic vibration parameters. The atomic scattering factor is modified by the term  $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{23}kl - B_{31}lh - B_{12}hk)$

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{23}$	$B_{31}$	$B_{12}$
Sb .....	0.0069	0.0075	0.0768	0.0035	-0.0238	0.0024
Br <sub>1</sub> .....	0.0040	0.0042	0.0804	-0.0043	0.0177	-0.0016
Br <sub>2</sub> .....	0.0032	0.0059	0.0963	-0.0008	-0.0169	-0.0006
Br <sub>3</sub> .....	0.0075	0.0059	0.0257	0.0176	-0.0061	0.0068

own Mercury computer programmes, lie very close to the non-centric  $N(z)$ - $z$  curve,<sup>6</sup> although they are more widely and less convincingly scattered (see Fig. 1) about the  $P(y)$ - $y$  non-centric curve.<sup>7</sup>

Zero-, first-, and second-layer integrated Weissenberg photographs about the  $c$  axis and zero-layer photographs about the  $a$  axis were obtained by using Mo- $K_\alpha$  radiation to minimise absorption errors ( $\mu_{Cu} = 690$ ,  $\mu_{Mo} = 290$  cm.<sup>-1</sup>). The intensity of each reflection, recorded by the multiple-film technique, was estimated visually. No allowance was made for absorption or extinction, these effects being minimised by use of a small crystal. The intensities, after

<sup>5</sup> Groth, *Chem. Kryst.*, 1906, I, 227.

<sup>6</sup> Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

<sup>7</sup> Ramachandran and Srinivasan, *Acta Cryst.*, 1959, **12**, 410.

Lorentz polarisation correction, gave a set of 232 independent structure amplitudes recorded in Table 2.

**Structure Determination.**—The Patterson projection about the  $c$  axis was interpreted to yield the antimony atom positions. Of the several possible sets of bromine atom positions, that corresponding to the analogous arsenic tribromide structure<sup>3</sup> was found by means of an electron-density synthesis to be the most promising. The customary  $R$  factor for the  $hk0$  data was then 27%, which dropped to 24% after one round of least-square refinement. The final electron-density projection is shown in Fig. 2.

The  $z$  co-ordinates of the antimony atom positions were obtained from an interpretation of the  $a$  axis Patterson map, the ensuing electron-density map confirming the bromine atom positions which had been arrived at from packing considerations. Three difference syntheses improved all these positions and reduced  $R$  to 18% for this zone.

Further progress was made by seven rounds of least-square refinement, with full three-dimensional data, the last five rounds involving anisotropic temperature factors. The final  $R$  factor is 16% excluding absent reflections. With absent reflections included in the manner used for the  $\beta$ -antimony tribromide structure,<sup>1</sup>  $R$  increased to 18%. Standard deviations in atomic positions were computed in the final round of least-square refinement, and are recorded in Table 1, together with the final atomic co-ordinates.

TABLE 2.

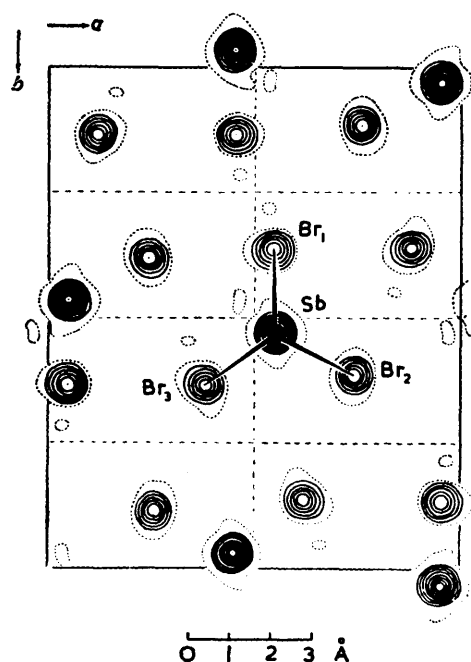
Observed structure amplitudes,  $F_o$ , calculated structure amplitudes,  $F_c$ , and phase angles,  $\alpha$ , for planes of index  $hkl$  (details of the atomic scattering and temperature factors used are given in the text).

$h$	$F_o$	$F_c$	$\alpha$	$h$	$F_o$	$F_c$	$\alpha$	$h$	$F_o$	$F_c$	$\alpha$	$h$	$F_o$	$F_c$	$\alpha$
0k0				4k0				8k0				2k1			
2	88	150	0	0	113	85	0	2	59	59	180-0	0	146	110	0
4	140	210	180-0	1	170	177	270-0	3	<17	15	270-0	1	185	175	48-1
6	76	70	0	2	72	56	0	4	109	95	180-0	2	188	199	67-3
8	162	150	0	3	70	53	270-0	5	<17	32	270-0	3	127	121	50-1
10	92	86	180-0	4	<13	11	180-0	6	<18	19	180-0	4	55	40	10-8
12	138	131	180-0	5	29	27	270-0	7	<18	31	270-0	5	105	103	159-5
14	<20	3	180-0	6	24	28	180-0	8	52	53	0	6	110	120	280-4
1k0				7	50	42	270-0					7	<15	15	191-1
1	30	24	90-0	8	22	25	0	9k0				8	<15	12	158-3
2	28	29	0	9	<17	26	90-0	1	70	69	90-0	9	81	84	347-7
3	85	90	90-0	10	<17	29	0	2	<17	4	180-0	10	86	84	113-6
4	78	85	0	11	78	76	90-0	3	<18	22	90-0				
5	116	136	90-0	12	27	28	180-0	4	30	27	0	3k1			
6	34	35	0	13	48	32	90-0	5	132	139	270-0	0	162	108	270-0
7	100	111	90-0	14	46	35	180-0	6	<19	26	0	1	82	61	72-0
8	24	28	180-0					7	70	86	270-0	2	79	66	198-7
9	58	53	90-0	5k0								3	88	90	96-1
10	16	20	0	1	47	36	270-0	10k0				4	88	80	127-3
11	41	31	90-0	2	129	105	0	0	141	148	180-0	5	84	59	102-2
12	54	52	0	3	13	16	270-0	1	<18	5	270-0	6	55	41	163-2
13	19	23	90-0	4	138	113	0	2	48	59	180-0	7	70	68	84-6
14	<21	5	180-0	5	52	37	90-0					8	70	68	216-9
				6	66	55	0	11k0				9	64	68	81-0
				7	<15	10	270-0	1	<20	15	270-0				
				8	42	39	0	2	34	65	180-0	4k1			
				9	34	32	270-0					0	143	123	0
				10	68	66	0	12k0				1	128	94	28-0
				11	<19	18	90-0	0	58	72	180-0	2	144	118	16-4
				12	51	48	0	1	36	61	90-0	3	91	67	15-2
2k0				6k0								4	98	85	329-0
0	126	135	0	0	149	130	180-0	0k1				5	68	67	162-5
1	95	85	270-0	1	209	228	270-0	1	94	131	90-0	6	<15	31	296-1
2	106	102	0	2	43	33	180-0	2	88	103	270-0	7	<15	22	134-8
3	108	106	270-0	3	78	55	90-0	3	104	164	90-0	8	57	56	113-6
4	103	88	0	4	71	57	0	4	<11	4	270-0	9	72	62	347-6
5	50	36	270-0	5	49	38	90-0	5	68	72	90-0				
6	83	74	0	6	<15	2	180-0	6	94	78	90-0	5k1			
7	<13	26	90-0	7	127	112	270-0	7	<14	32	270-0	0	200	192	90-0
8	<15	25	180-0	8	44	34	180-0	8	41	29	90-0	1	40	19	92-2
9	<15	17	90-0	9	<18	10	270-0	9	35	36	270-0	2	21	18	274-3
10	90	84	180-0	10	<18	14	0	10	<16	31	270-0	3	95	70	115-8
11	<17	15	90-0	11	109	108	90-0	11	<16	29	270-0	4	184	182	273-4
12	31	29	180-0									5	89	92	86-6
13	27	31	90-0	7k0				1k1				6	<15	13	85-4
14	<21	12	0	1	<15	15	90-0	0	111	56	90-0	7	76	86	73-7
				2	51	44	180-0	1	138	118	168-7	8	111	117	94-4
				3	<15	24	270-0	2	90	61	171-8	9	63	54	106-2
				4	43	39	0	3	140	157	11-1				
				5	82	85	270-0	4	107	121	207-3	6k1			
				6	125	120	0	5	82	75	17-2	0	106	67	0
				7	48	42	270-0	6	90	112	197-2	1	45	30	229-0
				8	60	66	0	7	107	114	180-7	2	124	106	29-0
				9	<19	7	90-0	8	91	82	156-7	3	<15	36	245-5
				8k0				9	44	37	123-8	4	72	83	358-9
				0	<15	6	180-0	10	66	57	146-4	5	<15	19	316-6
				1	61	54	270-0	11	75	68	1-0	6	45	51	277-9
												7	<17	22	31-1

TABLE 2. (Continued.)

$k$	$F_o$	$F_c$	$\alpha$	$k$	$F_o$	$F_c$	$\alpha$	$k$	$F_o$	$F_c$	$\alpha$	$k$	$F_o$	$F_c$	$\alpha$
7k1				0k2				3k2				6k2			
0	24	43	90.0	4	165	256	180.0	3	116	103	290.3	3	167	152	85.5
1	24	15	88.7	5	45	9	0	4	57	53	151.4	4	63	62	0.3
2	49	42	329.3	6	<13	8	0	5	29	32	54.8	5	86	87	77.1
3	56	51	116.6	7	38	8	180.0	6	54	56	355.4	6	<17	10	266.2
4	63	51	311.3	8	120	139	0	7	<17	12	218.4	7	66	82	280.6
5	59	59	106.4					8	61	70	189.4				
6	55	58	53.4	1k2				9	75	84	266.4	7k2			
7	40	44	82.4	0	71	76	90.0					0	<17	31	270.0
				1	52	35	288.6	4k2				1	60	34	69.8
8k1				2	56	22	154.7	0	<14	10	180.0	2	85	80	196.0
0	45	53	0	3	80	73	283.8	1	99	72	73.0	3	44	43	112.9
1	83	83	303.6	4	<13	29	272.2	2	19	26	224.1	4	45	51	186.6
2	153	144	287.4	5	64	72	265.9	3	124	100	85.1				
3	66	62	316.6	6	28	36	129.3	4	58	44	151.3	8k2			
4	<17	21	11.9	7	62	71	261.8	5	61	50	112.7	0	111	104	0
5	<18	48	204.7	8	53	60	158.4	6	40	46	132.0	1	37	41	133.3
6	87	94	85.7	9	62	60	280.5	7	24	34	294.1	2	46	54	336.8
								8	<17	16	22.5	3	38	52	100.3
9k1				2k2				5k2				9k2			
0	40	52	90.0	0	164	100	180.0	0	<14	14	270.0	0	<19	4	270.0
1	<18	25	163.6	1	127	86	76.1	1	79	60	332.4	1	80	77	105.1
2	<18	54	10.2	2	118	104	201.7	2	<15	8	223.3	2	<19	22	223.0
3	<18	12	72.1	3	39	29	60.0	3	<15	28	206.5	3	77	81	88.8
4	51	55	321.8	4	53	57	143.0	4	54	46	176.2				
				5	39	31	165.7	5	<16	36	109.6	0k3			
10k1				6	29	47	66.2	6	<16	96	191.9	1	114	128	270.0
0	<19	3	0	7	32	30	144.8	7	84	36	358.9	2	60	54	270.0
1	52	54	283.5	8	<17	18	295.7	8	<17	36	179.8	3	28	10	90.0
				9	<17	16	289.3					4	40	24	270.0
0k2				3k2				6k2				0k4			
0	108	108	0	0	58	23	270.0	0	39	35	180.0	0	120	116	0
1	<12	35	180.0	1	142	91	274.7	1	<15	8	296.4				
2	88	117	180.0	2	200	200	178.0	2	<16	36	53.5				
3	24	34	180.0												

FIG. 2. Electron-density projection on to (001). Zero contour (broken) at  $5.0 \text{ e}/\text{\AA}^2$ . Thereafter contours are at intervals of  $9.4 \text{ e}/\text{\AA}^2$ .



From these 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."<sup>8</sup> Because the wavelength of Mo- $K_{\alpha}$  radiation is close to the  $K$  absorption edge of bromine, a small correction<sup>9</sup> ( $-0.65$  electron) was applied to the atomic scattering factor of that atom.

<sup>8</sup> Bragg, "The Crystalline State," Bell, London, 1955, Vol. I, Table XV, p. 332.

<sup>9</sup> Henry, Lipson, and Wooster, "The Interpretation of X-Ray Diffraction Photographs," Macmillan, London, 1960, p. 208.

## DISCUSSION

Just as antimony trichloride can be obtained in two forms, one from the melt<sup>10</sup> and the other from carbon disulphide solution,<sup>5</sup> so we have found antimony tribromide can exist in two forms at room temperature. This polymorphism was overlooked by Bowles *et al.* in their recent Paper<sup>11</sup> on melting and polymorphism in antimony trihalides, although it would appear to constitute an additional argument in favour of the law of corresponding states. It is particularly relevant because of the structural parallel between one form of antimony trichloride<sup>10</sup> and  $\beta$ -antimony tribromide.

*Cell Dimensions and Morphology.*—From the cell dimensions determined above, the simple axial ratios  $a : b : c$  do not correspond to those recorded for antimony tribromide by Nicklès, Slawson, or Cooke. We have already identified Nicklès and Slawson's ratios with  $\beta$ -antimony tribromide,<sup>1</sup> and if we write for the  $\alpha$ -antimony tribromide structure the ratio  $2b : 2a : 5c$  (*i.e.*, 1.216 : 1 : 1.092) fair agreement with Cooke<sup>2</sup> (1.224 : 1 : 1.064) is obtained.

The isomorphism of arsenic tribromide and antimony tribromide reported by Braekken<sup>3</sup> may now be seen to refer to this  $\alpha$ -antimony tribromide structure, our dimensions (10.12, 12.30, and 4.42) corresponding to 10.17, 12.09, and 4.32 for arsenic tribromide.

*Molecular Dimensions.*—Like  $\beta$ -SbBr<sub>3</sub>,  $\alpha$ -SbBr<sub>3</sub> contains discrete pyramidal molecules. The observed bond distances and angles for the two structures are listed in Table 3, where the estimated standard deviations are also given. The results for the  $\alpha$  structure are

TABLE 3.  
Sb—Br bond distances in Å with angles at Sb (see ref. 1 for  $\beta$ -SbBr<sub>3</sub> data).

	$\alpha$ -SbBr <sub>3</sub>		$\beta$ -SbBr <sub>3</sub>
Sb—Br <sub>1</sub>	2.46 (e.s.d. 0.03)		2.46 (e.s.d. 0.02)
Sb—Br <sub>2</sub>	2.50 ( „ 0.04)	}	2.52 ( „ 0.02)
Sb—Br <sub>3</sub>	2.54 ( „ 0.03)		
Mean = 2.50 ± 0.05 = 2.49 ± 0.03.			
Br <sub>1</sub> —Sb—Br <sub>2</sub>	97.4 (e.s.d. 1.0)	}	97.5 (e.s.d. 1.3)
Br <sub>1</sub> —Sb—Br <sub>3</sub>	95.5 ( „ )		
Br <sub>2</sub> —Sb—Br <sub>3</sub>	93.6 ( „ )		92.8 ( „ 1.1)
Mean = 95.5 ± 2.0 = 95.2 ± 2.4.			

comparable with other Sb—Br distances,<sup>1</sup> and there is reasonable agreement with the  $\beta$ -structure.

The molecular packing corresponds to layers of bromine atoms in the planes at  $z = 0$  and  $\frac{1}{2}$ , the antimony atoms lying alternately above and below these planes. A small shift of one plane in the  $a$ -direction relative to its neighbour, combined with an expansion in the  $c$ -direction and a corresponding contraction in  $b$ , leads to the packing observed in the  $\beta$ -structure: \*  $\frac{1}{2}b_\alpha \sim a_\beta$ ,  $2c_\alpha \sim b_\beta$ ,  $a_\alpha \sim c_\beta$ . Interatomic distances between unbound atoms are all greater than 3.71 Å, the smallest *unbound* Br—Sb distance being 3.75 Å, compared with values of 3.66 and 3.66 Å in the  $\beta$ -structure. Thus, at room temperature, there is no evidence for even the “indistinct” existence of a molecular dimer as has been suggested by Shimomura<sup>12</sup> from the nuclear quadrupole resonance spectrum of antimony tribromide at 77°K.

We are grateful to the University of London Computer Unit for the provision of computing facilities, and one of us (D. W. C.) is indebted to this College for the award of a maintenance grant.

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[Received, December 5th, 1963.]

\* A typographical error occurs in Fig. 2b of the  $\beta$ -antimony tribromide structure. Fig. 2b should be rotated through 180° to correspond to Fig. 2a, the origin remaining at the bottom left-hand corner.

<sup>10</sup> Lindqvist and Niggli, *J. Inorg. Nuclear Chem.*, 1956, **2**, 345.

<sup>11</sup> Bowles, Scott, and Babb, *J. Chem. Phys.*, 1963, **39**, 831.

<sup>12</sup> Shimomura, *J. Phys. Soc. Japan*, 1957, **12**, 1389, footnote.