Synthesis and structure of tetraphenylantimony hydrogen phthalate

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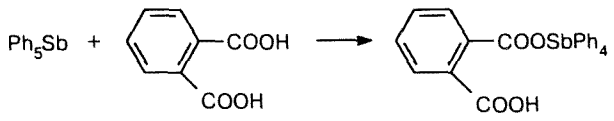
Tetraphenylantimony hydrogen phthalate, $Ph_4SbOC(O)C_6H_4COOH$-*o*, was prepared by the reaction of pentaphenylantimony with phthalic acid. According to the data of X-ray structural analysis, the resulting compound is a trigonal-bipyramidal complex of antimony with three phenyl groups in equatorial positions; the fourth phenyl group and the carboxyl fragment are in axial positions. The CSbO angle is 177.5(1)°; the Sb—$C(Ph)_{eq}$ and Sb—$C(Ph)_{ax}$ distances are 2.099(4)—2.177(4) Å and 2.129(4) Å, respectively. The H atom of the free carboxyl group and the carbonyl O atom of another carboxylate group form an intramolecular hydrogen bond.

Key words: tetraphenylantimony hydrogen phthalate, synthesis, X-ray structural study, molecular structure.

In the majority of antimony compounds of the general formula Ph_4SbX (X is an organic or inorganic ligand), the trigonal-bipyramidal coordination with the coordination number of 5 is typical of the Sb atom.[1] However, when other potentially coordinating centers are present in ligands, their additional interaction with the Sb atom is possible. This can result in a distorted bipyramidal or octahedral coordination environment about the Sb atom. For example, in tetraphenylantimony acetate[2] (the coordination number is 6) and in triphenylantimony dibenzoate[3] (the coordination number is 7), the Sb...O distances (2.81 and 2.70 Å, respectively) are shortened as compared to the sum of the van der Waals radii (3.60 Å),[4] which is indicative of the additional coordination about the Sb atom in these compounds.

Undoubtedly, studies of the salts of dicarboxylic acids are of interest because of the possibility for interactions between one or two O atoms of carbonyl groups and the central Sb atom. We have carried out an X-ray structural study of tetraphenylantimony hydrogen phthalate (**1**), which was obtained from pentaphenylantimony and phthalic acid.



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The data of X-ray structural analysis demonstrated that the coordination about the Sb atom (Fig. 1) is a trigonal bipyramid typical of antimony compounds with the coordination number of 5 (the sum of the C(Ph)SbC(Ph) bond angles in the equatorial plane is 352.7°; the C(7)SbO(1) angle for the atoms in apical positions is 177.5(1)°).

The Sb—$C(Ph)_{eq}$ distances are in the range of 2.099(4)—2.117(4) Å and are slightly shorter than the Sb—$C(Ph)_{ax}$ distance (2.129(4) Å). This is consistent with the valence-shell electron pair repulsion theory,[1,5] which explains well the structural features of the trigonal-bipyramidal complexes of the Group V elements. The range of the Sb—$C(Ph)_{eq}$ bond lengths is comparable to those for $Ph_4SbOC_6H_4NO_2$-*o* (2.115(4)—2.123(3) Å)[6], $Ph_4SbOC_6H_4COH$-*p* (2.118(4)—2.139(5) Å),[6] and $Ph_4SbOC(O)CH{=}CHPh$ (2.103(4)—2.140(5) Å).[7] However, the Sb—$C(Ph)_{ax}$ bond in mol-

† Deceased.

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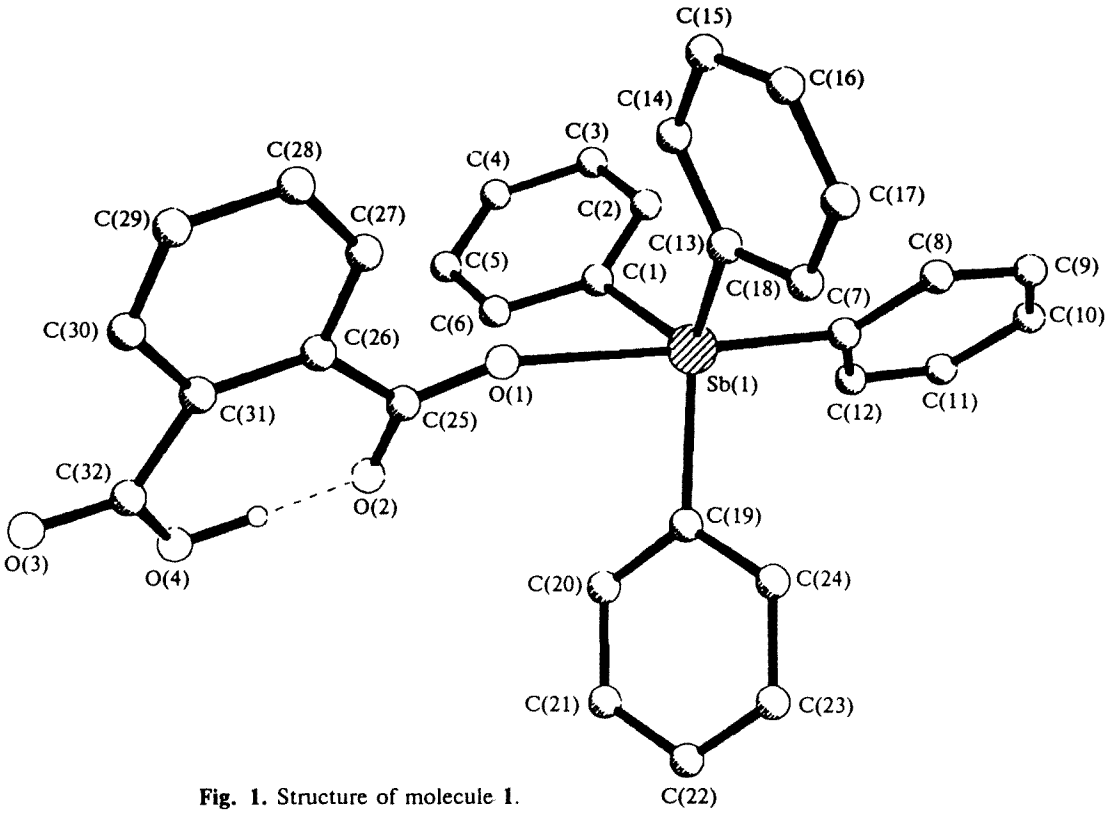

Fig. 1. Structure of molecule **1**.

ecule **1** (2.129(4) Å) is the shortest compared to the Sb–C $(Ph)_{ax}$ bonds in analogous complexes (2.181(5), 2.188(5), and 2.167(5) Å in $Ph_4SbOC_6H_4NO_2$-*o*, $Ph_4SbOC_6H_4COH$-*p*, and $Ph_4SbOC(O)CH{=}CHPh$, respectively). Note that in molecule **1**, the minimum value of the Sb—$C(Ph)_{ax}$ bond length is accompanied by the maximum values of the Sb—O bond length and the SbOC angle (Table 1).

In molecule **1**, the intramolecular H(4′)...O(2) hydrogen bond occurs (see Fig. 1). The O(4)—H(4′) and H(4′)...O(2) distances are 1.00(6) and 1.41(6) Å, respectively; the O(4)H(4′)O(2) angle is 175.3(5.4)°. The intramolecular O(2)...O(4) distance is 2.407 Å; this value is intermediate between the "normally" and "strongly" shortened O...O contacts (2.43 and 2.33 Å, respectively).[8] The planar seven-membered O(2)C(25)C(26)—C(31)C(32)O(4)H(4′) cycle (the maximum deviation from the mean plane is 0.037 Å) is formed through the intramolecular H(4′)...O(2) hydrogen bond. The presence of the hydrogen bond causes no considerable changes in the bond angles at the C(25) (116.8(4)—122.8(4)°) and C(32) (119.7(5)—120.3(5)°) atoms, but substantially increases the bond length in the carbonyl group: the O(2)—C(25) bond length is 1.259(5) Å. This bond is significantly longer than the analogous O(3)—C(32) distance not only in the second carbonyl group of molecule **1** (1.216(6) Å), but in the $Ph_4SbOC(O)CH{=}CHPh$ compound as well (1.219(7) Å).[7] Besides, the O(2)—C(25) distance is somewhat larger than the O(1)—C(25) bond length (1.245(5) Å) in which the O(1) atom is covalently bonded to the Sb(1) atom. Apparently, this elongation of the O(2)—C(25) bond is indicative of significant O(2)...H(4′) interaction. This conclusion correlates with the data on the O...H bond length (d(O...H) < 2.1 Å)[9], which exceeds substantially the experimental value of the O(2)...H(4′) bond length (1.41(6) Å) in molecule **1**. It may be suggested that the O(2)...H(4′) hydrogen bond is retained in solutions as well.

Note that the presence of the hydrogen bond in the adducts of the $Me_4SbOC(O)Me \cdot PhC(O)OH$ type is also assumed[10,11] based on the data of IR and ^1H NMR spectroscopy.

The O(1)—C(25) and O(2)—C(25) distances differ little (1.245(5) and 1.259(5) Å, respectively) and are close to the length of the delocalized double bond in carboxylate anions (1.255 Å).[12] The O(4)—C(32) bond

Table 1. Selected bond lengths (d) and bond angles (ω) in the compounds of the general formula Ph_4SbOR

Compound	d/Å		ω/deg,
	Sb—$C(Ph)_{ax}$	Sb—O	SbOC
1	2.129(4)	2.530(3)	151.8(3)
$Ph_4SbOC(O)CH{=}CHPh$[7]	2.167(5)	2.246(3)	122.6(3)
$Ph_4SbOC_6H_4NO_2$-*o*[6]	2.181(5)	2.221(4)	123.8(3)
$Ph_4SbOC_6H_4COH$-*p*[6]	2.188(5)	2.202(3)	129.6(3)

Table 2. Atomic coordinates ($\times 10^4$) and equivalent temperature factors (U_{eq}) in molecule **1**

Atom	*x*	*y*	*z*	$U_{eq} \cdot 10^3/Å^2$	Atom	*x*	*y*	*z*	$U_{eq} \cdot 10^3/Å^2$
Sb(1)	1235(1)	9074(1)	−3559(1)	40(1)	C(27)	2399(2)	6967(5)	−2006(2)	56(2)
O(1)	1558(1)	7622(3)	−2623(1)	57(1)	C(28)	2855(2)	6672(6)	−1743(3)	70(2)
O(2)	1068(1)	6589(4)	−1916(2)	70(1)	C(29)	2882(2)	5722(2)	−1242(3)	81(2)
O(3)	1670(2)	3769(4)	−503(2)	106(2)	C(30)	2458(2)	5136(7)	−1007(2)	78(2)
O(4)	1109(1)	4984(3)	−1018(2)	72(1)	C(31)	1987(2)	5429(5)	−1251(2)	51(1)
C(1)	1013(2)	10433(4)	−2802(2)	45(1)	C(32)	1569(2)	4658(5)	−903(2)	64(2)
C(2)	1018(2)	11848(5)	−2934(2)	64(2)	H(2)	113(2)	1214(5)	−333(3)	8(1)
C(3)	879(2)	12794(5)	−2458(3)	79(2)	H(3)	87(2)	1373(5)	−256(2)	8(2)
C(4)	722(2)	12303(6)	−1859(3)	83(2)	H(4)	61(2)	1285(6)	−154(3)	11(2)
C(5)	708(2)	10905(6)	−1725(3)	74(2)	H(5)	58(2)	1051(6)	−132(3)	11(2)
C(6)	856(2)	9959(5)	−2195(2)	58(2)	H(6)	82(2)	902(5)	−212(3)	8(2)
C(7)	995(2)	10316(4)	−4358(2)	46(1)	H(8)	166(1)	1046(4)	−485(2)	6(1)
C(8)	1312(2)	10763(5)	−4850(2)	59(2)	H(9)	137(2)	1194(6)	−567(3)	12(2)
C(9)	1134(2)	11589(6)	−5352(3)	80(2)	H(10)	52(2)	1259(5)	−573(3)	9(2)
C(10)	647(2)	11977(5)	−5378(3)	72(2)	H(11)	1(2)	1183(4)	−487(2)	7(1)
C(11)	332(2)	11555(6)	−4895(3)	75(2)	H(12)	27(2)	1051(5)	−402(3)	9(2)
C(12)	510(2)	10719(5)	−4388(3)	67(2)	H(14)	220(2)	1026(5)	−302(2)	7(1)
C(13)	2002(1)	8958(4)	−3759(2)	41(1)	H(15)	309(2)	1020(6)	−319(3)	12(2)
C(14)	2329(2)	9718(5)	−3379(2)	64(2)	H(16)	333(2)	898(4)	−422(2)	8(2)
C(15)	2829(2)	9744(7)	−3547(3)	79(2)	H(17)	281(2)	772(6)	−484(3)	11(2)
C(16)	2996(2)	8980(6)	−4067(3)	74(2)	H(18)	196(2)	781(4)	−459(2)	7(1)
C(17)	2672(2)	8251(6)	−4445(3)	73(2)	H(20)	42(1)	728(4)	−293(2)	5(1)
C(18)	2168(2)	8219(5)	−4286(2)	59(2)	H(21)	−7(2)	538(4)	−311(2)	7(1)
C(19)	806(1)	7294(4)	−3729(2)	40(1)	H(22)	4(2)	417(4)	−407(2)	8(1)
C(20)	456(2)	6808(5)	−3287(2)	56(2)	H(23)	62(2)	496(6)	−488(3)	10(2)
C(21)	166(2)	5678(5)	−3429(2)	63(2)	H(24)	111(1)	692(4)	−464(2)	5(1)
C(22)	232(2)	4986(5)	−4009(2)	63(2)	H(27)	235(2)	758(4)	−233(2)	5(1)
C(23)	577(2)	5445(5)	−4453(2)	66(2)	H(28)	316(2)	717(5)	−192(2)	8(2)
C(24)	860(2)	6613(5)	−4318(2)	54(1)	H(29)	321(2)	551(5)	−107(3)	8(2)
C(25)	1493(2)	6879(4)	−2134(2)	46(1)	H(30)	246(2)	445(6)	−70(3)	10(2)
C(26)	1958(2)	6388(4)	−1776(2)	43(1)	H(4')	110(3)	562(7)	−140(3)	12(2)

length in the carbonyl group is 1.299(6) Å, which coincides with analogous distances in carboxylic acids.[12]

Experimental

X-ray structural analysis of the crystal of $Ph_4SbOC(O)C_6H_4C(O)OH$ (**1**) was carried out on a four-circle automated Siemens P3/PC diffractometer (Mo-Kα radiation, graphite monochromator, $2° < 2\theta < 52°$). Crystals of **1** are orthorhombic, at 20 °C, $a = 26.900(4)$, $b = 9.650(2)$, $c = 20.493(4)$ Å, $V = 5320(3)$ Å^3, $d_{calc} = 1.487$ g cm^{-3}, $Z = 8$, space group *Pbcn*. Intensities of 5736 reflections were measured using the $\theta/2\theta$ scanning technique of which 3369 reflections with $I > 3\sigma(I)$ were used in the final refinement. The structure of **1** was solved by the heavy-atom method and refined by the block-diagonal least-squares method with anisotropic thermal parameters for nonhydrogen atoms to $R = 0.034$, $R_w = 0.042$, $S = 1.11$ using the following weighting scheme: $w^{-1} = \sigma^2(F) + 0.008F^2$. Positions of all H atoms were located from the difference electron density synthesis.

Calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS program.[13] Atomic coordinates and their equivalent isotropic temperature factors, the principal bond lengths, and bond angles are given in Tables 2—4, respectively.

Table 3. Bond lengths (*d*) in molecule **1**

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Sb(1)—O(1)	2.530(3)	C(2)—C(3)	1.387(8)	C(13)—C(14)	1.384(6)	C(22)—C(23)	1.374(7)
Sb(1)—C(1)	2.117(4)	C(3)—C(4)	1.381(9)	C(13)—C(18)	1.370(6)	C(23)—C(24)	1.388(7)
Sb(1)—C(7)	2.129(4)	C(4)—C(5)	1.377(8)	C(14)—C(15)	1.390(7)	C(25)—C(26)	1.525(6)
Sb(1)—C(13)	2.107(4)	C(5)—C(6)	1.386(7)	C(15)—C(16)	1.372(8)	C(26)—C(27)	1.393(6)
Sb(1)—C(19)	2.099(4)	C(7)—C(8)	1.388(6)	C(16)—C(17)	1.361(8)	C(26)—C(31)	1.422(6)
O(1)—C(25)	1.245(5)	C(7)—C(12)	1.387(6)	C(17)—C(18)	1.394(7)	C(27)—C(28)	1.370(7)
O(2)—C(25)	1.259(5)	C(8)—C(9)	1.388(7)	C(19)—C(20)	1.388(6)	C(28)—C(29)	1.379(9)
O(3)—C(32)	1.216(6)	C(9)—C(10)	1.363(9)	C(19)—C(24)	1.381(6)	C(29)—C(30)	1.362(9)
O(4)—C(32)	1.299(6)	C(10)—C(11)	1.364(8)	C(20)—C(21)	1.371(7)	C(30)—C(31)	1.389(7)
C(1)—C(2)	1.392(6)	C(11)—C(12)	1.392(8)	C(21)—C(22)	1.375(7)	C(31)—C(32)	1.525(7)
C(1)—C(6)	1.392(6)						

Table 4. Bond angles (ω) in molecule **1**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(1)—Sb(1)—C(1)	83.4(1)	Sb(1)—C(7)—C(8)	123.1(3)	C(20)—C(21)—C(22)	119.7(4)
O(1)—Sb(1)—C(7)	177.5(1)	Sb(1)—C(7)—C(12)	118.8(3)	C(21)—C(22)—C(23)	120.2(4)
C(1)—Sb(1)—C(7)	97.5(2)	C(8)—C(7)—C(12)	118.1(4)	C(22)—C(23)—C(24)	120.0(4)
O(1)—Sb(1)—C(13)	77.3(1)	C(7)—C(8)—C(9)	120.3(5)	C(19)—C(24)—C(23)	120.1(4)
C(1)—Sb(1)—C(13)	116.8(2)	C(8)—C(9)—C(10)	121.2(5)	O(1)—C(25)—O(2)	122.8(4)
C(7)—Sb(1)—C(13)	100.2(2)	C(9)—C(10)—C(11)	119.1(5)	O(1)—C(25)—C(26)	116.8(4)
O(1)—Sb(1)—C(19)	82.0(1)	C(10)—C(11)—C(12)	120.9(5)	O(2)—C(25)—C(26)	120.3(4)
C(1)—Sb(1)—C(19)	118.3(1)	C(7)—C(12)—C(11)	120.4(5)	C(25)—C(26)—C(27)	114.3(3)
C(7)—Sb(1)—C(19)	99.6(1)	Sb(1)—C(13)—C(14)	119.0(3)	C(25)—C(26)—C(31)	127.7(4)
C(13)—Sb(1)—C(19)	117.6(1)	Sb(1)—C(13)—C(18)	120.0(3)	C(27)—C(26)—C(31)	118.0(4)
Sb(1)—O(1)—C(25)	151.8(3)	C(14)—C(13)—C(18)	120.8(4)	C(26)—C(27)—C(28)	123.1(4)
Sb(1)—C(1)—C(2)	117.6(3)	C(13)—C(14)—C(15)	119.1(5)	C(27)—C(28)—C(29)	118.6(5)
Sb(1)—C(1)—C(6)	122.5(3)	C(14)—C(15)—C(16)	119.9(5)	C(28)—C(29)—C(30)	119.6(5)
C(2)—C(1)—C(6)	120.0(4)	C(15)—C(16)—C(17)	120.8(5)	C(29)—C(30)—C(31)	123.6(5)
C(1)—C(2)—C(3)	120.4(4)	C(16)—C(17)—C(18)	120.1(5)	C(26)—C(31)—C(30)	117.0(4)
C(2)—C(3)—C(4)	118.8(5)	C(13)—C(18)—C(17)	119.3(4)	C(26)—C(31)—C(32)	129.1(4)
C(3)—C(4)—C(5)	121.5(5)	Sb(1)—C(19)—C(20)	122.7(3)	C(30)—C(31)—C(32)	113.8(4)
C(4)—C(5)—C(6)	119.9(5)	Sb(1)—C(19)—C(24)	118.4(3)	O(3)—C(32)—O(4)	120.3(5)
C(1)—C(6)—C(5)	119.5(4)	C(20)—C(19)—C(24)	118.8(4)	O(3)—C(32)—C(31)	119.7(5)
		C(19)—C(20)—C(21)	121.0(4)	O(4)—C(32)—C(31)	120.0(4)

Tetraphenylantimony hydrogen phthalate (1). Pentaphenylantimony (4.9 mmol) was added to a 25 % solution of phthalic acid (4.9 mmol) in a 4:1 toluene—dioxane mixture in an evacuated glass tube, and the reaction mixture was heated at 90 °C for 30 min. After the removal of the solvent, the residue was recrystallized from a 5:3:1 benzene—chloroform—isopropyl alcohol mixture. Compound **1** (2.82 g, 96 %) was isolated as colorless needle-like crystals, m.p. 190—191 °C.

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