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Synthesis and Structure of Tetraphenylantimony 2-Furoinate and Benzoate

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Abstract—Tetraphenylantimony 2-furoinate $Ph_4SbOC(O)C_4H_3O$ is synthesized by the reaction of pentaphenylantimony with triphenylantimony bis(2-furoinate). The structure of the compound is determined by X-ray diffraction analysis. The Sb atom in the compound has a distorted trigonal-bipyramidal coordination with the phenyl and 2-furoinate groups in the axial positions. The Sb(1)–$C(Ph)_{eq}$ distances lie in the 2.119(1)–2.121(1) Å interval; the Sb–O(1) and Sb–$C(Ph)_{ax}$ bond lengths are equal to 2.273(1) and 2.161(1) Å, respectively; and the Sb(1)··O(2) intramolecular contact is 3.234(1) Å.

INTRODUCTION

In the majority of antimony compounds with the general formula Ar_4SbX (X is an organic or inorganic ligand), the Sb atom has the trigonal bipyramid configuration with coordination number (CN) 5 [1]. However, when the ligands contain potential coordination sites, they can additionally interact with the Sb atom. As a result, a coordination environment of the Sb atom with CN 6 can be realized. For example, most tetraarylantimony acylates [2–8] exhibit shortened Sb··O distances as compared to the sum of van der Waals radii, thus indicating an additional coordination of the Sb atom in these compounds.

In continuation of our studies on the structures of tetraphenylantimony acylates [2–8], we examined the molecular and crystal structures of tetraphenylantimony 2-furoinate (**I**) and tetraphenylantimony benzoate (**II**), which are antimony derivatives that differ only in the nature of the arene ring of the carboxylic acid. The structure of compound **II** determined with lower accuracy than in the present work, was reported in [8].

EXPERIMENTAL

Synthesis of tetraphenylantimony 2-furoinate was carried out in an evacuated glass tube as follows. Pentaphenylantimony (1.00 g, 1.97 mmol) and triphenylantimony bis(2-furoinate) (1.13 g, 1.96 mmol) in toluene (10 ml) were heated at 90°C for 1 h. The solvent was removed, and the residue was recrystallized from a benzene–heptane (3 : 1) mixture. The complex was obtained in 96% yield (2.05 g), mp 166°C.

IR (ν, cm^{-1}): 1630 vs, 1395 vs, 1180 vs, 1125 s, 1060 vs.

Tetraphenylantimony benzoate was synthesized similarly.

X-ray diffraction analysis of crystals **I** and **II** was performed on a SMART-1000 CCD automated diffractometer (Bruker). The data for compound **I** were collected in sets of 606, 435, and 230 frames at the angle $\varphi = 0°$, 90°, and 180°, respectively (ω scan mode with an increment of 0.3° and exposure of 10 s per frame for compound **I** and 20 s per frame for compound **II**).

The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for all non-hydrogen atoms. The positions of hydrogen atoms were calculated geometrically and included in the refinement by the "rider" model.

The data collection and editing and the refinement of the unit cell parameters were performed using the SMART and SAINT-*Plus* program packages [9]. All calculations for determination and refinement of the structures were performed using the SHELXTL/PC program package [10].

The main crystallographic data and results of refinement of the structures are presented in Table 1. The atomic coordinates[1] are presented in Table 2, and the bond lengths and angles are given in Table 3.

RESULTS AND DISCUSSION

Compounds **I** and **II** were synthesized by the disproportionation of pentaphenylantimony and triphenylantimony diacylates in toluene at 90°C. The reaction was

[1] The coordinates of hydrogen atoms and their thermal isotropic parameters can be made available by the authors.

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Table 1. Summary of data collection and refinement of structures **I** and **II**

Parameter	**I**	**II**
Empirical formula	$C_{29}H_{23}O_3Sb$	$C_{31}H_{25}O_2Sb$
Molecular weight	541.22	551.26
Temperature, K	293(2)	295(2)
Wavelength	MoK_α (0.71073 Å)	MoK_α (0.71073 Å)
Space group	$P2_1/c$	$P2_1/n$
a, Å	9.863(1)	10.395(1)
b, Å	14.867(2)	14.643(2)
c, Å	17.102(2)	17.199(2)
β, deg	105.286(2)	103.508(2)
V, Å^3	2414.0(5)	2545.6(6)
Z	4	4
ρ(calcd), g/cm^3	1.489	1.438
μ, mm^{-1}	1.171	1.109
F(000)	1088	1112
Crystal shape	Prism (0.20 × 0.20 × 0.27 mm)	Prism (0.2 × 0.26 × 0.4 mm)
Range of θ, deg	2.14–30.05	1.85–30.01
Intervals of refractive indices	$-13 \le h \le 13$, $-13 \le k \le 20$, $-24 \le l \le 21$	$-14 \le h \le 14$, $-15 \le k \le 20$, $-21 \le l \le 24$
Measured reflections	18252	19119
Independent reflections	7004 (R_{int} = 0.0370)	7402 (R_{int} = 0.0378)
Reflections with $I > 2\sigma(I)$	4913	4829
Refinement method	Full-matrix least-squares for F^2	Full-matrix least-squares for F^2
Refinement variables	299	307
GOOF	0.905	0.884
R factors for $F^2 > 2\sigma(F^2)$	R_1 = 0.0264, wR_2 = 0.0555	R_1 = 0.029, wR_2 = 0.056
R factors for all reflections	R_1 = 0.0454, wR_2 = 0.0602	R_1 = 0.0561, wR_2 = 0.0633
Molar absorption coefficient	0.00096(8)	Was not applied
Residual electron density (min/max), e/Å^3	–0.336/0.323 (near Sb atom)	–0.454/0.558 (near Sb atom)

almost complete after 1-h heating of the reaction mixture.

$$Ph_5Sb + Ph_3Sb[OC(O)R]_2 \longrightarrow 2Ph_4SbOC(O)R$$
$$(R = C_4H_3O, C_6H_5).$$

X-ray diffraction analysis of compounds **I** and **II** showed that the Sb atoms have a distorted trigonal-bipyramidal coordination (Figs. 1, 2) with the O atoms of the carboxylate ligands in the axial positions. The sums of the C(Ph)SbC(Ph) angles in the equatorial plane are 356.56(5)° and 356.17(6)°, and the axial angles O(1)SbC(11) in **I** and O(1)SbC(21) in **II** are 176.46(4)° and 176.66(5)°, respectively. The C(Ph)SbC(Ph) angles between the equatorial phenyl ligands are different: 130.75(5)°, 116.55(5)°, and 109.26(5)° in **I** and 129.14(6)°, 115.28(5)°, and 111.75(6)° in **II**.

The Sb–O(1) bond length in compound **I** (2.273(1) Å) is much longer than that in **II** (2.245(1) Å), which can be explained by the higher electron-withdrawing ability of the furan fragment as compared to that of the phenyl substituent. The C(1)–C(2) bond in **I** equal to 1.482(2) Å is much shorter than the analogous bond in **II** (1.507(2) Å), indicating that the *p* electrons of the carbonyl carbon atom are involved to a greater extent in the conjugation with the π-system of the furan ring in compound **I** than in compound **II**. The angles between the planes of the arene ring and carboxyl groups in the carboxylate fragment (16.12° and 30.58° in **I** and **II**, respectively) also confirm this fact.

The Sb··O(2) distances, which are equal to 3.234(1) and 3.305(1) Å for compounds **I** and **II**, respectively, are much shorter than the sum of the van der Waals radii of the Sb and O atoms (3.7 Å [11]), and the longer Sb–O(1) bond corresponds to the shorter Sb··O(2) contact in **I**. As in other tetraarylantimony acylates [2–8], the value of the angles on the side of the intramolecular Sb··O(2) contacts in **I** and **II** exceeds the standard value of 120°. Thus, the coordination number of the Sb atom in compounds **I** and **II** is 6 (5 + 1).

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

Atom	*x*	*y*	*z*	U_{eq}, Å^2	Atom	*x*	*y*	*z*	U_{eq}, Å^2
		I					**II**		
Sb	2502.73(9)	9847.80(6)	1930.98(5)	36.99(2)	Sb	4621.93(9)	5241.31(7)	2017.77(6)	41.66(3)
O(1)	4652(1)	9182.3(7)	2196.6(6)	49.8(3)	O(1)	2864.4(9)	5925.7(7)	2315.7(6)	52.1(3)
O(2)	5655(1)	10342.3(7)	2972.8(7)	57.2(3)	O(2)	2439.5(11)	4801.4(8)	3090.6(7)	63.1(3)
O(3)	8081(1)	9323(1)	3505.0(7)	82.5(4)	C(1)	2163.2(14)	5523.2(11)	2738.4(9)	45.6(4)
C(1)	5695(1)	9599(1)	2682(1)	44.3(4)	C(11)	908.1(13)	6025.6(11)	2762.5(9)	48.2(4)
C(2)	7009(2)	9063(1)	2866(1)	51.0(4)	C(12)	369.9(15)	5949.5(13)	3426.3(10)	64.9(5)
C(3)	7384(2)	8350(1)	2499(1)	57.4(5)	C(13)	–790.7(17)	6429.3(16)	3443.7(12)	85.1(7)
C(4)	8775(2)	8131(1)	2914(1)	88.4(7)	C(14)	–1408.9(17)	6936.0(15)	2797.2(14)	88.6(7)
C(5)	9150(2)	8701(2)	3517(1)	92.8(7)	C(15)	–891.8(17)	6997.2(14)	2136.6(13)	79.1(7)
C(11)	518(1)	10556(1)	1660(1)	38.3(3)	C(16)	274.7(16)	6555.6(12)	2122.7(11)	60.7(5)
C(12)	–375(2)	10499(1)	2167(1)	52.4(4)	C(21)	6241.0(14)	4524.6(10)	1687.0(9)	43.8(4)
C(13)	–1654(2)	10932(1)	1981(1)	56.7(4)	C(22)	6023.3(14)	3992.5(11)	1002.8(8)	48.9(4)
C(14)	–2068(2)	11434(1)	1282(1)	54.5(4)	C(23)	7051.9(15)	3565.7(12)	764.0(9)	56.2(5)
C(15)	–1205(2)	11505(1)	775(1)	53.4(4)	C(24)	8313.1(15)	3668.3(12)	1204.7(10)	60.2(5)
C(16)	71(2)	11071(1)	960(1)	45.1(4)	C(25)	8567.6(15)	4190.8(13)	1890.1(11)	63.3(5)
C(21)	2836(1)	9845(1)	3207(1)	39.7(3)	C(26)	7531.7(15)	4611.0(11)	2131.6(11)	57.7(5)
C(22)	3047(2)	9038(1)	3610(1)	49.9(4)	C(31)	5451.9(13)	5262.2(11)	3264.8(9)	46.2(4)
C(23)	3207(2)	9005(1)	4437(1)	60.2(5)	C(32)	5929.6(19)	4487.0(13)	3669.3(10)	70.7(6)
C(24)	3146(2)	9776(1)	4861(1)	60.2(5)	C(33)	6490.7(19)	4512.4(15)	4482.6(11)	79.7(7)
C(25)	2918(2)	10582(1)	4457(1)	64.1(5)	C(34)	6628.0(17)	5324.2(14)	4889.1(10)	68.4(6)
C(26)	2755(2)	10629(1)	3634(1)	57.6(5)	C(35)	6184.7(17)	6106.3(14)	4475.7(10)	69.9(6)
C(31)	3356(1)	10680(1)	1173(1)	41.3(4)	C(36)	5589.8(15)	6077.6(12)	3667.2(9)	57.3(5)
C(32)	3739(2)	11559(1)	1381(1)	55.3(4)	C(41)	3128.3(12)	4376.2(11)	1348.9(8)	42.4(4)
C(33)	4123(2)	12121(1)	832(1)	68.6(6)	C(42)	2345.5(17)	4699.8(13)	643.1(11)	63.6(5)
C(34)	4134(2)	11811(1)	88(1)	71.7(6)	C(43)	1440.4(17)	4135.5(15)	159.5(11)	74.7(6)
C(35)	3757(2)	10947(1)	–129(1)	75.7(6)	C(44)	1297.5(15)	3252.8(14)	372.0(11)	66.6(6)
C(36)	3365(2)	10372(1)	414(1)	61.9(5)	C(45)	2062.8(16)	2926.0(13)	1072.8(12)	70.8(6)
C(41)	1759(1)	8563(1)	1464(1)	38.6(3)	C(46)	2986.7(15)	3482.3(13)	1561.1(10)	61.2(5)
C(42)	329(2)	8450(1)	1149(1)	49.5(4)	C(51)	4835.3(13)	6520.5(10)	1478.0(8)	40.9(4)
C(43)	–223(2)	7612(1)	873(1)	62.0(5)	C(52)	4151.3(15)	7299.9(11)	1607.8(9)	53.3(4)
C(44)	657(2)	6886(1)	914(1)	62.6(5)	C(53)	4358.9(16)	8123.2(12)	1273.1(10)	61.7(5)
C(45)	2077(2)	6987(1)	1229(1)	57.2(5)	C(54)	5237.2(16)	8183.5(12)	791.9(10)	62.2(5)
C(46)	2641(2)	7826(1)	1500(1)	49.4(4)	C(55)	5911.1(15)	7421.2(13)	653.0(10)	61.2(5)
					C(56)	5729.8(14)	6589.2(11)	995.6(9)	48.7(4)

Table 3. Interatomic distances and bond angles in structures **I** and **II**

I				**II**			
Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
Sb–C(31)	2.119(1)	C(31)SbC(21)	130.75(5)	Sb–C(31)	2.117(2)	C(31)SbC(41)	129.14(6)
Sb–C(21)	2.120(1)	C(31)SbC(41)	116.55(5)	Sb–C(41)	2.122(1)	C(31)SbC(51)	111.75(6)
Sb–C(41)	2.121(1)	C(21)SbC(41)	109.26(5)	Sb–C(51)	2.125(2)	C(41)SbC(51)	115.28(5)
Sb–C(11)	2.161(1)	C(31)SbC(11)	93.96(5)	Sb–C(21)	2.169(2)	C(31)SbC(21)	96.61(6)
Sb–O(1)	2.273(1)	C(21)SbC(11)	96.19(5)	Sb–O(1)	2.245(1)	C(41)SbC(21)	94.78(5)
Sb–O(2)	3.234(1)	C(41)SbC(11)	98.73(5)	Sb–O(2)	3.305(1)	C(51)SbC(21)	98.36(6)
O(1)–C(1)	1.295(2)	C(31)SbO(1)	82.84(4)	O(1)–C(1)	1.286(2)	C(31)SbO(1)	85.59(5)
O(2)–C(1)	1.215(2)	C(21)SbO(1)	84.84(4)	O(2)–C(1)	1.219(2)	C(41)SbO(1)	81.89(5)
O(3)–C(2)	1.361(2)	C(41)SbO(1)	84.08(4)	C(1)–C(11)	1.507(2)	C(51)SbO(1)	83.10(5)
O(3)–C(5)	1.398(2)	C(11)SbO(1)	176.46(4)	C(11)–C(16)	1.381(2)	C(21)SbO(1)	176.66(5)
C(1)–C(2)	1.482(2)	C(2)O(3)C(5)	104.3(2)	C(11)–C(12)	1.388(2)	C(31)SbO(2)	66.90(4)
C(2)–C(3)	1.332(2)	O(2)C(1)O(1)	126.2(1)	C(12)–C(13)	1.403(2)	C(41)SbO(2)	71.07(4)
C(3)–C(4)	1.407(2)	O(2)C(1)C(2)	121.4(1)	C(13)–C(14)	1.366(3)	C(51)SbO(2)	124.82(4)
C(4)–C(5)	1.309(3)	O(1)C(1)C(2)	112.5(1)	C(14)–C(15)	1.369(3)	C(21)SbO(2)	136.72(5)
C(11)–C(16)	1.390(2)	C(3)C(2)O(3)	110.6(1)	C(15)–C(16)	1.379(3)	O(1)SbO(2)	42.13(3)
C(11)–C(12)	1.392(2)	C(3)C(2)C(1)	131.4(1)	C(21)–C(22)	1.385(2)	O(2)C(1)O(1)	125.41(1)
C(12)–C(13)	1.376(2)	O(3)C(2)C(1)	118.0(1)	C(21)–C(26)	1.386(2)	O(2)C(1)C(11)	121.0(1)
C(13)–C(14)	1.377(2)	C(2)C(3)C(4)	107.4(2)	C(22)–C(23)	1.381(2)	O(1)C(1)C(11)	113.6(1)
C(14)–C(15)	1.369(2)	C(5)C(4)C(3)	106.5(2)	C(23)–C(24)	1.361(2)	C(16)C(11)C(12)	119.4(2)
C(15)–C(16)	1.375(2)	C(4)C(5)O(3)	111.1(2)	C(24)–C(25)	1.378(2)	C(16)C(11)C(1)	120.5(1)
C(21)–C(22)	1.369(2)	C(16)C(11)C(12)	117.4(1)	C(25)–C(26)	1.386(2)	C(12)C(11)C(1)	120.1(1)
C(21)–C(26)	1.386(2)	C(13)C(12)C(11)	121.4(1)	C(31)–C(32)	1.363(2)	C(11)C(12)C(13)	119.4(2)
C(22)–C(23)	1.383(2)	C(12)C(13)C(14)	119.8(2)	C(31)–C(36)	1.371(2)	C(14)C(13)C(12)	119.9(2)
C(23)–C(24)	1.365(2)	C(15)C(14)C(13)	120.1(1)	C(32)–C(33)	1.385(2)	C(13)C(14)C(15)	120.7(2)
C(24)–C(25)	1.371(2)	C(14)C(15)C(16)	120.1(1)	C(33)–C(34)	1.369(3)	C(14)C(15)C(16)	120.1(2)
C(25)–C(26)	1.375(2)	C(15)C(16)C(11)	121.3(1)	C(34)–C(35)	1.370(3)	C(15)C(16)C(11)	120.5(2)
C(31)–C(36)	1.377(2)	C(22)C(21)C(26)	119.5(1)	C(35)–C(36)	1.384(2)	C(22)C(21)C(26)	117.7(1)
C(31)–C(32)	1.379(2)	C(21)C(22)C(23)	120.4(1)	C(41)–C(46)	1.376(2)	C(23)C(22)C(21)	121.5(1)
C(32)–C(33)	1.381(2)	C(24)C(23)C(22)	120.4(2)	C(41)–C(42)	1.378(2)	C(24)C(23)C(22)	119.8(2)
C(33)–C(34)	1.356(3)	C(23)C(24)C(25)	119.2(2)	C(42)–C(43)	1.376(2)	C(23)C(24)C(25)	120.4(2)
C(34)–C(35)	1.359(3)	C(24)C(25)C(26)	121.3(2)	C(43)–C(44)	1.361(3)	C(24)C(25)C(26)	119.7(1)
C(35)–C(36)	1.389(3)	C(25)C(26)C(21)	119.3(2)	C(44)–C(45)	1.366(2)	C(25)C(26)C(21)	120.9(2)
C(41)–C(42)	1.381(2)	C(36)C(31)C(32)	119.2(2)	C(45)–C(46)	1.384(2)	C(32)C(31)C(36)	119.0(2)
C(41)–C(46)	1.389(2)	C(31)C(32)C(33)	120.1(2)	C(51)–C(56)	1.387(2)	C(31)C(32)C(33)	120.7(2)
C(42)–C(43)	1.388(2)	C(34)C(33)C(32)	120.3(2)	C(51)–C(52)	1.390(2)	C(34)C(33)C(32)	120.5(2)
C(43)–C(44)	1.374(2)	C(33)C(34)C(35)	120.5(2)	C(52)–C(53)	1.375(2)	C(33)C(34)C(35)	118.6(2)
C(44)–C(45)	1.370(2)	C(34)C(35)C(36)	120.0(2)	C(53)–C(54)	1.371(2)	C(34)C(35)C(36)	120.9(2)
C(45)–C(46)	1.392(2)	C(31)C(36)C(35)	119.9(2)	C(54)–C(55)	1.368(2)	C(31)C(36)C(35)	120.2(2)
		C(42)C(41)C(46)	119.0(1)	C(55)–C(56)	1.385(2)	C(46)C(41)C(42)	118.9(1)
		C(41)C(42)C(43)	120.7(1)			C(43)C(42)C(41)	120.4(2)
		C(44)C(43)C(42)	120.0(2)			C(44)C(43)C(42)	120.7(2)
		C(45)C(44)C(43)	120.0(2)			C(43)C(44)C(45)	119.5(2)
		C(44)C(45)C(46)	120.5(2)			C(44)C(45)C(46)	120.5(2)
		C(41)C(46)C(45)	120.0(1)			C(41)C(46)C(45)	120.1(2)
						C(56)C(51)C(52)	118.4(1)
						C(53)C(52)C(51)	121.1(2)
						C(54)C(53)C(52)	120.1(2)
						C(55)C(54)C(53)	119.6(2)
						C(54)C(55)C(56)	121.2(2)
						C(55)C(56)C(51)	119.7(2)

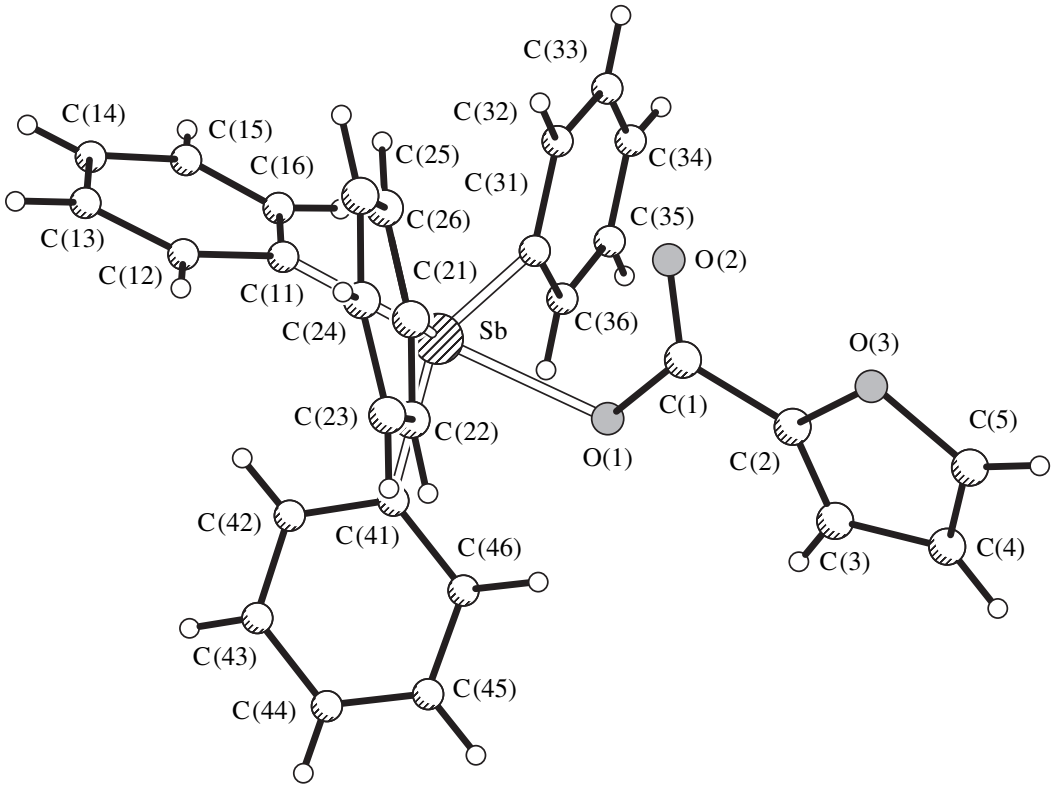

Fig. 1. Molecular structure of tetraphenylantimony 2-furoinate (**I**).

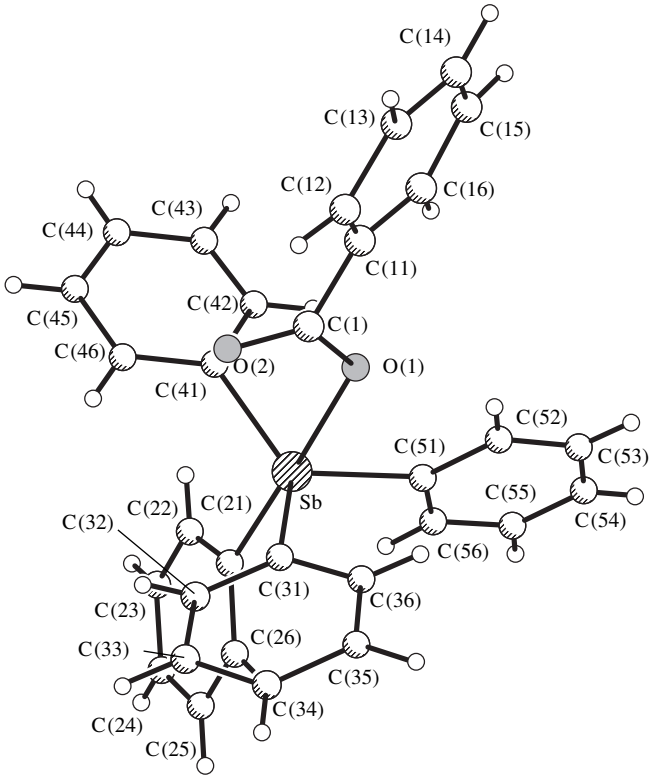

Fig. 2. Molecular structure of tetraphenylantimony benzoate (**II**).

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