

Second Determination of the Structure of Dimeric Triphenylstibine Oxide

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Abstract. $C_{36}H_{30}O_2Sb_2$, $M_r = 738.14$, triclinic, $P\bar{1}$, $a = 10.716$ (3), $b = 14.135$ (7), $c = 10.542$ (4) Å, $\alpha = 96.11$ (4), $\beta = 104.04$ (3), $\gamma = 89.90$ (3)°, $V = 1539.8$ Å³, $Z = 2$, $D_x = 1.59$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 17.9$ cm⁻¹, $F(000) = 728$, $T = 293$ K, $R = 0.024$ for 5714 observed reflections. The structure consists of dimeric $(\text{Ph}_3\text{SbO})_2$ molecules containing the 1,3,2,4-dioxadistibetane ring: each Sb atom exhibits regular trigonal-bipyramidal coordination by three C and two O atoms: the ring O atoms occupy one apical and one equatorial site. The two crystallographically independent molecules show only trivial structural differences.

Introduction. There has been much uncertainty about the structures of compounds described as triphenylstibine oxide (Briles & McEwen, 1966; Doak & Freedman, 1970; Venezky, Sink, Nevett & Fortescue, 1972; Lumbroso, Lloyd & Harris, 1974; Bowen & Long, 1978; Bordner, Doak & Everett, 1986). We have recently obtained, from the hydrolysis of triphenylstibonium bis(*p*-toluenesulfonyl)methylide, $\text{Ph}_3\text{SbC}(\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3)_2$ (Glidewell, Lloyd & Metcalfe, 1986; cf. Ferguson, Glidewell, Lloyd, Metcalfe & Ruhl, 1987), a product whose elemental analysis, and spectra, showed it to be a triphenylstibine oxide. Structure analysis shows it to comprise centrosymmetric dimeric molecules $(\text{Ph}_3\text{SbO})_2$: this hydrolysis product is thus the same compound as that recently characterized (Bordner *et al.*, 1986) from the thermal decomposition of Ph_4SbOH , although the structure analysis here reported is of rather higher precision.

Experimental. Colourless small block crystals grown from hexane/dichloromethane. Accurate cell dimensions and crystal orientation matrix determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 23 reflections in the range $8 \leq \theta \leq 15^\circ$. Crystal dimensions $0.53 \times 0.41 \times 0.40$ mm; intensities of reflections with indices $h - 13$ to 13 , $k - 18$ to 0 , $l - 13$ to 13 with $2 \leq 2\theta \leq 54^\circ$ measured; $\omega - 2\theta$ scans, ω -scan width $(0.60 + 0.35 \tan \theta)^\circ$, graphite-monochromatized Mo $K\alpha$ radiation; intensities of three reflections measured every 2 h showed no evidence of crystal decay. 7190 reflections measured, 6550 unique, 5714 with $F \geq 3\sigma(F)$ labelled observed and used in structure solution and refinement; $R_{\text{int}} = 0.008$. Data corrected for Lorentz, polarization and absorption effects (max. and min. transmission factors 0.574, 0.467). Gaussian integration, grid $10 \times 8 \times 8$. Space group $P\bar{1}$ or $P1$, $P\bar{1}$ chosen and confirmed by the successful refinement. The coordinates of the two Sb atoms in the asymmetric unit were determined from a detailed analysis of the three-dimensional Patterson function and the coordinates of the remaining non-H atoms found *via* the heavy-atom method. There are two independent half molecules of the complex lying about inversion centres in the asymmetric unit. Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed maxima in positions consistent with the expected locations of the H atoms; in the final rounds of calculations the H atoms were positioned on geometrical grounds (C–H 0.95 Å) and included (as riding atoms) in the structure-factor calculations with an overall B_{iso} of 5.0 Å². The final cycle of refinement on F

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included 362 variable parameters, $R = 0.024$, $wR = 0.044$, goodness-of-fit 1.19, $w = 1/[\sigma^2(F_o) + 0.07(F_o)^2]$. Max. shift/e.s.d. = 0.09; density in final difference map $\pm 0.72(7)e \text{ \AA}^{-3}$; no chemically significant features. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (Frenz, 1982). Atomic parameters and details of molecular geometry are given in Tables 1 and 2.* Fig. 1 is a view of one of the molecules prepared using *ORTEPII* (Johnson, 1976).

Discussion. The crystalline product from the hydrolysis of the stibonium ylide $\text{Ph}_3\text{SbC}(\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3)_2$ was shown by analysis to be a triphenylstibine oxide, but no combination of spectroscopic measurements could

provide definitive structural information. The X-ray analysis shows it to be the dimeric form containing the 1,3,2,4-dioxadistibetane ring, and to be identical to the product obtained (Bordner *et al.*, 1986) by thermal decomposition of Ph_4SbOH . The structure analysis reported here is of higher precision than the previous study (Bordner *et al.*, 1986) as shown by comparison of a few key parameters for the present determination with those for the earlier work in parentheses: number of unique reflections, 6550 (3317); number of observed reflections, 5714 (3169); R , 0.024 (0.036); $\sigma(\text{Sb}-\text{C})$, 0.002 \AA (0.006 \AA); $\sigma(\text{Sb}-\text{O})$, 0.002 \AA (0.004 \AA); $\sigma[\angle(\text{XSbY})]$ ($X, Y = \text{O}, \text{C}$), 0.08° (0.2°).

Table 2. Bond distances (\AA) and angles ($^\circ$)

Numbers in parentheses are e.s.d.'s in the least-significant digits.

* Lists of structure factors, anisotropic thermal parameters and calculated H coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43549 (70 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional and equivalent isotropic thermal parameters and their e.s.d.'s

| | x | y | z | B_{eq}^* (\AA^2) |
|--------|--------------|--------------|-------------|--------------------------------------|
| Sb(1) | -0.05579 (1) | -0.00463 (1) | 0.12319 (1) | 2.636 (3) |
| O(1) | -0.1016 (2) | 0.0416 (1) | -0.0479 (1) | 3.42 (3) |
| C(111) | 0.0727 (2) | 0.0712 (2) | 0.2896 (2) | 2.97 (4) |
| C(112) | 0.2027 (2) | 0.0569 (2) | 0.3137 (2) | 3.62 (5) |
| C(113) | 0.2875 (3) | 0.1057 (2) | 0.4235 (3) | 4.37 (6) |
| C(114) | 0.2404 (3) | 0.1686 (2) | 0.5092 (3) | 4.62 (6) |
| C(115) | 0.1105 (3) | 0.1818 (2) | 0.4860 (3) | 5.23 (7) |
| C(116) | 0.0275 (3) | 0.1337 (2) | 0.3784 (3) | 4.23 (6) |
| C(121) | -0.2352 (2) | 0.0465 (2) | 0.1603 (2) | 3.21 (4) |
| C(122) | -0.2810 (2) | 0.0155 (2) | 0.2634 (2) | 3.78 (5) |
| C(123) | -0.3967 (3) | 0.0455 (2) | 0.2851 (2) | 4.21 (5) |
| C(124) | -0.4689 (3) | 0.1077 (2) | 0.2063 (3) | 5.35 (7) |
| C(125) | -0.4268 (3) | 0.1373 (3) | 0.1056 (3) | 6.16 (7) |
| C(126) | -0.3089 (3) | 0.1088 (2) | 0.0831 (3) | 4.90 (6) |
| C(131) | 0.0787 (2) | -0.1497 (2) | 0.1524 (2) | 3.10 (4) |
| C(132) | -0.1976 (3) | -0.1930 (2) | 0.1309 (3) | 3.98 (5) |
| C(133) | 0.2096 (3) | -0.2880 (2) | 0.1539 (3) | 4.52 (6) |
| C(134) | -0.0996 (3) | -0.3374 (2) | 0.2021 (3) | 4.56 (6) |
| C(135) | 0.0183 (3) | -0.2947 (2) | 0.2222 (3) | 4.73 (6) |
| C(136) | 0.0308 (3) | -0.2007 (2) | 0.1966 (3) | 3.98 (5) |
| Sb(2) | 0.48119 (1) | 0.51942 (1) | 0.14329 (1) | 2.758 (3) |
| O(2) | 0.4913 (2) | 0.5883 (1) | -0.0031 (2) | 3.37 (3) |
| C(211) | 0.6508 (2) | 0.4810 (2) | 0.2766 (2) | 3.72 (5) |
| C(212) | 0.7120 (3) | 0.3983 (2) | 0.2475 (3) | 5.10 (7) |
| C(213) | 0.8189 (3) | 0.3706 (3) | 0.3388 (4) | 6.70 (9) |
| C(214) | 0.8646 (3) | 0.4229 (3) | 0.4564 (4) | 7.21 (9) |
| C(215) | 0.8041 (3) | 0.5058 (3) | 0.4845 (3) | 6.66 (9) |
| C(216) | 0.6986 (3) | 0.5352 (2) | 0.3960 (3) | 4.82 (6) |
| C(221) | 0.4394 (2) | 0.6490 (2) | 0.2523 (2) | 3.40 (5) |
| C(222) | 0.4059 (3) | 0.6459 (2) | 0.3717 (3) | 4.68 (6) |
| C(223) | 0.3752 (3) | 0.7281 (3) | 0.4388 (3) | 5.74 (7) |
| C(224) | 0.3767 (3) | 0.8152 (2) | 0.3886 (3) | 5.13 (7) |
| C(225) | 0.4039 (3) | 0.8176 (2) | 0.2714 (3) | 4.90 (7) |
| C(226) | 0.4373 (3) | 0.7358 (2) | 0.2036 (3) | 4.00 (5) |
| C(231) | 0.3170 (2) | 0.4407 (2) | 0.1567 (2) | 3.13 (4) |
| C(232) | 0.1969 (3) | 0.4802 (2) | 0.1321 (3) | 4.04 (6) |
| C(233) | 0.0898 (3) | 0.4269 (2) | 0.1339 (3) | 5.21 (7) |
| C(234) | 0.1021 (3) | 0.3354 (2) | 0.1652 (3) | 5.38 (7) |
| C(235) | 0.2190 (3) | 0.2958 (2) | 0.1929 (3) | 5.72 (7) |
| C(236) | 0.3289 (3) | 0.3497 (2) | 0.1899 (3) | 4.68 (6) |

* Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $\frac{1}{3}(a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3))$.

| | | | |
|----------------------|------------|----------------------|------------|
| Sb(1)-O(1) | 1.934 (2) | Sb(2)-O(2) | 1.935 (2) |
| Sb(1)-O(1') | 2.075 (2) | Sb(2)-O(2') | 2.079 (2) |
| Sb(1)-C(111) | 2.134 (2) | Sb(2)-C(211) | 2.120 (2) |
| Sb(1)-C(121) | 2.161 (2) | Sb(2)-C(221) | 2.163 (2) |
| Sb(1)-C(131) | 2.129 (2) | Sb(2)-C(231) | 2.125 (2) |
| C(111)-C(112) | 1.373 (3) | C(211)-C(212) | 1.382 (4) |
| C(111)-C(116) | 1.391 (4) | C(211)-C(216) | 1.384 (4) |
| C(112)-C(113) | 1.401 (3) | C(212)-C(213) | 1.391 (4) |
| C(113)-C(114) | 1.382 (4) | C(213)-C(214) | 1.355 (5) |
| C(114)-C(115) | 1.370 (5) | C(214)-C(215) | 1.378 (6) |
| C(115)-C(116) | 1.374 (4) | C(215)-C(216) | 1.375 (4) |
| C(121)-C(122) | 1.404 (4) | C(221)-C(222) | 1.395 (4) |
| C(121)-C(126) | 1.379 (4) | C(221)-C(226) | 1.377 (4) |
| C(122)-C(123) | 1.373 (4) | C(222)-C(223) | 1.377 (4) |
| C(123)-C(124) | 1.379 (4) | C(223)-C(224) | 1.392 (5) |
| C(124)-C(125) | 1.355 (5) | C(224)-C(225) | 1.340 (5) |
| C(125)-C(126) | 1.393 (4) | C(225)-C(226) | 1.388 (4) |
| C(131)-C(132) | 1.372 (3) | C(231)-C(232) | 1.379 (4) |
| C(131)-C(136) | 1.385 (3) | C(231)-C(236) | 1.367 (4) |
| C(132)-C(133) | 1.402 (4) | C(232)-C(233) | 1.379 (4) |
| C(133)-C(134) | 1.384 (4) | C(233)-C(234) | 1.366 (5) |
| C(134)-C(135) | 1.360 (4) | C(234)-C(235) | 1.350 (4) |
| C(135)-C(136) | 1.397 (4) | C(235)-C(236) | 1.412 (5) |
| O(1)-Sb(1)-O(1') | 77.56 (7) | O(2)-Sb(2)-O(2') | 77.34 (6) |
| O(1)-Sb(1)-C(111) | 122.95 (8) | O(2)-Sb(2)-C(211) | 120.63 (9) |
| O(1)-Sb(1)-C(121) | 89.69 (8) | O(2)-Sb(2)-C(221) | 90.74 (8) |
| O(1)-Sb(1)-C(131) | 123.26 (7) | O(2)-Sb(2)-C(231) | 124.96 (7) |
| O(1')-Sb(1)-C(111) | 88.61 (8) | O(2')-Sb(2)-C(211) | 90.34 (8) |
| O(1')-Sb(1)-C(121) | 167.24 (7) | O(2')-Sb(2)-C(221) | 167.39 (8) |
| O(1')-Sb(1)-C(131) | 89.02 (8) | O(2')-Sb(2)-C(231) | 87.70 (8) |
| C(111)-Sb(1)-C(121) | 98.49 (8) | C(211)-Sb(2)-C(221) | 99.40 (9) |
| C(111)-Sb(1)-C(131) | 111.30 (8) | C(211)-Sb(2)-C(231) | 111.96 (9) |
| C(121)-Sb(1)-C(131) | 98.14 (9) | C(221)-Sb(2)-C(231) | 95.96 (9) |
| Sb(1)-O(1)-Sb(1') | 102.44 (7) | Sb(2)-O(2)-Sb(2') | 102.66 (7) |
| Sb(1)-C(111)-C(112) | 120.4 (2) | Sb(2)-C(211)-C(212) | 119.9 (2) |
| Sb(1)-C(111)-C(116) | 121.4 (2) | Sb(2)-C(211)-C(216) | 121.1 (2) |
| C(112)-C(111)-C(116) | 118.2 (2) | C(212)-C(211)-C(216) | 118.2 (2) |
| C(111)-C(112)-C(113) | 120.7 (2) | C(211)-C(212)-C(213) | 119.3 (3) |
| C(112)-C(113)-C(114) | 120.0 (3) | C(212)-C(213)-C(214) | 121.4 (3) |
| C(113)-C(114)-C(115) | 119.3 (2) | C(213)-C(214)-C(215) | 118.8 (3) |
| C(114)-C(115)-C(116) | 120.6 (3) | C(214)-C(215)-C(216) | 121.1 (3) |
| C(111)-C(116)-C(115) | 121.2 (3) | C(211)-C(216)-C(215) | 120.1 (3) |
| Sb(1)-C(121)-C(122) | 120.5 (2) | Sb(2)-C(221)-C(222) | 120.3 (2) |
| Sb(1)-C(121)-C(126) | 121.4 (2) | Sb(2)-C(221)-C(226) | 121.7 (2) |
| C(122)-C(121)-C(126) | 118.1 (2) | C(222)-C(221)-C(226) | 117.9 (2) |
| C(121)-C(122)-C(123) | 120.8 (2) | C(221)-C(222)-C(223) | 120.2 (3) |
| C(122)-C(123)-C(124) | 120.0 (3) | C(222)-C(223)-C(224) | 120.7 (3) |
| C(123)-C(124)-C(125) | 119.9 (3) | C(223)-C(224)-C(225) | 119.1 (3) |
| C(124)-C(125)-C(126) | 120.9 (3) | C(224)-C(225)-C(226) | 120.9 (3) |
| C(121)-C(126)-C(125) | 120.2 (3) | C(221)-C(226)-C(225) | 121.1 (3) |
| Sb(1)-C(131)-C(132) | 122.2 (2) | Sb(2)-C(231)-C(232) | 120.9 (2) |
| Sb(1)-C(131)-C(136) | 118.2 (2) | Sb(2)-C(231)-C(236) | 120.3 (2) |
| C(132)-C(131)-C(136) | 119.6 (2) | C(232)-C(231)-C(236) | 118.8 (3) |
| C(131)-C(132)-C(133) | 120.8 (2) | C(231)-C(232)-C(233) | 120.5 (3) |
| C(132)-C(133)-C(134) | 119.1 (3) | C(232)-C(233)-C(234) | 120.3 (3) |
| C(133)-C(134)-C(135) | 120.0 (3) | C(233)-C(234)-C(235) | 120.4 (3) |
| C(134)-C(135)-C(136) | 121.1 (3) | C(234)-C(235)-C(236) | 119.6 (3) |
| C(131)-C(136)-C(135) | 119.3 (3) | C(231)-C(236)-C(235) | 120.3 (3) |

Symmetry code: (i) $-x, -y, -z$; (ii) $1-x, 1-y, -z$.

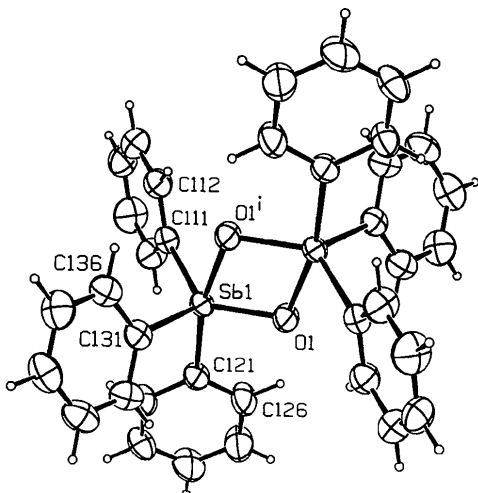
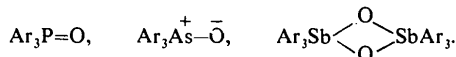


Fig. 1. Perspective view of molecule (1), showing the atom-numbering scheme.

The molecules comprise centrosymmetric dimers: the two crystallographically independent molecules show only trivial structure differences (Table 2). Each Sb atom exhibits rather exact trigonal-bipyramidal coordination with one O atom apical and one equatorial, as expected for a four-membered ring. For Sb(1), the apical atoms are C(121) and O(1') and the equatorial atoms are C(111), C(131) and O(1): of the three Sb—C distances, the apical Sb(1)—C(121) distance is significantly longer than the other two; likewise the apical Sb—O distance is much longer than the corresponding equatorial distance. These observations on $(\text{Ph}_3\text{SbO})_2$ neatly encapsulate most of the familiar generalizations

made by VSEPR theory about trigonal-bipyramidal structures.

The dimeric structure found for triphenylstibine oxide is in sharp contrast to the monomeric structure, containing near-tetrahedral Sb, found for triphenylstibine sulfide (Pebler, Weller & Dehnicke, 1982). It is interesting to note the changes in structure of the triaryl element oxides Ar_3MO ($M = \text{P}, \text{As}$ or Sb) which may most simply be summarized thus:



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Bis(isothiocyanato)(2,2',2''-trihydroxytriethylamine-*N,O,O',O''*)nickel(II)

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Abstract. $[\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_{15}\text{NO}_3)]$, $M_r = 324.06$, monoclinic, $P2_1/c$, $a = 9.4048$ (10), $b = 10.4130$ (7), $c =$

14.0647 (16) Å, $\beta = 101.05$ (1)°, $V = 1351.9$ (3) Å³, $Z = 4$, $D_x = 1.59$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.54051$ Å, $\mu = 49.34$ cm⁻¹, $F(000) = 672$, $T = 290$ K. Final $R = 0.034$ for 2234 'observed' reflections and 192 variables. Ni^{2+} is octahedrally coordinated ($\text{NiN}_2\text{O}_3\text{N}$ chromophore) by the N atoms of the NCS^- ions (in mutually

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