Redeterminations of the solid-state structures of trimethylarsenic dibromide, Me$_3$AsBr$_2$, and trimethylantimony dibromide, Me$_3$SbBr$_2$, by X-ray crystallography and solid state ^{13}C MAS NMR evidence for a highly symmetrical D_{3h}, non-ionic structure for Me$_3$SbBr$_2$ [1]

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Abstract

The crystal structure of trimethylantimony dibromide, Me$_3$AsBr$_2$, has been redetermined 24 years after its first characterization and that of trimethylarsenic dibromide, Me$_3$SbBr$_2$, 57 years later. Unlike the earlier As structure, the new determination provides bond distances and angles similar to those found in related compounds, but it does confirm the ionic nature of the structure, i.e. [MeAsBr]$^+$ Br. The new Sb determination reveals a rigorously trigonal bipyramidal, D_{3h}, structure. This is in contrast to the earlier determination which described the structure in terms of ionic (axial) distortions. It has been determined that refinement of the current data for Me$_3$SbBr$_2$ in the space groups previously reported for the "ionic" structures produces ionic distortions, whereas none is found in the correct centrosymmetric space group $P6_3/mmc$. From a variety of perspectives, the results are crystallographically inferior in the space groups that produce the "ionic" distortions. In support of the crystallographic results, the solid-state MAS ^{13}C NMR spectrum has also been obtained. The narrow single line observed is consistent only with a high symmetry electrical environment in the vicinity of the Sb and Br quadrupolar nuclei.

Keywords: Arsenic; Antimony; Crystal structure

1. Introduction

Empirical schemes for the prediction of covalent molecular structures assign to trimethylpnictogen dihalides, Me$_3$EX$_2$ (E = As or Sb; X = halogen), a regular trigonal bipyramidal structure with methyl groups equatorial and halogen atoms axial. Indeed, a large number of spectroscopic, conductivity and dipole moment studies in fluid phases [1] confirm this expectation. However, in the solid state, ionic structures such as Me$_3$EX$^+$X$^-$, or partially ionic distorted C_{3v} structures are possible. Solid-state nuclear quadrupole resonance (NQR) studies of Me$_3$SbCl$_2$ and Me$_3$SbBr$_2$ are consistent with idealized D_{3h} symmetry, [2] but both Me$_3$AsBr$_2$ and Me$_3$AsI$_2$ appear to be ionic from their IR spectra [3], and NQR data for Me$_3$AsBr$_2$ show that

the electric field gradient at As is much less symmetrical for Me$_3$AsBr$_2$ than for the F and Cl analogs.

Crystallographic characterizations of several Me$_3$EX$_2$ species have been reported. Me$_3$AsCl$_2$ is rigorously trigonal bipyramidal [4]. Me$_3$AsBr$_2$ is described as "ionic"; the geometry at As is pyramidal and there is one very short and one very long As–Br bond [4]. Three Me$_3$SbX$_2$ (X = Cl, Br or I) structures have been determined to be isomorphous [5]; all are described as showing evidence for ionicity in the Sb–X bonds, but are much less distorted from ideal D_{3h} symmetry than was Me$_3$AsBr$_2$. The structures of Me$_3$AsCl$_2$ and Me$_3$AsBr$_2$ were elucidated 24 years ago with photographic data and were refined to 7% and 10%, respectively. The Sb (X = Cl, Br and I) structures were characterized 57 years ago and were not refined. Me$_3$SbF$_2$ is, within experimental e.s.d.s, a regular trigonal bipyramid, but no crystallographic symmetry is imposed.

The structure of Me$_3$AsBr$_2$ contains some troubling features; the As–Br distance found, 2.15(4) Å, is 0.2–0.3

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[1] Dedicated to Professor Marvin Rausch on the occasion of his 65th birthday.

Table 1
Crystallographic data for Me_3AsBr_2 (As) and Me_3SbBr_2 (Sb)

Formula	$C_3H_9AsBr_2$	$C_3H_9SbBr_2$
Crystal system	hexagonal	hexagonal
Space group	$P6_3mc$ (no. 186)	$P6_3/mmc$ (no. 194)
a, c (Å)	7.1200(10), 9.354(2)	7.356(2), 8.878(2)
V (Å^3)	410.6(2)	416.2(2)
Z	2	2
d_{calc} (g cm^{-3})	2.263	2.607
T (K)	293	293
μ (Mo-Kα) (cm^{-1})	137.64	128.12
Absorption correction		ψ-scan, 216 reflections
Max./min./transmission	0.944/0.538	0.535/0.329
Diffractometer		Siemens P4 (Mo-Kα, graphite monochromator)
2θ range (deg)	7–45	4–45
Reflections (collected, independent, obs.)	1287, 261, 187 ($5\sigma F_o$)	1075, 262, 193 ($5\sigma F_o$)
$R(F), R(wF)$ [b] (%)	2.92 (5.69) [a], 2.68 (3.68)	2.92 (5.32) [a], 3.96 (8.46)
N_o/N_v	9.8	19.3
Max./min., $\Delta\rho$ (e Å^{-3})	1.07/− 0.87	0.65/− 0.83

[a] All data.
[b] $R(F) = \Sigma\Delta/\Sigma(F_o)$; $R(wF) = \Sigma[\Delta w^{1/2}]/[F_o w^{1/2}]$; $\Delta = |F_o - F_c|$; $w^{-1} = \sigma^2(F_o) + gF_o^2$

Å shorter than any As–Br bond previously found in an As^{III} or As^V bromide [6], and refinement of the crystallographically unique carbon atom produced a negative thermal parameter (which was attributed to disorder). Bond distance anomalies as large as this one are not chemically plausible and must be a demonstration of an error in the crystallographic characterization. Owing to the several problems associated with these earlier structures, we have undertaken a redetermination of the structures of Me_3AsBr_2 (As) and Me_3SbBr_2 (Sb) using modern diffractometer methods.

2. Results and discussion

All of the structurally characterized members of the group, except for Me_3SbF_2, crystallize as hexagonal prisms and have been identified as belonging to the hexagonal crystal system; Me_3SbF_2 is monoclinic [7]. For all of the hexagonal cases, the same systematic absences in the diffraction data are found and accommodate the same set of three space groups with $6/mmm$ Laue symmetry. Since, additionally, the unit-cell volume accommodates two molecules, and the ratios of the

c and a unit-cell axes are all 1.25 ± 0.05, it may be assumed that all studied Me_3EX_2 species pack similarly in the solid state. Of the three allowed space groups, two are noncentrosymmetric, $P6_3mc$ (#186) and $P\bar{6}2c$ (#190), and one is centrosymmetric, $P6_3/mmc$ (#194). All three space groups have been variously reported for Me_3EX_2 compounds: $P6_3mc$ for Me_3AsBr_2, $P\bar{6}2c$ for the three Me_3SbX_2 structures and $P6_3/mmc$ for Me_3AsCl_2.

The Group-15 element site symmetries differ in the three space groups. For $P6_3mc$, E is located on a three-fold axis which contains a mirror plane; this produces crystallographically nonequivalent axial X groups and allows pyramidalization at E. In this space group, z is a polar axis. Wells observed no piezoelectric effect in the crystals of any of the antimony species he studied [5]. For $P\bar{6}2c$, E is located on a $\bar{6}$ site which makes the two X groups equivalent and disallows pyramidalization. For $P6_3/mmc$, E is located on a $\bar{6}m2$ site which adds inversional symmetry to the previous case and imposes perfect D_{3h} symmetry.

A summary of the crystallographic experiments is given in Table 1, atomic coordinates are given in Tables 2 and 3, and molecular diagrams are provided in Figs. 1

Table 2
Atomic coordinates, equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) and site symmetry for Me_3AsBr_2

	Wyckoff site symmetry	x	y	z	U_{eq} [a]
As	c	1/3	2/3	0.5242	25(1)
Br(1)	c	1/3	2/3	0.8085(4)	40(1)
Br(2)	c	1/3	2/3	0.1694(4)	36(1)
C(1)	d	0.1842(8)	0.3685(15)	0.5121(18)	35(4)

[a] Equivalent isotropic U defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table 3
Atomic coordinates, equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) and site symmetry for Me_3SbBr_2

	Wyckoff site symmetry	x	y	z	U_{eq} [a]
Sb	d	2/3	1/3	1/4	31(1)
Br(1)	f	2/3	1/3	− 0.0483(2)	60(1)
C(1)	k	0.8273(8)	0.1727(8)	1/4	53(4)

[a] Equivalent isotropic U defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.
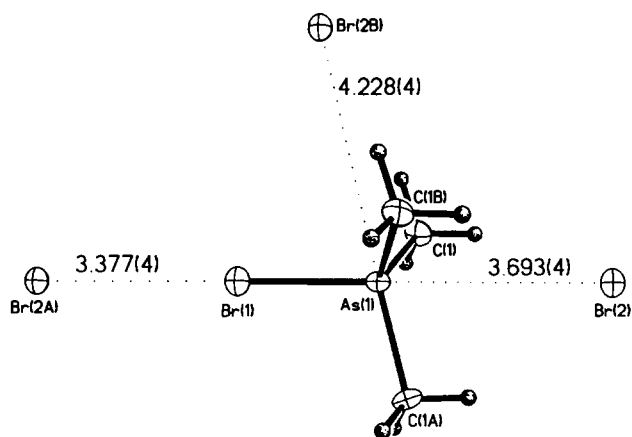
Fig. 1. Molecular structure of Me_3AsBr_2 drawn with 40% thermal ellipsoids.

Table 4
Bond distances (Å) and angles (deg) for CH_3AsBr_2 and CH_3SbBr_2

	CH_3AsBr_2	CH_3SbBr_2
E–Br	2.285(4)	2.649(2)
E–C	1.902(10)	2.047(5)
E···Br	3.693(4) (ax.)	
	4.228(4) (equ.)	
Br···Br	3.377(4)	
Br–E–Br		180
Br–E–C	104.8(4)	90
C–E–C	113.7(4)	120

and 2. With the understanding that heavy atoms on special positions may skew the statistical distribution of the magnitudes of the normalized structure factors, we noted that $|E^2 - 1| = 0.96$ for As and 1.01 for Sb, which is strongly indicative of centrosymmetry (theoretical: 0.968, centric; 0.736, acentric). For the Sb analog we carried out a refinement of the structure in all three allowed space groups and the comparative results are given in Table 5.

In confirmation of the earlier determination, satisfactory results could only be obtained for As in the non-centrosymmetric space group $P6_3mc$. The As atom environment (see Table 2 and Fig. 1) is distinctly tetrahedral (the unique Br–As–C and C–As–C angles are 104.8(5) and 113.7(4)°) with the fifth substituent at a distance considerably removed from the central atom. The As(1)–Br(1) distance is 2.285(4) Å and is similar to other As–Br distances, in contrast to the unreasonably short distance of 2.15(4) Å previously reported. [4] The Br· · ·Br non-bonded distance is 3.377(4) Å (see Table 4). The unit-cell packing arrangement is shown in Fig. 2. Clearly, the solid-state structure for As is $[Me_3AsBr]^+Br^-$.

For Sb a distorted trigonal bipyramidal structure is obtained in $P6_3mc$, although not nearly to the extent as found in the earlier determination of Me_3AsBr_2 in which the As–Br distances were reported as 2.15(4) and 3.82(4) Å. [4] Atomic coordinates for the 1971 study are not available either in the original literature or databases. However, we have simulated these extreme distortions with the current data by placing Sb on the screw axis at $0,0,z$; this leads to an unrefinable structure (as was observed for the As data) with very short and very long Sb–Br bond distances, resembling the earlier ionic As characterization. In Table 3, we report a structurally more plausible result in this space group based on placement of Sb on the three-fold axis at $1/3,2/3,z$. The pyramidalization at Sb is still evident in the 0.153 Å elevation of the Sb atom above the carbon-atom plane, but the independent Sb–Br distances differ by only 0.04 Å.

Refinement in $P\bar{6}2c$ leads to a chemically plausible result with reasonable bond distances and a regular trigonal bipyramidal structure, but a large residual unassigned electron density peak, 2.71 $e\text{Å}^3$ resides about 0.45 Å from Br suggesting that in the absence of a mirror plane there is instability along the three-fold axis.

Refinement in $P6_3/mmc$ produced the most satisfactory results for Sb: lowest e.s.d.s, lowest residuals, only background-level noise and chemically reasonable
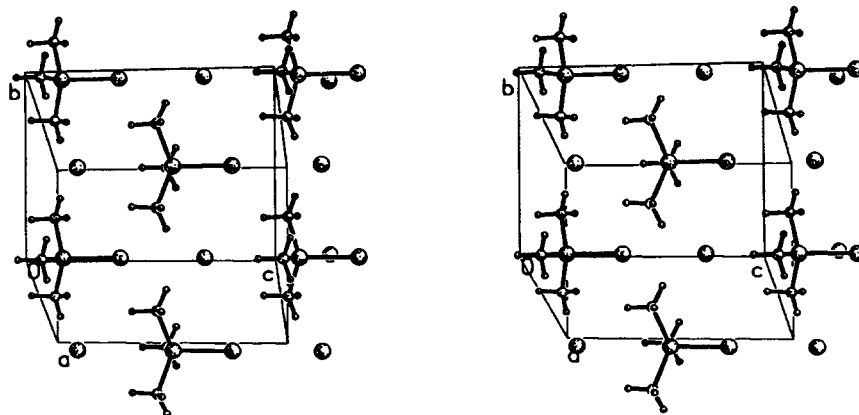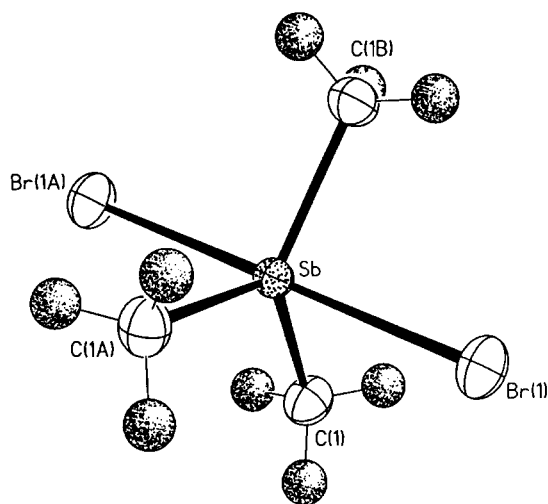

Fig. 2. Stereo unit-cell packing figure for Me_3AsBr_2.

Fig. 3. Molecular structure of Me_3SbBr_2 drawn with 40% thermal ellipsoids. The crystallographic disorder imposed on the methyl-group hydrogen atoms has been removed for clarity.

bond parameters. Crystallographic symmetry requires that all non-hydrogen bond angles be 90°, 120° or 180°. The stereoviews of the unit-cell packing in Fig. 3 show an unambiguously centrosymmetric arrangement of molecules. (In the two noncentrosymmetric space groups the basic packing arrangements are essentially unchanged, but they are far less regular.)

Another factor that differs among the three refinements for Sb is the symmetry of the methyl group environments. Whereas the variation in bonded intramolecular parameters is not dramatically large, the non-bonded contacts, in particular the intra- and intermolecular $dC \cdots Br$ distances differ more extensively Table 5 gives a comparison of the three refinements. In Table 5, the distances of 3.3–3.5 Å are intramolecular, and those of 3.9–4.1 Å represent interactions with neighboring molecules. In both of the noncentrosymmetric space group choices, the electrostatic field of the bromine atoms found at the methyl groups is of very low symmetry, whereas in $P6_3/mmc$ the field is much

more symmetrical. As a method of checking the correctness of our centrosymmetric assignment, we determined the solid-state ^{13}C MAS spectrum of a polycrystalline sample of Me_3SbBr_2. The observed spectrum consists of a single symmetric line at 19.75 ppm broadened by unresolved weak couplings to Sb. No anisotropy is present that would indicate that the carbon atom is coupled to antimony subject to a strong quadrupolar coupling [8]. Such an observation is consistent with the assignment of a centrosymmetric space group, with the antimony nucleus at a center of high symmetry.

3. Experimental

Trimethylarsenic dibromide [9] and trimethylantimony dibromide [10] were prepared following literature procedures.

3.1. Crystallographic studies of Me_3AsBr_2 (As) and Me_3SbBr_2 (Sb)

Crystallographic data are collected in Table 1. Crystals of As were grown from acetone and those of Sb were grown from water. Colorless rods of each were mounted on fine glass fibers with epoxy cement. From a combination of photographic evidence and diffraction symmetry, it was determined that both crystals possessed 6/mmm Laue symmetry. Systematic absences in the data allowed three space groups, as discussed in the text. Refinement was carried to convergence in all three for both analogs with all non-hydrogen atoms anisotropic; comparative results are given in Table 2 for the Sb. The structures were solved intuitively. For As, the noncentrosymmetric space group $P6_3mc$ produced the most chemically reasonable set of bond parameters and the lowest residuals. Despite E-statistics which suggested that As was centrosymmetric, it was not possible to achieve a stable refinement in the centrosymmetric alternative. In $P\bar{6}2c$, the alternative non-

Table 5
Comparison of refinement results for the three possible hexagonal space groups for Me_3SbBr_2

	$R(F)$ (%) [a]	$dSb-Br$ (Å)	$dSb-C$ (Å)	$dC \cdots Br$ (Å)	d(Sb out of plane) (Å)	$\Delta\rho$ (e Å^{-3})
$P6_3mc$	4.1	2.621(7) 2.663(10)	2.12(4)	3.29–1 [b] 3.49–1 4.04–2 4.15–2	0.153	1.65
$P\bar{6}2c$	3.6	2.642(4)	2.09(2)	3.37–2 3.94–2 4.25–2	0.0	2.71
$P6_3/mmc$	2.9	2.649(2)	2.047(5)	3.35–2 4.09–4	0.0	0.65

[a] $5\sigma(F_o)$ data, non-hydrogen atoms anisotropic, hydrogen atoms idealized.
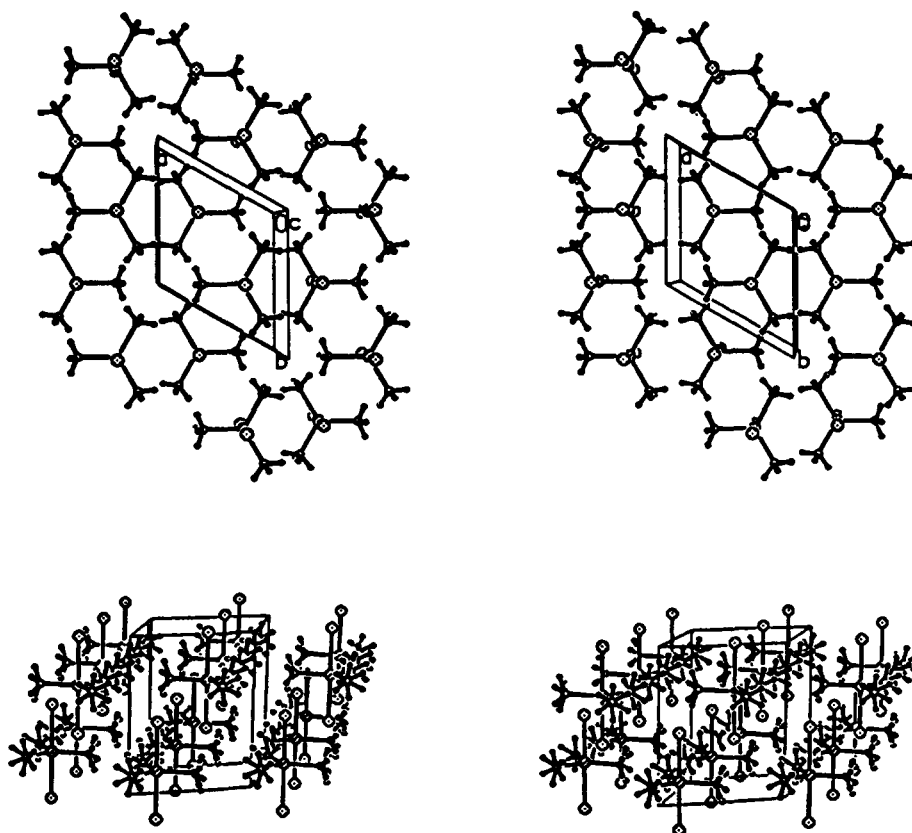[b] Redundancy of this distance.

Fig. 4. Two stereoviews of the crystal packing of Me_3SbBr_2; the upper view is down the c axis, and the lower view is down the b axis.

centrosymmetric space group, bond distance excursions from chemically reasonable values were unacceptable. A Rogers test which determines a multiplier for $\Delta f''$ refined to 1.2(2) indicating that the hand reported is correct. For Sb, in the most satisfactory space group, $P6_3/mmc$, the hydrogen atoms on the methyl group are rotationally disordered in two equivalent sets. Two stereoviews of the crystal packing of Me_3SbBr_2 are shown in Fig. 4. All computations used SHELXTL software (ver. 4.2, G. Sheldrick, Siemens XRD, Madison, WI).

3.2. ^{13}C CPMAS NMR study of Me_3SbBr_2

Solid state NMR spectra of the methyl group carbon atoms were determined using magic angle spinning at approximately 3.5 kHz and high-power proton decoupling on a Chemagnetics m100S spectrometer at a frequency of 25.012 MHz. The 90° pulse length was 6.8 μs and the cross-polarization contact time was 8 ms.

4. Supplementary material available

Tables of thermal parameters, hydrogen-atom coordinates and structure factors are available from one of the authors (ALR) at arnrhein@strauss.udel.edu.

Acknowledgments

References and notes

[1] For summaries of these studies, see: G.O. Doak and L.D. Freedman, Organometallic Compounds of Arsenic, Antimony and Bismuth, Wiley, New York, 1970, pp. 205, 333; Gmelin Handbook of Inorganic Chemistry, Organoantimony Compounds, Vol. 4, Springer, Berlin, 1986.
[2] T.B. Brill and G.G. Long, Inorg. Chem., 9 (1970) 1980.
[3] M.H. O'Brien, G.O. Doak and G.G. Long, Inorg. Chim. Acta, 1 (1967) 34.
[4] M.B. Hursthouse, I.A. Steer, J. Organomet. Chem., 27 (1971) C11.
[5] A.F. Wells, Z. Kryst., 99 (1938) 367.
[6] As–Br bond distances were obtained from the Cambridge Structural Database: F.H. Allen and O. Kennard, Chem. Design Automat. News, 8 (1993) 31.
[7] W. Schwartz and H.J. Guder, Z. Anorg. Allgem. Chem., 444 (1978) 105.
[8] J.G. Hexem, M.H. Frey and S.J. Opella, J. Am. Chem. Soc., 103 (1981) 224.
[9] W.J.C. Dyke, G. Davies and W.J. Jones, J. Chem. Soc., (1931) 185.
[10] H. Schmidbaur and K.H. Mitschke, Chem. Ber., 104 (1971) 1837.