Synthesis and Structure of (4-Acetyl-3-hydroxyphenoxy)tetraphenylantimony

V. V. Sharutin, O. K. Sharutina, E. A. Bondar', O. V. Subacheva, A. P. Pakusina, A. V. Gerasimenko, and S. S. Sergienko

Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russia

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Abstract — Pentaphenylantimony was reacted with 4-acetyl-1,3-dihydroxybenzene in toluene at elevated temperature to obtain (4-acetyl-3-hydroxyphenoxy)tetraphenylantimony in 93% yield. According to X-ray diffraction data, the antimony atom in (4-acetyl-3-hydroxy-phenoxy)tetraphenylantimony has a distorted trigonal-bipyramidal configuration. The Sb–O and Sb–C distances are 2.237(1) and 2.112(1), 2.114(2), 2.118(2), 2.170(2) Å, respectively, and the CSbO angle is 177.86(5)°.

It is known that reactions of pentaarylantimony with dicarboxylic acids may involve, depending on the starting reagent ratio, substitution of one or two carboxyl hydrogen atoms to give derivatives like $Ar_4SbOC(O)RC(O)OH$ or $Ar_4SbOC(O)RC(O)OSb$. Ar_4 , respectively [1]. No reactions of pentaarylantimony with dihydroxybenzenes have not yet been reported.

We showed that the reaction of pentaphenylantimony with resorcinol (1:1 molar ratio, toluene, 20°C, 12 h) gives (3-hydroxyphenoxy)tertaphenylantimony.



Changing the reagent ratio to 2:1 leads to substitution of hydrogen in the second hydroxy group. More rigid conditions are needed in this case, which is explained by decrease in the lability of the free hydroxyl hydrogen upon introduction of the electron-donor Ph_4Sb substituent into the starting phenol.

It was found that pentaphenylantimony reacts with 4-acetyl-1,3-dihydroxybenzene analogously, i.e. by way of substitution of the most active hydrogen atom, to give (4-acetyl-3-hydroxyphenoxy)tetraphenylantimony (\mathbf{I}); (toluene, 100°C, 1 h).



The hydrogen atom of the hydroxy group *ortho* to the acetyl group in the starting phenol takes part in intramolecular hydrogen bonding, and its lability is decreased. To substitute this hydrogen atom by Ph_4Sb requires more rigid conditions (130–150°C, 2 h).



X-ray diffraction data show that the antimony atom in compound I has a trigonal-bipyramidal coordinaton. The sum of equatorial bond angles is 356.73° , and the axial C¹³SbO¹ angle is 177.86(5)°. The equatorial positions are occupied by phenyl substituents. The angles between them are slightly smallerthan 120° (117.98, 119.04, and 119.71). The axial positions are occupied by the fourth phenyl substituent and the aroxy group. The Sb–C_e distances [2.112(1), 2.114(2), and 2.118(2) Å] are shorter than Sb–C_a [2.170(2) Å].

Note, that among all the structurally characterized aroxytetraphenyl derivatives of antimony compound **I** has the longest Sb–O bond [2.237(1) Å] and the shortest O–C_{ar} bond [1.316(2)Å]. The Sb–O and O–C_{ar} bond lengths in other tetraphenylantimony phenolates are as follows, Å: 2.128(3) and 1.333(5) in (5-ethyl-2-isopropyl-phenoxy); 2.132(6) and 1.41(2) in (2,6-dimethylphenoxy)tetraphenylantimony [2]; 2.202(3) and 1.321(5) in (4-formylphenoxy)tetraphenylantimony; and 2.221(4) and 1.317(6) in tetraphenyl(2-nitrophenoxy)antimony [3]. The Sb–O and O–C_{ar} distances in aroxytetraphenyl derivatives of



General view of the molecule of (4-acetyl-3-hydroxyphenoxy)tetraphenylantimony.

antimony vary over a wide range and are determined by the electron density on the aroxy group [4]. The oxygen unshared electron pair interacts with the benzene π -electron system, thereby depleting the oxygen atom of electron density. This effect is compensated for by electron density shift from the antimony atom, which results in polarization of the Sb-O bond. The above electron interaction shortens the O-C_{ar} distance. Electron-acceptor substituents in the benzene ring favor stronger electron density shift from oxygen, rendering the Sb-O distance longer. Electrondonor substituents exert the opposite effect. The aroxy group of compound I both an electron-donor and an electron-acceptor group. The lengthening of the Sb-O bond and the attendant shortening of the O-C_{ar} bond can be explained by prevailing effect of the electronacceptor acetyl substituent.

The presence of a potential coordinating center (carbonyl group) in the aroxyl ligand does not lead to intermolecular Sb···O=C bonding, probably because of the existence of an $O^2-H^1\cdots O^3$ intramolecular hydrogen bond between the carbonyl and hydroxy groups, with the following parameters: O^2-H^1 0.92(3) Å, $H^1\cdots O^3$ 1.68(3) Å, and $O^2H^1O^3$ angle 158(2)°. The $C^{31}-O^3$ bond [1.240(2) Å] is slightly longer than the C=O bond in aldehydes and ketones [1.215(5) Å] [5]. The $C^{28}-C^{31}$ bond length is 1.450(2) Å.

The C=O stretching absorption bands in the IR spectra of compounds I and I are observed at 1608 and 1600 cm⁻¹. From that it follows that this bond in compound II is longer than in I. The C=O bond length in compound II is probably increased by intramolecular interaction between the antimony atom and the carbonyl oxygen. The same effect is observed in tetraphenylantimony acylates, where the Sb…O=C distances are shorter than the sum of the van der Waals radii of antimony and oxygen [6].

EXPRIMENTAL

The IR spectra were measured on a Hitachi-215 spectrometer in Vaselive oil between NaCl plates.

X-ray diffraction analysis was performed on a Bruker SMART-1000 diffractometer for a balled single crystal. Data collection was perfomed in groups of 606 images at φ 0, 90, and 180°, with ω -scanning in 0.3° steps and a dwell time of 10 s. Correction for absorption was applied. The crystal data and experimental and refinement parameters for structure I were as follows: empirical formula C₃₂H₂₇O₃Sb, molecular weight 591,29, temperature 293(2) K, MoK_a radiation (0.71073 Å), space group *P*1, *a* 9.454(2), *b* 9.874(2), *c* 15.168(4) Å; α 101.454(4)°, β 92.332(4)°, γ 104.869(4)°; *V* 1334.9(6) Å³, *Z* 2, *d*_{calc} 1.446 g/cm³, μ 1.064 mm⁻¹, *F*(000) 588; θ range 3.12–31.51°,

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Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Angle	o, deg	Angle	ω, deg
$\begin{array}{c} Sb-O^{1}\\ Sb-C^{1}\\ Sb-C^{7}\\ Sb-C^{13}\\ Sb-C^{19}\\ O^{1}-C^{25}\\ O^{2}-C^{29}\\ O^{3}-C^{31}\\ C^{1}-C^{6}\\ C^{1}-C^{2}\\ C^{2}-C^{3}\\ C^{3}-C^{4}\\ C^{4}-C^{5}\\ C^{5}-C^{6}\\ C^{7}-C^{8}\\ C^{7}-C^{12}\\ C^{8}-C^{9}\\ C^{9}-C^{10}\\ C^{10}-C^{11}\\ C^{11}-C^{12}\\ \end{array}$	$\begin{array}{c} 2.237(1)\\ 2.112(1)\\ 2.114(2)\\ 2.170(2)\\ 2.118(2)\\ 1.316(2)\\ 1.359(2)\\ 1.240(2)\\ 1.377(2)\\ 1.380(2)\\ 1.379(2)\\ 1.366(3)\\ 1.365(3)\\ 1.365(3)\\ 1.381(2)\\ 1.381(2)\\ 1.382(2)\\ 1.382(2)\\ 1.386(2)\\ 1.362(3)\\ 1.371(2)\\ 1.386(2)\\ \end{array}$	$\begin{array}{c} C^{13}-C^{18}\\ C^{13}-C^{14}\\ C^{14}-C^{15}\\ C^{15}-C^{16}\\ C^{16}-C^{17}\\ C^{17}-C^{18}\\ C^{19}-C^{24}\\ C^{19}-C^{20}\\ C^{20}-C^{21}\\ C^{21}-C^{22}\\ C^{22}-C^{23}\\ C^{23}-C^{24}\\ C^{25}-C^{30}\\ C^{25}-C^{26}\\ C^{26}-C^{27}\\ C^{27}-C^{28}\\ C^{28}-C^{29}\\ C^{28}-C^{31}\\ C^{29}-C^{30}\\ C^{31}-C^{32} \end{array}$	1.389(2) 1.393(2) 1.373(2) 1.378(3) 1.390(2) 1.381(2) 1.383(2) 1.390(3) 1.372(3) 1.367(3) 1.367(3) 1.384(2) 1.393(2) 1.415(2) 1.417(2) 1.450(2) 1.374(2) 1.500(3)	$\begin{array}{c} C^{1}SbC^{7}\\ C^{1}SbC^{19}\\ C^{7}SbC^{19}\\ C^{7}SbC^{13}\\ C^{7}SbC^{13}\\ C^{19}SbC^{13}\\ C^{19}SbC^{1}\\ C^{19}SbO^{1}\\ C^{19}SbO^{1}\\ C^{19}SbO^{1}\\ C^{13}SbO^{1}\\ C^{25}O^{1}Sb\\ C^{6}C^{1}C^{2}\\ C^{6}C^{1}Sb\\ C^{2}C^{1}Sb\\ C^{3}C^{2}C^{1}\\ C^{4}C^{3}C^{2}\\ C^{5}C^{4}C^{3}\\ C^{4}C^{5}C^{6}\\ C^{1}C^{6}C^{5}\\ C^{9}C^{10}C^{11}\\ C^{7}C^{12}C^{11}\\ C^{18}C^{13}C^{14}\\ C^{18}C^{13}Sb\\ C^{14}C^{13}Sb\\ C^{15}C^{14}C^{13}\\ C^{24}C^{19}C^{20}\\ C^{20}C^{19}Sb\\ C^{20}C^{19}Sb\\ \end{array}$	$\begin{array}{c} 117.98(6)\\ 119.04(6)\\ 119.71(6)\\ 97.75(5)\\ 96.03(6)\\ 94.32(6)\\ 84.01(5)\\ 82.05(5)\\ 85.84(5)\\ 177.86(5)\\ 124.35(9)\\ 119.0(1)\\ 121.3(1)\\ 119.6(1)\\ 120.7(2)\\ 119.9(2)\\ 119.8(2)\\ 120.9(2)\\ 119.7(2)\\ 120.1(2)\\ 120.1(2)\\ 120.0(2)\\ 117.7(1)\\ 123.8(1)\\ 118.5(1)\\ 121.3(2)\\ 119.3(2)\\ 122.2(1)\\ 118.5(1)\\ \end{array}$	$\begin{array}{c} C^{16}C^{15}C^{14}\\ C^{15}C^{16}C^{17}\\ C^{16}C^{17}C^{18}\\ C^{13}C^{18}C^{17}\\ C^{8}C^{7}C^{12}\\ C^{8}C^{7}Sb\\ C^{12}C^{7}Sb\\ C^{7}C^{8}C^{9}\\ C^{10}C^{9}C^{8}\\ C^{22}C^{23}C^{24}\\ C^{19}C^{24}C^{23}\\ 0^{1}C^{25}C^{26}\\ C^{30}C^{25}C^{26}\\ C^{27}C^{26}C^{25}\\ C^{26}C^{27}C^{28}C^{29}\\ C^{27}C^{28}C^{29}\\ C^{27}C^{28}C^{31}\\ C^{29}C^{28}C^{31}\\ C^{29}C^{28}C^{31}\\ C^{29}C^{28}C^{31}\\ C^{29}C^{28}C^{31}C^{22}\\ C^{30}C^{25}C^{26}\\ C^{30}C^{25}C^{26}\\ C^{30}C^{25}C^{28}\\ C^{29}C^{30}C^{25}\\ C^{30}C^{25}C^{28}\\ C^{29}C^{30}C^{25}\\ C^{31}C^{28}\\ C^{31}C^{32}\\ C^{28}C^{31}C^{32}\\ C^{19}C^{20}C^{21}\\ C^{22}C^{21}C^{20}\\ C^{23}C^{22}C^{21}\\ \end{array}$	120.2(2) $120.0(2)$ $119.8(2)$ $120.9(2)$ $119.4(2)$ $121.7(1)$ $118.9(1)$ $119.8(2)$ $120.5(2)$ $119.8(2)$ $120.4(2)$ $123.5(1)$ $119.6(1)$ $116.9(2)$ $121.2(2)$ $122.5(2)$ $116.3(2)$ $123.0(2)$ $120.7(2)$ $118.0(2)$ $121.1(2)$ $121.2(2)$ $121.2(2)$ $121.2(2)$ $121.2(2)$ $121.2(2)$ $121.2(2)$ $121.2(2)$ $121.2(2)$ $121.2(2)$ $121.2(2)$ $117.7(2)$ $121.1(2)$ $120.1(2)$ $119.6(2)$ $120.7(2)$

Table 1. Bond lengths and angles in structure I

-13 < h < 13, -14 < k < 14, and -22 < l < 22. We measured 20915 reflections, 8477 of which were unique (R_{int} 0.0352) and 6480 had $I > 2\sigma(I)$. The extinction coefficient was not refined. Residual electron density (max/min) $-0.300/0.461 \ e/A^3$.

The structure was solved by the direct method and refined by the least-squares procedure anisotropically for non-hydrogen atoms [330 variables, *GOOF* 0.889, *R*1 0.0291 and $\omega R2$ 0.0578 for $F^2 > 4\sigma(F^2)$ and *R*1 0.0436 and $\omega R2$ 0.0611 for all reflections]. The H¹ atom was located by difference synthesis and refined isotropically. The other H atoms were placed in geometrically calculated positions and refined by the rider model.

Data collection and edition, as well as refinement of unit cell parameters were carried out using the SMART and SAINT Plus programs [7]. All structural calculations were carried out using the SHELXTL/PC program package [8]. Reaction of pentaphenylantimony with 4-acetyl-1,3-dihydroxybenzene (molar ratio 1:1). A mixture of 1.00 g of pentaphenylantimony, 0.30 g of 4-acetyl-1,3-dihydroxybenzene, and 10 ml of toluene was heated at 100°C for 1 h. The solvent was removed, and the residue was crystallized from toluene– heptane (1:1) to obtain 1.05 g (92%) of pinkish crystals, mp 194–195°C. IR spectrum, v, cm⁻¹: 1800 s, 1745 m, 1330 s, 1275 v.s, 1220 m, 1180 s, 1120 s, 1060 s.

The reaction of pentaphenylantimony with resorcinol was carried out analogously. Crystals of (3-hydroxyphenoxy)tetraphenylantimony (67%) were obtained, mp 159°C.

Reaction of pentaphenylantimony with 4-acetyl-1,3-dihydroxybenzene (molar ratio 2:1). A mixture of 3.00 g of pentaphenylantimony, 0.44 g of 4-acetyl-1,3-dihydroxybenzene, and 15 ml of toluene were heated at 130–150°C for 2 h. The reaction mixture

Table 2. Atomic coordinates and isotropic equivalent thermal parameters ($\times\,10^5$ for Sb and $\times\,10^4$ for the rest atoms) in structure I

x	У	Z	U _{eq}
-1766(1)	23777(1)	21601(1)	3727(3)
1161(1)	2562(1)	3452(1)	494(3)
4679(1)	-16(2)	2686(1)	695(4)
4883(2)	-1905(2)	3584(1)	819(4)
-758(2)	160(1)	2144(1)	377(3)
-1679(2)	-361(2)	2754(1)	524(4)
-2022(2)	-1794(2)	2785(1)	614(5)
-1469(2)	-2718(2)	2194(1)	648(5)
-565(2)	-2214(2)	1584(2)	808(6)
-202(2)	-778(2)	1553(1)	620(5)
-1218(2)	3691(1)	3028(1)	399(3)
-433(2)	4782(2)	3727(1)	558(5)
-1154(2)	5643(2)	4265(1)	667(5)
-2639(2)	5398(2)	4126(1)	614(5)
-3433(2)	4299(2)	3445(1)	584(5)
-2723(2)	3454(2)	2885(1)	493(4)
-1489(2)	2275(2)	929(1)	408(4)
-1363(2)	3534(2)	618(1)	497(4)
-2171(2)	3543(2)	-153(1)	605(5)
-3115(2)	2299(2)	-640(1)	653(5)
-3275(2)	1036(2)	-351(1)	659(6)
-2475(2)	1029(2)	438(1)	533(4)
1845(2)	3312(2)	1688(1)	425(4)
2164(2)	2681(2)	848(1)	568(5)
3523(2)	3202(2)	543(1)	718(6)
4528(2)	4372(2)	1069(2)	719(6)
4200(2)	5041(2)	1883(1)	656(5)
2868(2)	4498(2)	2202(1)	540(5)
1865(2)	1626(2)	3598(1)	423(4)
1530(2)	926(2)	4322(1)	508(4)
2207(2)	-73(2)	4478(1)	517(4)
3267(2)	-470(2)	3939(1)	436(4)
3630(2)	257(2)	3228(1)	458(4)
2944(2)	1268(2)	3071(1)	476(4)
3955(2)	-1577(2)	4077(1)	557(5)
3577(2)	-2355(2)	4826(1)	744(6)
491(3)	-75(3)	291(2)	114(9)
	x -1766(1) 1161(1) 4679(1) 4883(2) -758(2) -1679(2) -2022(2) -1469(2) -565(2) -202(2) -1218(2) -433(2) -1154(2) -2639(2) -3433(2) -2723(2) -1489(2) -1363(2) -2171(2) -3115(2) -3275(2) -2475(2) 1845(2) 2164(2) 3523(2) 4528(2) 4528(2) 4528(2) 4528(2) 1865(2) 1530(2) 2207(2) 3630(2) 2944(2) 3955(2) 3577(2) 491(3)	x y $-1766(1)$ $23777(1)$ $1161(1)$ $2562(1)$ $4679(1)$ $-16(2)$ $4883(2)$ $-1905(2)$ $-758(2)$ $160(1)$ $-1679(2)$ $-361(2)$ $-2022(2)$ $-1794(2)$ $-1469(2)$ $-2718(2)$ $-565(2)$ $-2214(2)$ $-202(2)$ $-778(2)$ $-1218(2)$ $3691(1)$ $-433(2)$ $4782(2)$ $-1154(2)$ $5643(2)$ $-2639(2)$ $5398(2)$ $-3433(2)$ $4299(2)$ $-2723(2)$ $3454(2)$ $-1489(2)$ $2275(2)$ $-1363(2)$ $3534(2)$ $-2171(2)$ $3543(2)$ $-3115(2)$ $2299(2)$ $-3275(2)$ $1036(2)$ $-2475(2)$ $1029(2)$ $1845(2)$ $3312(2)$ $2164(2)$ $2681(2)$ $3523(2)$ $3202(2)$ $4528(2)$ $4372(2)$ $4200(2)$ $5041(2)$ $2868(2)$ $4498(2)$ $1865(2)$ $1626(2)$ $1530(2)$ $926(2)$ $207(2)$ $-73(2)$ $3267(2)$ $-470(2)$ $3630(2)$ $257(2)$ $2944(2)$ $1268(2)$ $3955(2)$ $-1577(2)$ $3577(2)$ $-2355(2)$ $491(3)$ $-75(3)$	x y z -1766(1)23777(1)21601(1)1161(1)2562(1)3452(1)4679(1)-16(2)2686(1)4883(2)-1905(2)3584(1)-758(2)160(1)2144(1)-1679(2)-361(2)2754(1)-2022(2)-1794(2)2785(1)-1469(2)-2718(2)2194(1)-565(2)-2214(2)1584(2)-202(2)-778(2)1553(1)-1218(2)3691(1)3028(1)-433(2)4782(2)3727(1)-1154(2)5643(2)4265(1)-2639(2)5398(2)4126(1)-3433(2)4299(2)3445(1)-2723(2)3454(2)2885(1)-1489(2)2275(2)929(1)-1363(2)3534(2)618(1)-2171(2)3543(2)-153(1)-3115(2)2299(2)-640(1)-3275(2)1029(2)438(1)1845(2)3312(2)1688(1)2164(2)2681(2)848(1)3523(2)3202(2)543(1)4528(2)4372(2)1069(2)4200(2)5041(2)1883(1)2868(2)4498(2)2202(1)1865(2)1626(2)3598(1)1530(2)926(2)4322(1)207(2)-73(2)4478(1)3267(2)-470(2)3939(1)3630(2)257(2)3228(1)2944(2)1268(2)3071(1)3955(2)-1577(2)4077(1)3577(2)-2355(2)482

was cooled to room temperature to form yellow crystals which were filtered off and dried to obtain 2.45 g (84%) of yellow crystals, mp 123–131°C. IR spectrum, v, cm⁻¹: 1600 s, 1290 v.s, 1150 s, 1060 s.

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