J. Am. Chem. Soc. 1986, 108, 4206–4213

Crystal Structure of 2,2,4,4-Tetrahydro-2,2,2,4,4,4-hexaphenyl-1,3,2,4-dioxadistibetane (Triphenylstibine Oxide Dimer) and Related Compounds

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Abstract: The structure of triphenylstibine oxide has long been the subject of considerable controversy in the chemical literature. Crystals, obtained by the slow cooling of a xylene solution of the crystalline form of the compound I, were subjected to a single-crystal X-ray analysis and shown to exist as a dimer with a four-membered ring containing Sb–O–Sb linkages. Molecular weight determinations and the infrared spectrum showed that this structure was unchanged in solution. The oxidation of triphenylstibine with hydrogen peroxide in acetone solution under carefully controlled conditions led to the formation of a cyclic peroxide in which a mole of acetone was incorporated into the molecule II. Its structure was determined by X-ray analysis. A compound III, previously believed to be diphenylstibinic acid anhydride, was a byproduct of this oxidation. An X-ray analysis of this material showed it to be a complex tricyclic compound with four antimony and six oxygen atoms in the rings. In addition to the crystalline form, one or more amorphous forms of triphenylstibine oxide, of unknown structure, have been prepared. The crystal data (Mo Kα, $\lambda = 0.71069$ Å) are as follows. I: $a = 10.703$ (5) Å, $b = 10.521$ (5) Å, $c = 14.225$ (8) Å, space group $P\bar{1}$. II: $a = 18.124$ (2) Å, $b = 9.327$ (1) Å, $c = 11.390$ (1) Å, space group $Pna2_1$. III: $a = 11.677$ (5) Å, $b = 9.745$ (3) Å, $c = 10.586$ (6) Å, space group $P\bar{1}$.

The structure of triphenylstibine oxide has long been the subject of controversy among those chemists whose research interests include organic compounds of arsenic, antimony, and bismuth. Triphenylstibine oxide has been synthesized a number of times by a wide variety of methods with highly discordant results. A summary of the research results before 1970 was published in that year.[1] At that time three crystalline samples, prepared by three different synthetic procedures, had been reported.[2–4] All melted in the range 221–223 °C. Other samples of the compound, prepared by other groups of workers, were apparently noncrystalline. Their melting points varied from 209 to 295 °C.[1]

In 1972 Venezky and co-workers[5] published a long paper on the structure and properties of triphenylstibine oxide. Previous work was reviewed, and a number of experiments, designed to afford a final solution to the structural problem of this compound, were performed. These authors were unable to obtain the crystalline product previously described by McEwen and co-workers.[3] Instead they obtained only amorphous material by several different synthetic procedures. All samples melted at 280 °C. They concluded that triphenylstibine oxide existed only as a polymer of unknown molecular weight. In that same year (1972) another paper from McEwen's laboratory again described, in much greater detail, the preparation of crystalline triphenylstibine oxide. A molecular weight determination in refluxing benzene by vapor-phase osmometry gave a value of 367 ± 3 (calculated for the monomer 369). In spite of these molecular weight results, McEwen and co-workers believed the compound existed as an equilibrium mixture of monomer and a more highly associated form. This conclusion was based solely on the IR spectral data. Two absorption bands at 664 and 478 cm^{-1} were assigned to Sb═O and Sb—O—, respectively. The assignments were based on an earlier paper of Chremos and Zingaro[7] who had reported on the IR spectra of a series of trialkylstibine oxides. McEwen's group further concluded that triphenylstibine oxide existed in two different forms: a polymeric material of unknown molecular weight which melted at 280 °C and a crystalline form, mp 221.5–222 °C, which was a monomer in equilibrium with a more highly associated form.

Other recent work has not solved the structural problem. Razuvaev and co-workers[8] prepared crystalline triphenylstibine oxide, mp 219 °C, by the oxidation of triphenylstibine with *tert*-butyl (or cumene) hydroperoxide. Although Nomura[9] obtained the same prooduct, mp 220–221 °C, by this procedure, Hiatt and co-workers[10] stated that this oxidation with *tert*-butyl hydroperoxide gave a polymeric product similar to that obtained by Venezky.[5] Pichuk and co-workers[11] prepared crystalline triphenylstibine oxide, mp 220–221 °C, by the reaction between an *Sb*,*Sb*,*Sb*-triphenyl-*N*-(arylsulfonyl)stibine imide and benzaldehyde:

$$\mathrm{ArSO_2N{=}SbPh_3 + PhCHO \rightarrow ArSO_2N{=}CHPh + Ph_3SbO}$$

Molecular weight determinations ebullioscopically in boiling benzene or boiling dichloroethane gave values of 780 and 705, respectively, in agreement with values for a dimer. The authors suggested that triphenylstibine oxide exists as a dimer containing a four-membered ring with Sb–O–Sb bonds. The ^{121}Sb Mössbauer spectrum of crystalline triphenylstibine oxide has been reported by Bowen and Long.[12] They concluded that a structure containing a trigonal bipyramidal antimony atom, with bridging oxygen atoms in apical positions, was the only simple structure that fitted the Mossbauer data.

In view of the conflicting data, it would seem logical to determine the structure of crystalline triphenylstibine oxide by means of X-ray diffraction. In this regard, we prepared the crystalline material by most of the methods reported in the chemical literature.[2–4,6,8,13] All samples appeared to be identical as judged by mixed melting points and IR spectra. For X-ray diffraction, a

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(1) Doak, G. O.; Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony, and Bismuth*; Wiley: New York, 1970; pp 298–307 and references cited therein.

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(7) Chremos, G. N.; Zingaro, R. A. *J. Organomet. Chem.* **1970**, *22*, 637–646.

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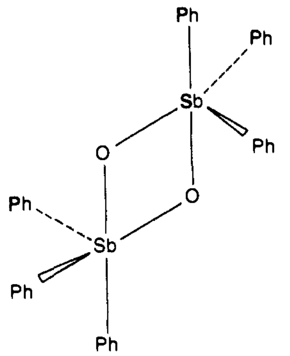

Figure 1. Structure of triphenylstibine oxide dimer, 2,2,4,4-tetrahydro-2,2,2,4,4,4-hexaphenyl-1,3,2,4-dioxadistibetane (compound I).

sample prepared by the thermal decomposition of hydroxytetraphenylantimony according to the directions of McEwen and coworkers[3,6] was recrystallized by slow cooling of a hot xylene solution of the compound. Beautiful prismatic crystals, mp 220–221 °C, suitable for X-ray diffraction and analyzing correctly for triphenylstibine oxide, were obtained. X-ray diffraction studies, reported in the Experimental Section, showed that this triphenylstibine oxide (I) was dimeric (Figure 1) with a structure similar to that proposed by Pichuk,[11] namely 2,2,4,4-tetrahydro-2,2,2,4,4,4-hexaphenyl-1,3,2,4-dioxadistibetane as shown in Figure 1.

Although this result applies only to the compound in the solid state, we believe that the same structure is present in solution. Thus, the IR spectrum of compound I was essentially the same in the solid state (Nujol mull and KBr pellets) and in solution (CS_2 and CCl_4). Furthermore, molecular weight determinations, both ebullioscopically in boiling benzene and by vapor-phase osmometry in carbon tetrachloride at 37 °C (Experimental Section) gave values in close agreement with those calculated for the dimer. From all of these results we are convinced that crystalline triphenylstibine oxide exists only as a dimer, both in the solid state and in solution.

In addition to the crystalline material, we have also carried out further studies on the amorphous forms of triphenylstibine oxide as reported by previous investigators[1,5,9,14,15] and also on a commercially available sample of the same material.[16] Oxidation of triphenylstibine with hydrogen peroxide in acetone solution has been the usual method for preparing the amorphous product.[1,5,9,14] The resulting material, after treatment with benzene, was reported to be a white powder, almost insoluble in organic solvents.[17] The melting point has been reported to vary between 249 and 285 °C. There is, however, one exception to this result. Nerdel and coworkers[18] reported that oxidation of triphenylstibine with hydrogen peroxide in acetone gave a product, mp 170 °C, the analysis of which corresponded to the formula $(C_6H_5)_3SbO_{1.4}$ and which they believed was a peroxide. It should be noted that Nerdel and co-workers were apparently the only investigators of this procedure who did not treat the oxidation product with benzene. With one possible exception,[19] no other worker has reported the formation of a peroxide by this reaction.

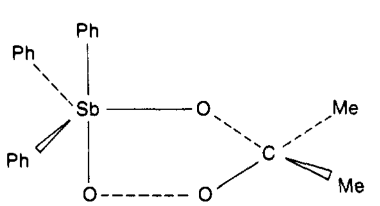

Figure 2. Structure of 3,3-dihydro-5,5-dimethyl-3,3,3-triphenyl-1,2,4,3-trioxastibolane (compound II).

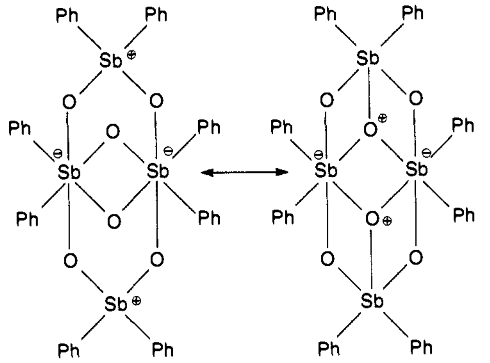

Figure 3. Structure of hexa-μ-oxooctaphenyltetraantimony (compound III).

We first attempted to repeat the oxidation of triphenylstibine in acetone solution following exactly the detailed directions of Goodgame and Cotton.[14] Our results, however, differed significantly from theirs. Instead of the 3 g of solid precipitate (from 12 g of triphenylstibine), we obtained from 7.4 to 10.3 g of crystalline material (average yield 9.4 g from six duplicate experiments). Elementary analyses of this solid (compound II), mp 165–167 °C dec, gave a C/Sb ratio of 21/1 and an empirical formula of $C_{21}H_{21}O_3Sb$. This result suggested that a mole of acetone had been incorporated into the molecule.

Compound II was unstable. On standing in the air, II gradually turned yellow (more slowly in a desiccator) and the percent of antimony increased. When the freshly prepared compound was stirred at room temperature with a variety of organic solvents other than acetone (benzene, toluene, xylene, chloroform, and carbon tetrachloride), it was rapidly transformed into an amorphous solid, mp 179–180 °C. Elemental analyses for this amorphous solid were in agreement with values for triphenylstibine oxide. It was essentially insoluble in organic solvents. The reaction of compound II with organic solvents was shown dramatically by the PMR spectral results. Compound II dissolved readily in $CDCl_3$ to form a clear solution which rapidly turned cloudy and soon deposited a white solid. If the PMR spectrum of the cloudy solution was obtained rapidly, two singlets at δ 1.4 and 2.1, as well as a multiplet centered at δ 7.45, were obtained. After about 2 min the heavy precipitate that formed in the NMR tube prevented further determinations. Integration of the spectrum showed that the ratio of aromatic protons at δ 7.45 vs. the sum of the two methyl protons was 15/6. If the spectrum was obtained in acetone-d_6, only the acetone methyl signal at δ 2.1 could be seen. However, when the spectrum was obtained in regular protonated acetone, the signal at δ 1.4 could be seen. These results are consistent with a compound containing a labile acetone molecule liberated by the solvent $CDCl_3$ and readily exchanged with acetone-d_6.

The formation of compound II was remarkably sensitive to the reaction conditions employed. Thus, if during the addition of

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(13) McEwen and co-workers (McEwen, W. E.; Briles, G. H.; Giddings, B. E. *J. Am. Chem. Soc.* **1969**, *91*, 7079–7084) have questioned a report from our laboratory[4] that methoxytetraphenylantimony underwent decomposition in xylene, under carefully controlled conditions, to yield crystalline triphenylstibine oxide. They suggested rather that our reported synthesis of methoxytetraphenylantimony had actually given hydroxytetraphenylantimony and that it was this latter matterial that we had actually heated in xylene solution. Accordingly we have carefully rechecked our previous results. These are reported in the Experimental Section and confirm that fact that our previously reported results were not in error.

(14) Goodgame, D. M. L.; Cotton, F. A. *J. Am. Chem. Soc.* **1960**, *82*, 5774–5776.

(15) Srinivasan, C.; Pitchumani, K. *Int. J. Chem. Kinet.* **1982**, *14*, 1315–1324.

(16) Obtained from Alfa Products, Catalog No. 87672. Also see Goel, R. G.; Ridley, D. R. *J. Organomet. Chem.* **1979**, *182*, 207–212.

(17) Goodgame and Cotton[14] state that amorphous triphenylstibine oxide is quite soluble in hot dimethylformamide. We have found, however, that triphenylstibine oxide undergoes rapid decomposition when heated in dimethylformamide.

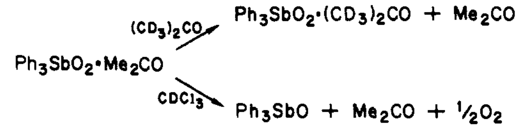
(18) Nerdel, F.; Buddrus, J.; Höher, K. *Chem. Ber.* **1964**, *97*, 124–131.

(19) Briles and McEwen[3] state that they obtained a peroxide by the oxidation of triphenylstibine with hydrogen peroxide. Their conclusion was based on the fact that the product liberated iodine from a glacial acetic acid solution of potassium iodide. However, almost all Sb(V) compounds oxidize iodide to iodine. A somewhat similar criticism of Briles and McEwen's conclusion has been given by Venezky and co-workers.[5]

Table I. Single-Crystal X-ray Crystallographic Analysis

	crystal		
	I	II	III
A. Crystal Parameters			
formula	$C_{36}H_{30}Sb_2O_2$ (738.13)	$C_{21}H_{21}O_8Sb$ (443.15)	$C_{48}H_{40}O_6Sb_4$ (1199.84)
crystallization medium	xylene	acetone	reaction mixture
crystal size, mm	0.21 × 0.30 × 0.31	0.31 × 0.31 × 0.36	0.19 × 0.23 × 0.25
cell dimensions			
a, Å	10.703 (5)	18.124 (2)	11.677 (5)
b, Å	10.521 (5)	9.327 (1)	9.745 (3)
c, Å	14.125 (8)	11.390 (1)	10.586 (6)
α, deg	96.09 (4)	90.0	99.69 (4)
β, deg	89.94 (4)	90.0	113.35 (3)
γ, deg	104.03 (4)	90.0	87.56 (3)
V, Å^3	1534 (1)	1925 (1)	1089.8 (8)
space group	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
molecules/unit cell	2	4	1
density obsd, g/cm^3	1.57	1.53	1.79
density calcd, g/cm^3	1.598	1.529	1.828
linear absorption coeff, cm^{-1}	18.1	14.7	25.3
B. Refinement Parameters			
no. of reflections	3317	2224	2357
non-zero reflections ($I > 1.0\sigma$)	3169	1722	2175
R^a	0.036	0.046	0.051
GOF^b	2.44	1.31	2.47
scale factor	0.957 (2)	0.936 (2)	0.682 (1)
secondary extinction coeff	0.6 (7) × 10^{-6}	0.0	0.7 (2) × 10^{-6}

$^a\Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b[\Sigma w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$.



hydrogen peroxide to the acetone solution of triphenylstibine the temperature was not controlled and the reaction mixture was not stirred at 0–5 °C but allowed to stand at room temperature, the crystalline solid which precipitated was not compound II but crystalline triphenylstibine oxide (I), mp 220–222 °C. The yield of this material, however, was never large (8–20%) even when the reaction mixture was allowed to stand for 24 h. This result may explain the findings of Boodts and Bueno[20] who reported the formation of triphenylstibine oxide, mp 220–221 °C, by this oxidation procedure. Furthermore, the IR spectrum in the region 950–400 cm^{-1}, which they reported,[20] was identical with the spectrum we have found for pure crystalline triphenylstibine oxide dimer (I).

Crystals of compound II, suitable for X-ray study, were obtained by recrystallization from acetone. The X-ray analysis gave the structure in Figure 2 for the compound, namely 3,3-dihydro-5,5-dimethyl-3,3,3-triphenyl-1,2,4,3-trioxastibolane.

The geometry of the antimony atom was that of a slightly distorted trigonal bipyramid, with two phenyl groups in equatorial positions and the peroxide oxygen and one phenyl group in axial positions.

The procedure of Venezky and co-workers[5] differed from that of Goodgame and Cotton in that the product from the oxidation of triphenylstibine was refluxed with benzene and by the use of a Dean-Stark trap to remove any water. The resulting triphenylstibine oxide was reported to melt at 280 °C,[5] considerably higher than that reported by Goodgame and Cotton[14] (254–256 °C). Venezky and co-workers do not state how long the refluxing was carried out. In repeating their work, we refluxed the oxidation product with benzene for 3 h. The resulting material melted at 280–285 °C, but the C/Sb ratio was only 13.7/1, suggesting that considerable decomposition had occurred from this procedure.

In addition to acetone as a solvent for the oxidation of triphenylstibine with hydrogen peroxide, we have carried out the same reaction employing either ethanol or acetonitrile as the solvent. In both cases amorphous white powders, essentially insoluble in common organic solvents and giving analytical results in approximate agreement with those for triphenylstibine oxide, were obtained. When either of these powders was dissolved in hot glacial acetic acid and the resulting solution cooled, crystals, mp 209 °C, were obtained which gave analytical values in agreement with those for diacetatotriphenylantimony. A similar result was obtained when crystalline triphenylstibine oxide (I) or the amorphous commercial product was treated with acetic acid. Accordingly, we are in agreement with McEwen[6] that triphenylstibine oxide occurs in two forms, a crystalline material, mp 220–222 °C, and an amorphous form (probably several forms) of unknown molecular weight. We differ from McEwen and co-workers[6] in our belief that the crystalline form is dimeric rather than monomeric.

Various other methods for preparing triphenylstibine oxide have been reported in the chemical literature. These include the use of oxidizing agents other than hydrogen peroxide or organic hydroperoxides for oxidizing triphenylstibine,[1,15] the thermal dehydration of dihydroxytriphenylantimony,[1,5] and the hydrolysis of dichlorotriphenylantimony by prolonged boiling with water.[21] Often the reaction conditions were not adequately described nor were the reaction products always properly characterized. We have not attempted to duplicate all of the reported synthetic procedures. We did attempt, without success, to duplicate the hydrolysis of dichlorotriphenylantimony as reported by Bernstein and co-workers.[21] We have been similarily unsuccessful in hydrolyzing diacetatotriphenylantimony to dihydroxytriphenylantimony by methods described in the chemical literature[22-24] (see Experimental Section).

When triphenylstibine was oxidized in acetone by the procedure of Goodgame and Cotton[14] and the crystalline II was removed by filtration, the filtrate was kept in the refrigerator for 2 weeks. A second crystalline product III, mp 285–290 °C, slowly crystallized from this solution. Elemental analysis of this material gave a C/Sb ratio of 12/1. The high melting point and the analytical results suggested that III might be the same as the

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[20] Boodts, J. F. C.; Bueno, W. A. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1689.

[21] Bernstein, J.; Halman, M.; Pinchas, S.; Samuel, S. *J. Chem. Soc.* **1964**, 821–824.

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[24] Becke-Goehring, M.; Thielemann, H. *Z. Anorg. Allg. Chem.* **1961**, *308*, 33–51.

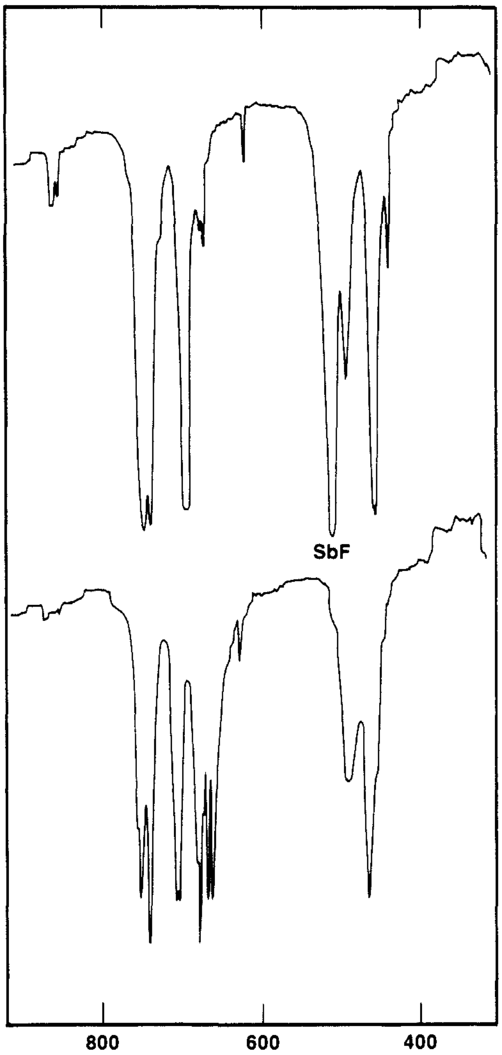


Figure 4. Comparison of the IR spectra of difluorotriphenylantimony (top) and triphenylstibine oxide dimer (bottom) in the region 300–900 cm^{-1}.

compound, mp 302–303 °C, reported by McEwen and co-workers[6] which was obtained by heating triphenylstibine oxide in xylene or dioxane without exclusion of oxygen. They also obtained the same product when a dioxane solution of triphenylstibine oxide was allowed to stand at room temperature for 20 days.[6] Accordingly, we prepared a sample from triphenylstibine oxide in xylene solution by McEwen's procedure.[6] The melting point of the resulting material, 302–303 °C, was not depressed by admixture with III, and the IR spectra of the two products were identical.

McEwen assigned the structure $Ph_2Sb(O)OSb(O)Ph_2$, i.e., the anhydride of diphenylstibinic acid, to this compound on the basis of its IR spectrum, independent synthesis, and chemical reactions. However, if it indeed is the acid anhydride, it should be soluble in aqueous alkali. We have found that the pure crystalline material was insoluble in sodium or potassium hydroxide solution, both in the cold or when heated. Accordingly we determined the structure of the pure compound, mp 302–303 °C, by X-ray diffraction. Rather than diphenylstibinic acid anhydride, it was found to be a complex oxide with four antimony atoms and six oxygen atoms in the unit cell (Figure 3). It is a resonance hybrid between two structures with the second canonical form contributing more to the structure, as judged by the Sb–O distances. Two different types of Sb atoms are present in the molecule, two hexacovalent Sb atoms bearing negative charges and two Sb atoms which are either tetracovalent, each with a positive charge, or pentacovalent, with positive charges on two oxygen atoms. The molecule does not contain an Sb=O bond as suggested by McEwen.[6]

Table II. Non-Hydrogen Atom Coordinates (×10^4) and Their Standard Deviations for Crystal I. The Values Have Been Multiplied by 10^4

	x/a	y/b	z/c
Sb1	188 (0)	3567 (0)	4806 (0)
01	88 (4)	5033 (4)	4122 (3)
C(1)	616 (6)	2471 (6)	3512 (4)
C(2)	944 (7)	1284 (7)	3543 (5)
C(3)	1244 (8)	594 (7)	2720 (6)
C(4)	1245 (7)	1100 (8)	1873 (6)
C(5)	951 (7)	2284 (8)	1830 (5)
C(6)	629 (7)	2975 (7)	2643 (5)
C(7)	−1504 (6)	2225 (6)	5195 (5)
C(8)	−1991 (7)	1034 (7)	4463 (6)
C(9)	−3055 (8)	149 (8)	4937 (8)
C(10)	−3639 (8)	438 (9)	5776 (8)
C(11)	−3177 (8)	1601 (10)	6305 (7)
C(12)	−2109 (7)	2527 (8)	6033 (6)
C(13)	1831 (6)	3431 (6)	5589 (4)
C(14)	3024 (7)	3695 (7)	5194 (5)
C(15)	4095 (7)	3653 (8)	5729 (6)
C(16)	3972 (8)	3335 (8)	6638 (6)
C(17)	2799 (8)	3063 (9)	7030 (5)
C(18)	1717 (7)	3103 (8)	6507 (5)
Sb2	4442 (0)	6232 (0)	9953 (0)
O1A	3979 (4)	4526 (4)	10419 (3)
C(1A)	2628 (6)	6597 (6)	10461 (5)
C(2A)	1896 (7)	5819 (7)	11076 (6)
C(3A)	743 (8)	6055 (9)	11367 (6)
C(4A)	289 (7)	7055 (8)	11052 (6)
C(5A)	1030 (7)	7844 (7)	10449 (5)
C(6A)	2200 (7)	7630 (7)	10154 (5)
C(7A)	5730 (6)	7909 (6)	10712 (4)
C(8A)	5256 (7)	8777 (7)	11337 (5)
C(9A)	6105 (8)	9860 (7)	11826 (5)
C(10A)	7415 (7)	10080 (7)	11686 (5)
C(11A)	7871 (7)	9232 (7)	11056 (5)
C(12A)	7043 (6)	8136 (6)	10572 (5)
C(13A)	4203 (6)	6533 (6)	8510 (4)
C(14A)	3022 (7)	6304 (7)	8074 (5)
C(15A)	2907 (7)	6545 (7)	7127 (5)
C(16A)	4004 (8)	7019 (7)	6630 (5)
C(17A)	5190 (7)	7235 (7)	7059 (5)
C(18A)	5321 (6)	6979 (7)	7994 (5)

Table III. Non-Hydrogen Coordinates (×10^4) and Their Standard Deviations for Crystal II

	x/a	y/b	z/c
Sb1	3094 (0)	9094 (4)	2500 (0)
C(1)	3772 (7)	8609 (11)	1034 (13)
C(2)	4442 (5)	9284 (10)	878 (9)
C(3)	4919 (5)	8948 (12)	−27 (11)
C(4)	4734 (7)	7827 (14)	−810 (10)
C(5)	4099 (8)	7107 (17)	−615 (12)
C(6)	3614 (6)	7462 (12)	264 (10)
C(7)	3702 (7)	8137 (12)	3908 (13)
C(8)	3429 (6)	8220 (12)	5043 (10)
C(9)	3831 (7)	7636 (15)	5958 (11)
C(10)	4501 (9)	7031 (17)	5757 (15)
C(11)	4776 (6)	6968 (13)	4651 (12)
C(12)	4377 (7)	7534 (12)	3716 (8)
C(13)	3217 (4)	11385 (9)	2410 (20)
C(14)	3337 (9)	12155 (21)	1402 (17)
C(15)	3415 (11)	13670 (18)	1468 (21)
C(16)	3363 (5)	14342 (8)	2565 (29)
C(17)	3245 (11)	13524 (21)	3521 (19)
C(18)	3189 (9)	12067 (16)	3508 (16)
O(19)	2189 (3)	9570 (7)	3525 (6)
O(20)	1795 (4)	8200 (7)	3624 (6)
C(21)	1674 (4)	7696 (10)	2433 (21)
C(22)	1428 (5)	6172 (9)	2623 (26)
C(23)	1112 (6)	8605 (11)	1813 (10)
O(24)	2359 (3)	7743 (7)	1857 (6)

Infrared and Raman Spectra: Sb=O Bond. The IR spectra of both the crystalline form[6,20] and of the amorphous form (or forms)[5,21,25] of triphenylstibine oxide have been previously reported, and assignments of some of the bands have been made. The

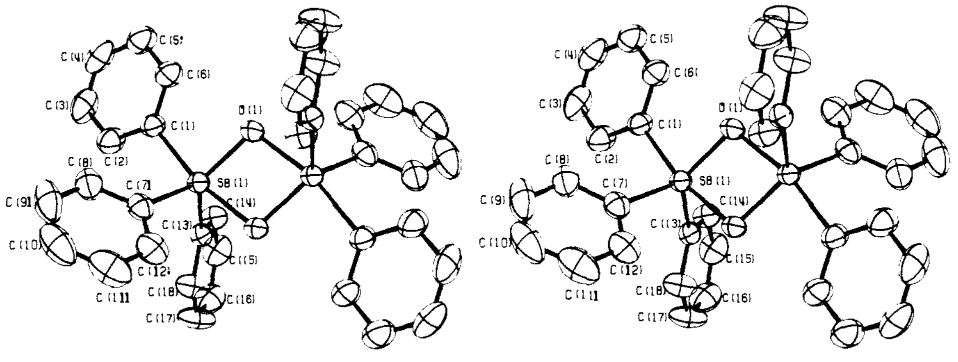


Figure 5. Stereoview of the molecule in crystal I.

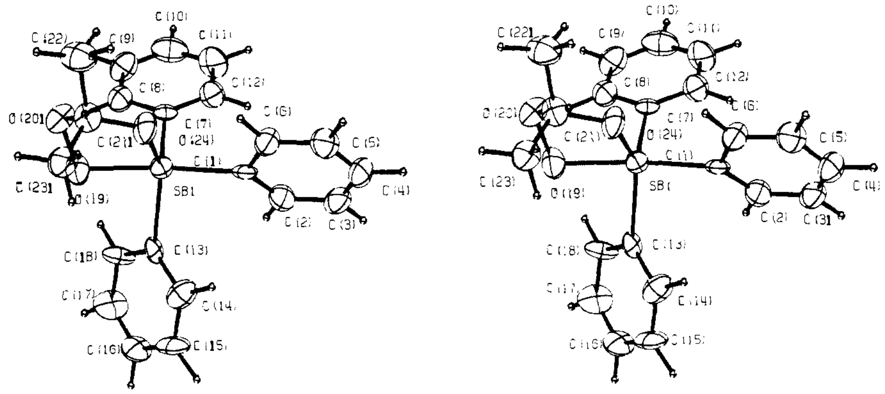


Figure 6. Stereoview of the molecule in crystal II.

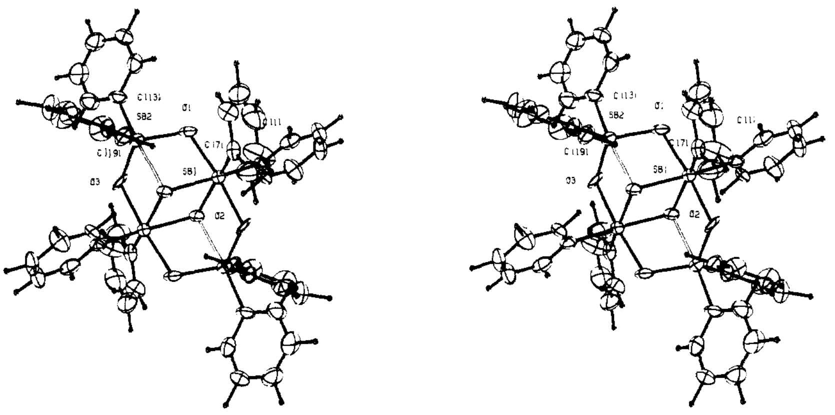
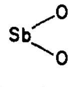


Figure 7. Stereoview of the molecule in crystal III.

present investigation has clearly established that crystalline triphenylstibine oxide possesses the



grouping and thus its vibrational spectrum might be expected to be somewhat similar to the spectra of the dihalotriphenylantimony compounds which have been thoroughly studied by Nevett and Perry.[26] Accordingly, we compared the IR and Raman spectra of crystalline triphenylstibine oxide (I) with those of difluorotriphenylantimony in the IR region 4000–300 cm^{-1} and in the Raman region 2000–160 cm^{-1} in order to locate bands associated with Sb–O stretching vibrations. Between 4000 and 800 cm^{-1} the two IR spectra are virtually superimposable. The band at 664 cm^{-1}, which McEwen and co-workers[6] have assigned to $Sb{=}O$, is clearly seen to occur at the same position in the difluoride (Figure 4). Although this band is somewhat weaker in the difluoride than in the oxide, the line shapes appear to be identical in both compounds. The band at 478 cm^{-1} in the oxide, which McEwen and co-workers have assigned to Sb–O, was found to occur at 485 cm^{-1} in the difluoride. The weak band at 430 cm^{-1} in the fluoride occurred as a shoulder at 438 cm^{-1} in the oxide.

There are two very distinct differences between the two spectra in the 800–300-cm^{-1} region, namely, the strong band at 508 cm^{-1} in the difluoride, which has been assigned to ν_{as}(Sb–F),[26] and the two strong, sharp bands at 643 and 651 cm^{-1} in the oxide, which are not present in the difluoride. These latter two bands must be associated with Sb–O vibrations. There do not appear to be any other bands in the 900–300-cm^{-1} region—where both Sb-F and Sb–O stretching vibrations should occur—which are not present in both compounds.

We have also compared the Raman spectra of crystalline triphenylstibine oxide and difluorotriphenylantimony in the region 1200–160 cm^{-1}. In the spectrum of the difluoride a medium band occurring at 488 cm^{-1} has been assigned to ν_s(Sb–F).[26] In the spectrum of the oxide a strong band at 649 cm^{-1} was not present in the difluoride. There were no other bands present in the Raman spectra that can be said with certainty to occur in one compound and not in the other. Are these IR and Raman spectra consistent

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(25) Jensen, K. A.; Nielsen, P. H. *Acta Chem. Scand.* **1963**, *17*, 1875–1885.

(26) Nevett, B. A.; Perry, A. *Spectrochim. Acta, Part A* **1977**, *33A*, 755–760.

with the four-membered antimony–oxygen bridge ring system for triphenylstibine oxide, found by X-ray diffraction? The vibrational spectra of four-membered metal–oxygen ring systems, of the type found in crystalline triphenylstibine oxide, have been considered by Wing and Callahan.[27] They point out that this system should give rise to four bridge vibrations which are linear combinations of the symmetric and antisymmetric vibrations of the two isolated monobridged species. These four vibrations are sensitive to the M–O–M angle ϕ. The frequencies of two of these vibrations (ν_1 and γ_3) increase rapidly as ϕ decreases, while ν_2 and ν_4 decrease as ϕ decreases. In the case of the molybdenum four-membered dioxo-bridged compounds, studied by Wing and Callahan,[27] ν_2 and ν_4 intercept ν_1 and ν_3 in the range ϕ 90–100°. The authors point out that the change in vibrational frequencies of the bridge modes as a function of the M–O–M angle, as illustrated graphically in their paper, was for illustrative purposes only. Nevertheless, it would be expected that the vibrational spectrum of the four-membered Sb–O ring system would be qualitatively similar to the spectra of the similar four-membered Mo–O ring systems studied by Wing and Callahan.[27] Since the four-membered ring system in triphenylstibine oxide is centrosymmetric, ν_1 should be infrared inactive. With the Sb–O–Sb angle $\phi = 102.1°$, as found by X-ray diffraction, the vibrational spectrum would be expected to consists of two IR and two Raman bands which should not be widely separated. Assuming that ν_1 is 649 cm^{-1} and ν_3 and ν_4 are 643 and 652 cm^{-1}, respectively, we can calculate values for k (the Sb–O force constant) and the $k_{\text{Sb–O–Sb}}$ and $k_{\text{O–Sb–O}}$ (the Sb–O–Sb and O–Sb–O bridge interaction constants, respectively) from the secular equations given by Wing and Callahan. These values are $k = 3.6$, $k_{\text{Sb–O–Sb}} = 0.54$, and $k_{\text{O–Sb–O}} = -0.08$ mdyn/Å. If we assume ν_3 is 652 cm^{-1} and ν_4 is 643 cm^{-1}, the values for k, $k_{\text{Sb–O–Sb}}$, and $k_{\text{O–Sb–O}}$ are 3.7, 0.67, and −0.15 mdyn/Å. These values lead to a frequency of either 658 or 664 cm^{-1} for ν_2, depending on which values for ν_3 and ν_4 are chosen. Either of these bands might be masked by the strong Raman band at 660 cm^{-1} which is found in both triphenylstibine oxide and difluorotriphenylantimony and assigned by Nevett and Perry to the *s* mode.[28] This interpretation of the vibrational spectrum of crystalline triphenylstibine oxide would seem to be more in accord with the actual structure (as found by X-ray diffraction) than the interpretations offered by previous investigators.

We believe it is useless to speculate on the structures of the various amorphous forms of triphenylstibine oxide. These materials cannot be purified by recrystallization or sublimation. Their melting points (or decomposition points) vary over a wide range depending on the method used for their preparation. Venezky and co-workers[5] have reported that different amorphous forms prepared by different synthetic procedures gave different thermograms. Furthermore, the IR spectra of the different preparations show significant differences. The two strong bands at 643 and 652 cm^{-1}, so characteristic of the crystalline preparations of triphenylstibine oxide, were absent from the spectra of all of the amorphous forms. Although Venezky and co-workers[5] have assigned a band at 744 cm^{-1} to the Sb–O–Sb stretching frequency in their samples of amorphous triphenylstibine oxide, this band was also present in difluorotriphenylantimony. There were no bands in the IR spectra of any of the amorphous samples of triphenylstibine oxide, prepared in our laboratory, that we could assign with certainty to Sb–O vibrations.

Table IV. Non-Hydrogen Coordinates (×10^4) and Their Standard Deviations for Crystal III

	x/a	*y/b*	*z/c*
	Molecule 1		
Sb(1)	8895 (1)	8954 (1)	3693 (1)
Sb(2)	11272 (1)	10049 (1)	3323 (1)
O(01)	9552 (10)	9638 (12)	2364 (10)
O(02)	9237 (10)	10856 (12)	5118 (11)
O(03)	11627 (10)	11592 (11)	4856 (12)
C(1)	7087 (15)	9576 (17)	2507 (17)
C(2)	6637 (16)	10810 (20)	2774 (16)
C(3)	5428 (17)	11163 (17)	2040 (19)
C(4)	4633 (15)	10252 (19)	991 (19)
C(5)	5061 (16)	8988 (20)	659 (19)
C(6)	6268 (17)	8648 (18)	1437 (18)
C(7)	8919 (15)	6781 (18)	2868 (18)
C(8)	9082 (18)	6349 (21)	1651 (19)
C(9)	9080 (20)	5025 (27)	1123 (24)
C(10)	8986 (21)	4024 (22)	1873 (26)
C(11)	8834 (24)	4399 (20)	3019 (21)
C(12)	8809 (21)	5753 (23)	3534 (21)
C(13)	11483 (17)	11183 (18)	1854 (17)
C(14)	12188 (18)	12377 (19)	2237 (18)
C(15)	12307 (19)	13036 (19)	1252 (22)
C(16)	11742 (17)	12528 (21)	−82 (20)
C(17)	10979 (16)	11380 (21)	−499 (17)
C(18)	10869 (16)	10728 (18)	454 (19)
C(19)	12638 (16)	8518 (18)	3504 (17)
C(20)	13742 (17)	8854 (18)	3495 (18)
C(21)	14616 (18)	7900 (26)	3601 (23)
C(22)	14488 (21)	6634 (24)	3866 (24)
C(23)	13407 (22)	6271 (22)	3898 (25)
C(24)	12481 (17)	7190 (21)	3746 (20)
	Molecule 2		
Sb(3)	9216 (1)	11460 (1)	4606 (1)
Sb(4)	7786 (1)	8567 (1)	4136 (1)
O(04)	7715 (9)	10189 (11)	3348 (11)
O(05)	10542 (8)	10141 (10)	4217 (10)
O(06)	9184 (8)	7533 (10)	4066 (10)
C(25)	9008 (14)	12480 (14)	2897 (16)
C(26)	8231 (15)	11992 (18)	1581 (18)
C(27)	8141 (16)	12651 (20)	484 (17)
C(28)	8874 (17)	13776 (18)	720 (19)
C(29)	9669 (19)	14327 (20)	2002 (22)
C(30)	9759 (15)	13667 (19)	3100 (17)
C(31)	8150 (14)	12701 (16)	5594 (15)
C(32)	7554 (17)	13843 (18)	5079 (20)
C(33)	6850 (20)	14577 (23)	5616 (28)
C(34)	6765 (21)	14282 (24)	6843 (26)
C(35)	7329 (18)	13185 (20)	7357 (20)
C(36)	8012 (17)	12356 (21)	6787 (19)
C(37)	6371 (14)	7352 (16)	2354 (16)
C(38)	6557 (16)	6008 (18)	1986 (18)
C(39)	5630 (20)	5246 (22)	880 (27)
C(40)	4619 (18)	5783 (25)	169 (21)
C(41)	4403 (16)	7181 (21)	478 (20)
C(42)	5316 (15)	7929 (18)	1594 (17)
C(43)	7088 (14)	8547 (16)	5697 (18)
C(44)	7879 (15)	8741 (20)	7170 (19)
C(45)	7383 (17)	8690 (24)	8119 (19)
C(46)	6155 (18)	8519 (21)	7698 (20)
C(47)	5384 (16)	8346 (21)	6348 (21)
C(48)	5857 (15)	8383 (18)	5365 (17)

From the results reported in the present paper, there can be little doubt that triphenylstibine oxide, in contrast to its phosphorus and arsenic analogues, does not contain a double bond between oxygen and the heteroelement. Likewise, the structure reported to be diphenylstibinic acid anhydride with Sb═O bonds does not contain this linkage. Organostibonic and organostibinic acids also differ significantly from the corresponding phosphorus and arsenic analogues in that the antimony compounds are high molecular weight amorphous materials, whereas the phosphorus and arsenic compounds are monomers.[29] Although Chremos and Zingaro[7] have interpreted the IR and Raman spectra of trialkylstibine oxides in terms of a monomer ⇌ polymer equilibrium, their molecular weight data are generally in better agreement with values for a dimer. Also in the mass spectrum of trimethylstibine oxide, reported from the same laboratory,[30] the base peak corresponds to the dimer which has lost one methyl group, and there are no peaks corresponding to associated forms higher than the dimer. We would suggest that evidence for the existence of any antimony

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(27) Wing, R. M.; Callahan, K. P. *Inorg. Chem.* **1968**, *8*, 871–874.

(28) Whiffen's nomenclature: Whiffen, D. H. *J. Chem. Soc.* **1956**, 1350–1356.

(29) Doak, G. O.; Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony, and Bismuth*; Wiley: New York, **1970**; pp 291–293.

(30) Morris, W.; Zingaro, R. A.; Laane, J. *J. Organomet. Chem.* **1975**, *91*, 295–306.

Table V. Distances and Angles Involving Antimony for Crystal I

dist or ang	molec 1	molec 2^b
Sb–Sb^a	3.129 (1)^c	3.120 (1)^d
O1–O1^a	2.494 (6)^c	2.522 (6)^d
Sb–O1	1.928 (4)	1.929 (4)
Sb–O1^a	2.071 (4)^c	2.080 (4)^d
Sb–C1	2.164 (6)	2.175 (6)
Sb–C7	2.121 (7)	2.141 (6)
Sb–C13	2.121 (6)	2.121 (6)
Sb–O1–Sb^a	102.9 (2)^c	102.1 (2)^d
C1–Sb–O1^a	167.5 (2)^c	167.1 (2)^d
C1–Sb–O1	91.2 (2)	89.3 (2)
C1–Sb–C7	99.5 (3)	98.7 (2)
C1–Sb–C13	95.5 (2)	97.6 (2)
O1^a–Sb–O1	77.1 (2)^c	77.9 (2)^d
O1^a–Sb–C7	90.4 (2)^c	88.8 (2)^d
O1^a–Sb–C13	87.9 (2)^c	89.4 (2)^d
O1–Sb–C7	121.0 (2)	123.0 (2)
O1–Sb–C13	124.9 (2)	123.6 (2)
C7–Sb–C13	111.7 (2)	111.1 (2)

[a] These atoms are not crystallographically unique and are generated by symmetry. [b] Coordinates for this molecule begin with Sb2 and have the suffix A. [c] Symmetry operation for indicated atom: $\bar{x}$, $\bar{y}$, + 1.0, $\bar{z}$ + 1.0. [d] Symmetry operation for indicated atom: $\bar{x}$ + 1.0, $\bar{y}$ + 1.0, $\bar{z}$ + 2.0.

Table VI. Distances and Angles Involving Antimony for Crystal II

dist or ang		dist or ang	
Sb1–C1	2.122 (14)	Sb1–O19	2.062 (6)
Sb1–C7	2.141 (14)	Sb1–O24	1.974 (7)
Sb1–C13	2.151 (8)		
C7–Sb1–C1	101.7 (5)	O24–Sb1–O19	79.1 (3)
C13–Sb1–C1	96.6 (6)	C2–C1–Sb1	120.9 (9)
O19–Sb1–C1	162.2 (4)	C6–C1–Sb1	122.2 (9)
O24–Sb1–C1	87.8 (4)	C8–C7–Sb1	119.2 (9)
C13–Sb1–C7	113.4 (6)	C12–C7–Sb1	120.9 (10)
O19–Sb1–C7	94.3 (4)	C14–C13–Sb1	125.2 (14)
O24–Sb1–C7	111.0 (4)	C18–C13–Sb1	113.8 (12)
O19–Sb1–C13	84.0 (4)	O20–O19–Sb1	104.1 (4)
O24–Sb1–C13	133.4 (4)	C21–O24–Sb1	116.3 (8)

Table VII. Distances and Angles Involving Antimony for Crystal III

molecule 1		molecule 2	
Sb$_1$–O1	2.057 (12)	Sb3–O4	2.039 (11)
Sb1–O2	2.125 (11)	Sb3–O5	2.092 (10)
Sb1–O2^a	2.039 (12)	Sb3–O5^a	2.098 (10)
Sb1–O3^a	2.014 (12)	Sb3–O6^a	2.011 (10)
Sb1–1	2.108 (18)	Sb3–25	2.135 (15)
Sb1–7	2.154 (18)	Sb3–31	2.141 (16)
Sb2–O1	1.881 (12)	Sb4–O4	1.891 (11)
Sb2–O2^a	2.273 (11)	Sb4–O5^a	2.283 (10)
Sb2–O3	1.940 (11)	Sb4–O6	1.901 (10)
Sb2–13	2.146 (18)	Sb4–37	2.153 (16)
Sb2–19	2.112 (18)	Sb4–43	2.116 (18)
O2–O2^a	2.444 (17)	O5–O5^a	2.504 (14)
O2–Sb1–O1	96.2 (4)	O5–Sb3–O4	95.4 (4)
O2^a–Sb1–O1	78.6 (4)	O5^a–Sb3–O4	79.2 (4)
O3^a–Sb1–O1	174.5 (5)	O6^a–Sb3–O4	171.9 (4)
1–S1–O1	90.0 (6)	25–Sb3–O4	90.0 (5)
7–Sb1–O1	94.6 (6)	31–Sb3–O4	92.3 (5)
O2^a–Sb1–O2	71.9 (5)	O5^a–Sb3–O5	73.4 (4)
O3^a–Sb1–O2	79.1 (4)	O6^a–Sb3–O5	78.6 (4)
1–Sb1–O2	90.9 (5)	25–Sb3–O5	91.1 (5)
7–Sb1–O2	161.2 (6)	31–Sb3–O5	163.7 (5)
O3^a–Sb1–O2^a	97.1 (5)	O6^a–Sb3–O5^a	93.8 (4)
1–Sb1–O2^a	157.9 (6)	25–Sb3–O5^a	159.9 (5)
7–Sb1–O2^a	95.4 (6)	31–Sb3–O5^a	94.1 (5)
1–Sb1–O3^a	93.0 (6)	25–Sb3–O6^a	95.5 (5)
7–Sb1–O3^a	89.1 (6)	31–Sb3–O6^a	92.2 (5)
7–Sb1–1	104.4 (7)	31–Sb3–25	103.3 (6)
O2^a–Sb2–O1	76.6 (4)	O5^a–Sb4–O4	77.8 (4)
O3–Sb2–O1	112.4 (5)	O6–Sb4–O4	108.5 (5)
13–Sb2–O1	97.3 (6)	37–Sb4–O4	97.7 (5)
19–Sb2–O1	122.7 (6)	43–Sb4–O4	120.9 (5)
O3–Sb2–O2^a	77.1 (4)	O6–Sb4–O5^a	76.2 (4)
13–Sb2–O2^a	169.1 (6)	37–Sb4–O5^a	170.4 (5)
19–Sb2–O2^a	88.8 (6)	43–Sb4–O5^a	88.1 (5)
13–Sb2–O3	97.4 (6)	37–Sb4–O6	97.6 (5)
19–Sb2–O3	117.5 (6)	43–Sb4–O6	123.3 (5)
19–Sb2–13	102.2 (7)	43–Sb4–37	101.5 (6)
Sb2–O1–Sb1	108.7 (5)	Sb4–O4–Sb3	109.0 (5)
Sb1^a–O2–Sb1	108.1 (5)	Sb3^a–O5–Sb3	106.6 (5)
Sb2–O2^a–Sb1	95.7 (4)	Sb4–O5^a–Sb3	93.8 (4)
Sb2–O2^a–Sb1^a	94.2 (4)	Sb4–O5^a–Sb3^a	94.5 (4)
Sb2–O3–Sb1^a	109.2 (5)	Sb4–O6^a–Sb3^a	110.5 (5)

[a] Atoms generated by symmetry operation: 2.0 − x, 2.0 − y, 1.0 − z.

comound containing the Sb═O (or Sb → O) group is questionable.

Experimental Section

General. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 521 infrared spectrometer. The Raman spectra were recorded on a Jarrell-Ash 25-300 monochrometer using the 488-nm line of the Spectra-Physics Model 171-17 Ar$^+$ laser. NMR spectra were determined on a Varian EM-390 spectrometer. A Syntax P1 diffractometer equipped with a graphite monochromator and molybdenum radiation (λ = 0.71069 Å) was used for the single-crystal X-ray analysis. Carbon and hydrogen analyses were performed by Galbraith Laboratoeis, Knoxville, TN. Antimony analyses were performed by Dolores Knight of this laboratory.

Hydroxytetraphenylantimony was prepared by the hydrolysis of tetraphenylstibonium bromide with aqueous ammonia.[31,32] ^{1}H NMR (CDCl$_3$): δ 0.75 (s, 1 H), 7.4 (m, 20 H).

Methoxytetraphenylantimony. Tetraphenylstibonium bromide (10.2 g, 0.02 mol) and sodium methoxide (1.1 g, 0.02 mol) were dissolved in 175 mL of methanol, and the solution was refluxed for 1 h. After the solution was cooled to room temperature, cold water (125 mL) was slowly added with stirring. The resulting precipitate was removed by filtration, washed with cold water, and dried in vacuo. ^{1}H NMR (CDCl$_3$): δ 2.85 (s, 2.7 H), 7.5 (m, 20 H). In addition there was a barely perceptible peak at δ 0.75, corresponding to a small amount of hydroxytetraphenylantimony. These results indicated that the crude precipitate contained approximately 90% methoxytetraphenylantimony. When the crude product was recrystallized from methanol, or better from water–methanol (1:5), analytically pure methoxytetraphenylantimony was obtained. In agreement with McEwen and co-workers,[13] we have found that hydroxytetraphenylantimony, when crystallized from methanol, was converted to the methoxy compound.

Crystalline Triphenylstibine Oxide [2,2,4,4-Tetrahydro-2,2,2,4,4,4-hexaphenyl-1,3,2,4-dioxadistibetane (I)]. Recrystallized methoxytetraphenylantimony (6 g) was suspended in 375 mL of xylene and heated at 60–70 °C for 6 days in a nitrogen atmosphere with the flask being covered with aluminum foil to exclude light. At the end of the heating period, all but 50 mL of xylene was removed by vacuum distillation and the residual liquid cooled to 0 °C. The yield of crystalline solid, mp 220–222 °C, which separated from solution, was 1.5 g, 31%. Crystalline triphenylstibine oxide was also prepared from hydroxytetraphenylantimony and from dimethoxytriphenylantimony by McEwen's procedures[6] and from triphenylstibine by the procedure of Razuvaez and co-workers.[8] Mixed melting points between any two samples gave no depression, and IR spectra were the same. The molecular weight of the crystalline material was determined ebullioscopically in benzene by using the familiar Cottrell apparatus. A sample (1.973 g) in 50 mL of benzene gave an elevation of 0.15 °C for a molecular weight of 757 (calculated for the dimer 738). The material recovered by evaporation of the benzene solution was unchanged triphenylstibine oxide. The molecular weight was also determined by vapor-phase osmometry (using the A. H. Thomas isothermal molecular weight apparatus thermostated at 37 °C) in carbon tetrachloride solution. The average value found from three determinations was 747.

3,3-Dihydro-5,5-dimethyl-3,3,3-triphenyl-1,2,4,3-trioxastibolane (II). A solution of 12 g of triphenylstibine in 240 mL of acetone in a three-neck flask, equipped with a thermometer, mechanical stirrer, and addition funnel, was treated dropwise with 5 mL of 30% H$_2$O$_2$. The temperature was maintained between 25 and 30 °C by a water–ice bath. After

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(31) Beauchamp, A. L.; Bennet, M. J.; Cotton, F. A. *J. Am. Chem. Soc.* **1969**, *91*, 297–301.

(32) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, 1962; Vol. 3, pp 204–214.

peroxide addition was complete, stirring was continued for 0.5 h and then for a further hour at 0–5 °C. The heavy crystalline precipitate (compound II) was removed by filtration and washed with a small amount of cold acetone. (The filtrate was placed in the refrigerator for 2 weeks to yield 2.4 g of crystalline material, compound III, mp 285–290 °C.) Compound II was recrystallized by dissolving in acetone at room temperature and slowly removing the solvent over calcium chloride under a slight vacuum. Crystals suitable for X-ray diffraction were obtained. Heating compound II in acetone resulted in decomposition. Anal. Calcd for $C_{21}H_{21}SbO_3$: C, 56.91; H, 4.78; Sb, 27.47. Found: C, 56.81; H, 4.82; Sb, 27.83.

Amorphous Triphenylstibine Oxide. (**a**) When the previous reaction was repeated without cooling, 1–2.5 g of triphenylstibine oxide, mp 220–222 °C, identical with I, separated from solution and were removed by filtration. The filtrate, when poured into cold water, gave 10–11 g of amorphous triphenylstibine oxide, mp 285–290 °C.

(**b**) Compound II (5 g) was stirred with 50 mL of benzene for 2 h. The resulting white powder was removed by filtration and excess solvent removed in vacuo. The yield was quantitative, mp 170–180 °C. Elemental analyses of both of the above samples gave results in agreement with theoretical for $(C_6H_5)_3SbO$.

(**c**) Oxidation of triphenylstibine in ethanol solution, when carried out under the same conditions as used to prepare compound II, gave a white amorphous powder, mp 215–220 °C, in 90% yield. If acetonitrile was used as a solvent, the yield of white powder, mp 288–294 °C, was essentially quantitative. Elemental analyses of these last two samples gave results which varied slightly from the theoretical for $(C_6H_5)_3SbO$ which suggested that these compounds were not quite pure.

Diacetatotriphenylantimony. When any of the above samples of amorphous triphenylstibine oxide were dissolved in hot glacial acetic acid and the resulting solution was cooled, beautiful crystals of the diacetate, mp 208–209 °C [lit. mp 215 °C], were obtained. Elemental analyses were in agreement with the diacetato compound. The same compound was also obtained by the same procedure from crystalline triphenylstibine oxide and from a commercial sample of triphenylstibine oxide.

When diacetatotriphenylantimony was dissolved in warm acetic acid and the solution poured into cold water, the diacetato compound was recovered unchanged in quantitative yield. The compound could not be hydrolyzed by boiling with water for several hours.

Attempted Hydrolysis of Dichlorotriphenylantimony. When dichlorotriphenylantimony was suspended in water and refluxed for periods up to several weeks, the dichloro compound was recovered unchanged essentially quantitatively. Titration of the filtrate with standard alkali showed that less than 10% of the dichloride had been hydrolyzed.

Hexa-μ-oxooctaphenyltetraantimony. The compound believed to be diphenylstibinic acid anhydride[6] was prepared by heating triphenylstibine oxide in xylene following exactly the procedure of McEwen and coworkers.[6] Beautiful crystals, mp 302–303 °C, suitable for X-ray diffraction, were obtained. These crystals were compared with the 2.5 g of crystalline material III, mp 285–290 °C, obtained from the filtrate after removal of compound II (when triphenylstibine was oxidized in acetone solution). Elemental analysis, IR spectra, and mixed melting points giving no depression were all convincing evidence that the two products were the same.

X-ray diffraction on the compound, mp 302–303 °C, showed that it was not diphenylstibinic acid anhydride but the complex antimony oxide, namely hexa-μ-oxooctaphenyltetraantimony.

Single-Crystal X-ray Analysis. All three X-ray analyses reported in this paper were conducted in a similar fashion by using conventional methods of X-ray crystallography. A representative crystal of each compound was surveyed, and a 1-Å data set (maximum $\sin \theta/\lambda = 0.5$) was collected on a Syntex P1 diffractometer. The diffractometer was equipped with a graphite monochromator and molybdenum radiation ($\lambda = 0.71069$ Å). Atomic scattering factors for C and O were taken from the *International Tables for X-ray Crystallography*,[32] hydrogen was taken from Stewart et al.,[33] and Sb was taken from Cromer and Mann.[34] All crystallographic calculations were facilitated by the CRYM system.[35] All diffractometer data were collected at room temperature. Pertinent crystal, data collection, and refinement parameters are summarized in Table I.

The trial structures were obtained by using conventional Patterson and Fourier techniques. Hydrogen positions were calculated wherever possible. Hydrogen positions which could not be calculated were located by difference Fourier techniques. The hydrogen parameters were added to the structure factor calculations but were not refined. The final cycles of full matrix least-squares refinement contained the scale factor, secondary extinction coefficient, coordinates, and anisotropic temperature factors in a single matrix. The shifts calculated in the final cycle were all less than 0.3 of their corresponding standard deviation. The final data fit criteria are presented in Table I. A final difference Fourier on each structure revealed no missing or misplaced electron density. The refined structures were plotted by using the ORTEP computer program of Johnson[36] (Figures 5–7).

Crystal I contained a dimeric compound with two dimers in the unit cell. Both molecules used a center of symmetry (0, $^1/_2$, $^1/_2$ and $^1/_2$, $^1/_2$, 0) to generate the second half of the molecule. The atomic positions for non-hydrogen atoms are given in Table II. Bond distances and angles, anisotropic temperature factors, hydrogen parameters, and a structure factor table are presented as supplementary material (Tables S1–S5).

Crystal II was a routine structure analysis. The final refinement proved that the space group for this crystal did not contain a center of symmetry and was $Pna2_1$. A secondary extinction correction was tried on this crystal, but refinement proved that this correction was vanishingly small. The atomic positions for non-hydrogen atoms are given in Table III. Bond distances and angles, anisotropic temperature factors, hydrogen parameters, and a structure factor table are presented as supplementary material (Table S6–S9).

Crystal III was the most difficult structure to solve. Again the molecular structure was dimeric. The unit cell contained only one molecule. This required that the dimer use a center of symmetry (1, 1, $^1/_2$). However, the crystal was disordered. The dimer could take up two different positions in the unit cell. The population of these two possible positions was estimated by least-squares refinement to be 50/50. The atomic positions for the non-hydrogen atoms for both possibilities are given in Table IV. Some selected bond angles (degrees) for crystals I and II are given in Tables V–VII.

Acknowledgment. The authors wish to thank Professor Dennis Wertz for running the Raman spectra and for help in interpreting the electronic spectra.

Supplementary Material Available: Bond distances and angles, anisotropic temperature factors, hydrogen parameters, and a structure factor table (Tables S1–S14) (71 pages). Ordering information is given on any current masthead page.

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