Synthesis and Structure of 2-*tert*-Butylphenoxytetraphenylantimony

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Abstract—2-*tert*-Butylphenoxytetraphenylantimony $Ph_4SbOC_6H_4(Bu-t)$ -2 was prepared by the reaction of pentaphenylantimony with 2-*tert*-butylphenol in toluene at 20°C. The structure of the obtained compound was determined by X-ray diffraction. The Sb atom in this compound has a distorted trigonal-bipyramidal coordination with the aroxy group in the axial position. The Sb–C(Ph)_{eq} and Sb–C(Ph)_{ax} distances are 2.111(7)–2.138(7) and 2.180(7) Å; the Sb–O and O–C_{Ar} distances are 2.143(4) and 1.363(8) Å, respectively. The C(Ph)_{ax}SbO_{Ar} axial angle is 174.1(2)°, while the SbOC angle is 126.7(4)°.

In continuation of our studies into the synthesis, structure, and thermal decomposition of antimony aroxytetraaryl compounds [1–3], we investigated the interaction of pentaphenylantimony Ph_5Sb with 2-*tert*-butylphenol HOC₆H₄(Bu-*t*)-2. Reaction between the reagents in the toluene solution at 20°C run for 48 h results in formation of 2-*tert*-butylphenoxytetraphenyl-antimony (**I**) isolated from the reaction mixture as colorless crystals.

Ph₅Sb + HOC₆H₄(Bu-
$$t$$
)-2
→ Ph₄SbOC₆H₄(Bu- t)-2 + PhH.

The structure of compound **I** is determined by X-ray diffraction. The coordination of the Sb(1) atom in the $Ph_4SbOC_6H_4(Bu-t)-2$ molecule is a distorted trigonal bipyramid (figure), which is typical of pentavalent antimony compounds with the coordination number 5. The sum of the C(Ph)SbC(Ph) angles in the equatorial plane



Molecular structure of compound I.

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Compound	Bond length, Å			ShOC angla dag	Poforoncos
Compound	Sb–O	O–C _{Ar}	Sb–C _{ax}	SUCC aligie, deg	References
Ph ₄ SbOC ₆ H ₄ (NO ₂)-2	2.221(4)	1.317(6)	2.181(5)	123.8(3)	[1]
Ph ₄ SbOC ₆ H ₄ (CHO)-4	2.202(3)	1.321(5)	2.188(5)	126.9(3)	[1]
Ph ₄ SbOC ₆ H ₃ Me-2, <i>i</i> -Pr-5	2.128(3)	1.333(5)	2.187(4)	127.1(2)	[3]
$Ph_4SbOC_6H_4(t-Bu)-2$	2.143(4)	1.363(8)	2.180(7)	126.7(4)	In this work
$Ph_4SbOC_6H_3(Me)_2-2,6$	2.132(6)	1.41(2)	2.176(8)	124.0(8)	[3]

Table 1. The Sb–O and O–C bond lengths and SbOC angles in the molecules of antimony aroxytetraaryl compounds

Table 2. Atomic coordinates $(\times 10^4)$ and equivalent isotropic thermal parameters $(\times 10^3)$ in structure I

Atom	x	У	z	$U_{ m eq}$, Å 2
Sb(1)	2375(1)	1115(1)	6164(1)	37(1)
O(1)	2834(4)	1323(2)	7678(3)	44(1)
C(1)	2086(6)	962(4)	4586(5)	39(2)
C(2)	1818(8)	1517(4)	3997(6)	52(2)
C(3)	1582(9)	1449(5)	3001(6)	65(2)
C(4)	1614(8)	826(5)	2561(7)	63(2)
C(5)	1885(10)	265(5)	3124(6)	66(3)
C(6)	2128(8)	336(4)	4139(6)	51(2)
C(7)	3644(7)	1929(4)	5913(5)	41(2)
C(8)	4653(7)	1870(4)	5235(6)	50(2)
C(9)	5383(8)	2419(5)	4987(7)	59(2)
C(10)	5121(10)	3035(6)	5392(7)	69(3)
C(11)	4140(11)	3101(5)	6047(7)	71(3)
C(12)	3436(9)	2547(4)	6307(6)	57(2)
C(13)	447(7)	1437(3)	6440(5)	40(2)
C(14)	-509(7)	1284(4)	5791(7)	47(2)
C(15)	-1755(8)	1497(4)	5950(7)	55(2)
C(16)	-2031(8)	1867(4)	6770(6)	59(2)
C(17)	-1079(9)	2021(5)	7426(7)	69(3)
C(18)	166(8)	1800(4)	7276(6)	58(2)
C(19)	2951(7)	106(3)	6465(5)	39(2)
C(20)	2039(9)	-410(4)	6469(6)	48(2)
C(21)	2409(11)	-1051(5)	6717(7)	62(2)
C(22)	3657(11)	-1184(5)	6957(7)	74(3)
C(23)	4547(10)	-689(5)	6958(7)	73(3)
C(24)	4205(8)	-42(4)	6721(6)	54(2)
C(25)	2603(7)	914(4)	8466(5)	40(2)
C(26)	1560(8)	480(4)	8488(6)	50(2)
C(27)	1350(9)	49(4)	9265(7)	59(2)
C(28)	2195(10)	66(5)	10059(6)	65(3)
C(29)	3188(9)	507(5)	10055(6)	59(2)
C(30)	3449(7)	954(4)	9289(5)	43(2)
C(31)	4538(8)	1462(4)	9345(6)	56(2)
C(32)	4007(9)	2176(4)	9227(7)	73(3)
C(33)	5258(9)	1440(6)	10338(7)	87(3)
C(34)	5532(7)	1315(5)	8547(6)	68(3)

is $358.5(3)^{\circ}$, and the $O_{Ar}SbC(Ph)_{ax}$ angle is $174.1(2)^{\circ}$. The equatorial positions are occupied by the Ph groups, the C(Ph)_{eq}SbC(Ph)_{eq} angles vary in the $112.9(3)^{\circ}$ – $125.0(3)^{\circ}$ range. All the angles between the electronegative axial ligand and equatorial Ph groups are less than 90° ($82.7(2)^{\circ}$, $86.3(2)^{\circ}$, and $88.8(2)^{\circ}$). The Sb–C(Ph)_{eq} distances varying in the 2.111(7)–2.138(7) Å range are essentially shorter than the Sb–C(Ph)_{ax} distance 2.180(7) Å. The O_{Ar}–C bond length is 1.363(8) Å; the value of the Sb(1)O(1)C(25) angle is $126.7(4)^{\circ}$.

To date, the structures of four antimony aroxytetraphenyl compounds, containing electron-accepting [1] and electron-donating [3] substituents in the aroxy group, have been determined by X-ray diffraction (Table 1).

As is seen from Table 1, the Sb–O distances for the compounds with electron-donating substituents in the aroxy group (2.128(3)-2.143(4) Å) are somewhat shorter than the similar distances for the compounds with electron-accepting substituents (2.202(3) and 2.221(4) Å). However, the O– C_{Ar} distances for the compounds with electron-donating substituents in the aroxy group (1.333(5)-1.41(2) Å) are somewhat longer than similar distances for the compounds with electronaccepting substituents (1.317(6) and 1.321(5) Å). Note that the following regularity is found for the structures of four compounds (except Ph₄SbOC₆H₃Me-2,*i*-Pr-5): the decrease of the O-CAr bond length is accompanied by the increase of the Sb-O distance (Table 1). This fact may be explained by a redistribution of electron density in the system of conjugated Ar–O–Sb bonds involving π -electrons of the benzene ring of the aroxy group, the *p*-orbital of the oxygen atom, and the *d*-orbital of the antimony atom. The electron-accepting substituent in the aroxy group is responsible for the shift of electron density from the oxygen atom to the benzene ring of the aroxy group and for the strengthening of the O–C bond. On the other hand, the electron-donating substituents contained in the aroxy group make the electron density shift from the oxygen atom to the antimony atom and thus strengthen the Sb–O bond.



Bond	<i>d</i> , Å	Angle	ω, deg	Angle	ω, deg
Sb(1)–C(7)	2.111(7)	C(7)Sb(1)C(19)	125.0(3)	C(7)Sb(1)C(1)	91.7(2)
Sb(1)–C(19)	2.125(7)	C(7)Sb(1)C(13)	112.9(3)	C(19)Sb(1)C(1)	95.4(3)
Sb(1)–C(13)	2.138(7)	C(19)Sb(1)C(13)	120.6(6)	C(13)Sb(1)C(1)	95.1(3)
Sb(1)–O(1)	2.143(4)	C(7)Sb(1)O(1)	82.7(2)	O(1)Sb(1)C(1)	174.1(2)
Sb(1)–C(1)	2.180(7)	C(19)Sb(1)O(1)	86.3(2)	C(25)O(1)Sb(1)	126.7(4)
O(1)–C(25)	1.363(8)	C(13)Sb(1)O(1)	88.8(2)		

Table 3. Selected bond lengths and angles in structure I

EXPERIMENTAL

Synthesis of 2-*tert*-butylphenoxytetraphenylantimony (I). A mixture of 1.00 g (2.0 mmol) of pentaphenylantimony, 0.30 g (2.0 mmol) of 2-*tert*-butylphenol, and 10 ml of toluene was kept for 48 h at 25°C, after which crystals were formed; their quantity increased significantly on cooling the reaction mixture to -18°C. The solvent was decanted; the crystals were washed with hexane (5 ml) and dried. The yield was 0.96 g (84%), mp 211°C.

For C34H33OSb

anal. calcd. (%):	C, 70.47;	Н, 5.70;	Sb, 21.07.
Found (%):	C, 69.49;	Н, 5.32;	Sb, 21.25.

X-ray diffraction analysis of I was carried out using a Siemens P3/PC four-circle diffractometer (graphite monochromator, MoK_{α} radiation, $\theta/2\theta$ scan mode).

The crystals of **I** are monoclinic: a = 10.395(3) Å, b = 19.798(9) Å, c = 13.556(5) Å, $\beta = 90.36(3)^{\circ}$, V = 2790(2) Å³, space group $P_2(1)/n$, Z = 4, $\rho_{calcd} = 1.379$ g/cm³ at 20°C.

The structure of complex **I** was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms. The refinement converged to R = 0.046, $R_w = 0.107$, and S = 1.22 for 2842 reflections with $I > 2\sigma(I)$. The H atoms of the phenyl groups were

located from the difference syntheses and refined isotropically. The H atoms of the *tert*-butyl groups were placed in the geometrically calculated positions and refined in the rider model with fixed values of U_{iso} . All calculations were performed using the SHELX97 program package [4] on an IBM PC.

Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Bond lengths and angles are given in Table 3.

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