

798. *The Crystal and Molecular Structure of Antimony Tribromide: α -Antimony Tribromide.*

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There are two forms of antimony tribromide. The crystal structure of α -SbBr₃, 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 ± 0.05 Å, and the mean Br-Sb-Br angle is $95.5 \pm 1.9^\circ$.

PREVIOUSLY¹ we reported the existence of two forms of antimony tribromide and discussed the structure of the β -form. The present Paper is concerned with the structure of the acicular α -form, which we believe must correspond to the morphological data of Cooke² and to the preliminary X-ray data of Braekken.³ Apart from interpreting the morphological data, it is of interest to know whether or not the molecule which gives rise to the α -modification differs from that found in the β -structure.

EXPERIMENTAL

Preparation of Crystals.— α -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 β -form. Reported values⁴ for the m. p. of antimony tribromide range from 90.0 to 96.6°. We find the m. p. of α -SbBr₃ to be $96.0 \pm 0.5^\circ$, a value which is identical with that of β -SbBr₃. 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

¹ Cushen and Hulme, *J.*, 1962, 2218.

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

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

⁴ 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.— α -SbBr₃, 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, $U = 550$ Å³, as determined from Cu- K_{α} 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). Groth⁵ gives 4.15 g./c.c. Despite this difference we infer that there are four molecules of SbBr₃ in the unit cell, $D_c = 4.37$, so that $F(000) = 624$.

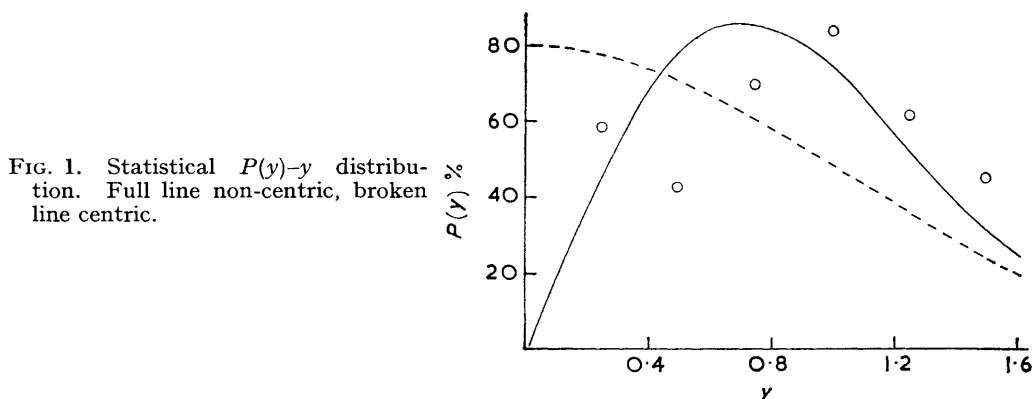


FIG. 1. Statistical $P(y)-y$ distribution. Full line non-centric, broken line centric.

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 I.

(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 ₁	0.4540, 4.594 (0.016)	0.1351, 1.662 (0.014)	-0.0221, -0.977 (0.026)
Br ₂	0.2612, 2.643 (0.015)	-0.1174, -1.444 (0.016)	-0.0207, -0.915 (0.035)
Br ₃	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 $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - E_{23}kl - B_{31}lh - B_{12}hk)$

	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 ₁	0.0040	0.0042	0.0804	-0.0043	0.0177	-0.0016
Br ₂	0.0032	0.0059	0.0963	-0.0008	-0.0169	-0.0006
Br ₃	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,⁶ although they are more widely and less convincingly scattered (see Fig. 1) about the $P(y)-y$ non-centric curve.⁷

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_{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, these effects being minimised by use of a small crystal. The intensities, after

⁵ Groth, *Chem. Kryst.*, 1906, I, 227.

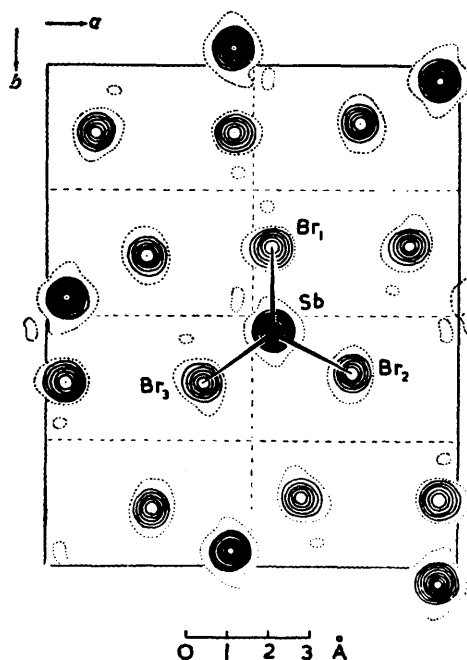
⁶ Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

⁷ Ramachandran and Srinivasan, *Acta Cryst.*, 1959, **12**, 410.

TABLE 2. (Continued.)

<i>k</i>	<i>F_o</i>	<i>F_c</i>	α	<i>k</i>	<i>F_o</i>	<i>F_c</i>	α	<i>k</i>	<i>F_o</i>	<i>F_c</i>	α	<i>k</i>	<i>F_o</i>	<i>F_c</i>	α	
7k1																
0	24	43	90.0	4	165	256	180.0	3	116	103	290.3	6k2	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	83	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					9	75	84	266.4	7k2	0	<17	31	270.0
7	40	44	82.4									1	60	34	69.8	
8k1																
0	45	53	0					4k2	0	<14	10	180.0	2	85	80	196.0
1	83	83	303.6					1	99	72	73.0	3	44	43	112.9	
2	153	144	287.4					2	19	26	224.1	4	45	51	186.6	
3	66	62	316.6					3	124	100	85.1					
4	<17	21	11.9					4	58	44	151.3	8k2	0	111	104	0
5	<18	48	204.7					5	61	50	112.7	1	37	41	133.3	
6	87	94	85.7					6	40	46	132.0	2	46	54	336.8	
9k1																
0	40	52	90.0					8	<17	16	22.5	3	38	52	100.3	
1	<18	25	163.6									9k2	0	<19	4	270.0
2	<18	54	10.2					0	<14	14	270.0	1	80	77	105.1	
3	<18	12	72.1					1	79	60	332.4	2	<19	22	223.0	
4	51	55	321.8					2	<15	8	223.3	3	77	81	88.8	
10k1																
0	<19	3	0					3	<15	28	206.5					
1	52	54	283.5					4	54	46	176.2	0k3	1	114	128	270.0
0k2																
0	108	108	0					5	<16	36	109.6	2	60	54	270.0	
1	<12	35	180.0					6	84	96	191.9	3	28	10	90.0	
2	88	117	180.0					7	<17	36	358.9	4	40	24	270.0	
3	24	34	180.0					8	66	80	179.8					
3k2																
0	58	23	270.0									0k4	0	120	116	0
1	142	91	274.7					6k2	0	39	35	180.0				
2	200	200	178.0					1	<15	8	296.4					
2k2																
0	71	76	90.0					2	<16	36	53.5					
1	52	35	288.6													
2	56	22	154.7													
3	80	73	283.8													
4	<13	29	272.2													
5	64	72	265.9													
6	28	36	129.3													
7	62	71	261.8													
8	53	60	158.4													
9	62	60	280.5													

FIG. 2. Electron-density projection on to (001). Zero contour (broken) at $5.0 e/A^2$. Thereafter contours are at intervals of $0.4 e/A^2$.



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."⁸ Because the wavelength of Mo- K_{α} radiation is close to the K absorption edge of bromine, a small correction⁹ (-0.65 electron) was applied to the atomic scattering factor of that atom.

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

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

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DISCUSSION

Just as antimony trichloride can be obtained in two forms, one from the melt¹⁰ and the other from carbon disulphide solution,⁵ 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 Paper¹¹ 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 trichloride¹⁰ and β -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 β -antimony tribromide,¹ and if we write for the α -antimony tribromide structure the ratio $2b : 2a : 5c$ (*i.e.*, 1.216 : 1 : 1.092) fair agreement with Cooke² (1.224 : 1 : 1.064) is obtained.

The isomorphism of arsenic tribromide and antimony tribromide reported by Braekken³ may now be seen to refer to this α -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 β -SbBr₃, α -SbBr₃ 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 α structure are

TABLE 3.
Sb-Br bond distances in Å with angles at Sb (see ref. 1 for β -SbBr₃ data).

	α -SbBr ₃	β -SbBr ₃
Sb-Br ₁	2.46 (e.s.d. 0.03)	2.46 (e.s.d. 0.02)
Sb-Br ₂	2.50 („ 0.04)	2.52 („ 0.02)
Sb-Br ₃	2.54 („ 0.03)	
	Mean = 2.50 ± 0.05 = 2.49 ± 0.03.	
Br ₁ -Sb-Br ₂	97.4 (e.s.d. 1.0)	97.5 (e.s.d. 1.3)
Br ₁ -Sb-Br ₃	95.5 („)	
Br ₂ -Sb-Br ₃	93.6 („)	92.8 („ 1.1)
	Mean = 95.5 ± 2.0 = 95.2 ± 2.4.	

comparable with other Sb-Br distances,¹ and there is reasonable agreement with the β -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 β -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 β -structure. Thus, at room temperature, there is no evidence for even the "indistinct" existence of a molecular dimer as has been suggested by Shimomura¹² from the nuclear quadrupole resonance spectrum of antimony tribromide at 77°K.

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

¹⁰ Lindqvist and Niggli, *J. Inorg. Nuclear Chem.*, 1956, **2**, 345.

¹¹ Bowles, Scott, and Babb, *J. Chem. Phys.*, 1963, **39**, 831.

¹² Shimomura, *J. Phys. Soc. Japan*, 1957, **12**, 1389, footnote.