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Synthesis and Structure of Tetraphenylantimony Oximates $Ph_4SbON=CRR'$ ($CRR' = C_6H_9–C_6H_9$-2 and R = Ph, R' = C(O)Ph)

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Abstract—The reaction of pentaphenylantimony and the oxime HON=CRR' taken in 1 : 1 molar ratio in toluene gave tetraphenylantimony oximates $Ph_4SbON=CRR'$ ($CRR' = C_6H_9–C_6H_9$-2 (**I**) and R = Ph, R' = C(O)Ph (**II**)). According to X-ray diffraction data, the Sb atoms in **I** and **II** have a distorted trigonal-bipyramidal coordination with oximate ligands in the axial positions. The $C_{ax}SbO$ angles are 177.6(1)° in **I** and 176.58(6)° in **II**. The Sb–C bond lengths lie in the ranges of 2.120(4)–2.203(4) Å for **I** and 2.122(2)–2.181(2) Å for **II**. The Sb–O bond lengths are 2.120(2) Å (**I**) and 2.166(1) Å (**II**). The lengths of the intramolecular Sb···N contacts are 2.806(3) and 2.918(2) Å in **I** and **II**, respectively.

The coordination number of the central atom in tetraphenylantimony oximates $Ph_4SbON=CRR'$ is known to increase to six due to additional coordination of the oximate nitrogen atom to antimony atom [1–4]. Evidently, the probability of Sb···N coordination in these compounds can be decreased by introducing an additional coordination site into the oximate ligand. A decrease in the Sb ⟵ N donor–acceptor interaction can also be expected in tetraphenylantimony oximates having bulky substituents near nitrogen atom.

In order to prepare organoantimony derivatives of sterically hindered oximes, we studied the reaction of pentaphenylantimony with cyclohexanone oxime containing a cyclohexenyl substituent in the *ortho*-position and with benzyl monooxime, which also contains several potential coordination sites.

RESULTS AND DISCUSSION

It was shown that reactions of pentaphenylantimony carried out in toluene at room temperature were complete in 24 h (the course of the reactions was monitored by TLC). The only organoantimony compound thus formed was tetraphenylantimony oximate, which was isolated from the reaction mixture in a yield of up to 99%

$$Ph_5Sb + HON=CRR' \longrightarrow Ph_4SbON=CRR' + PhH,$$

$$CRR' = C_6H_9–C_6H_9\text{-2 } (\mathbf{I});$$

$$R = Ph, \quad R' = C(O)Ph\ (\mathbf{II}).$$

According to X-ray diffraction data, the antimony atoms in compounds **I** and **II** have a trigonal-bipyramidal surrounding formed by the O atoms of the oximate ligands (Figs. 1, 2). The axial CSbO angles are 177.6(1)° in **I** and 176.58(6)° in **II** (Table 1). The $OSbC_{eq}$ bond

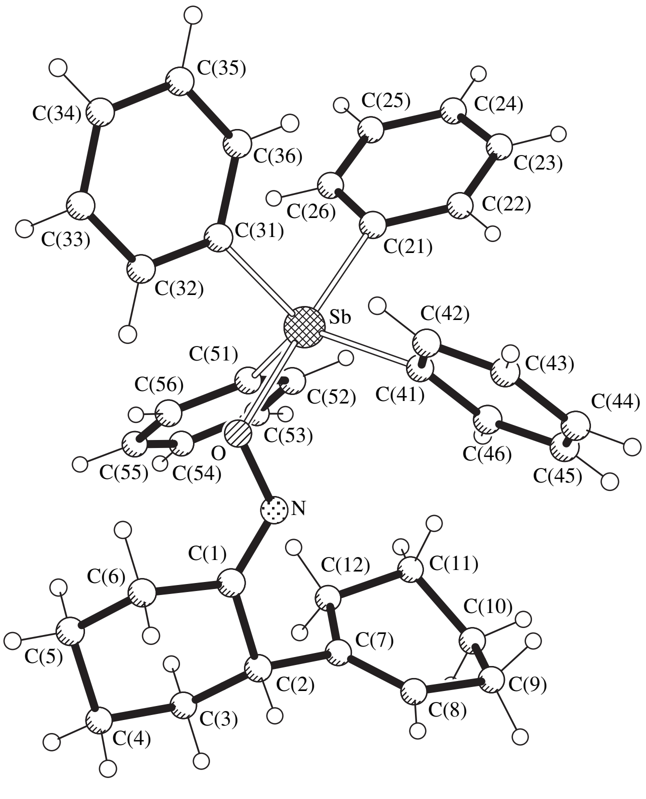

Fig. 1. Structure of molecule **I**.

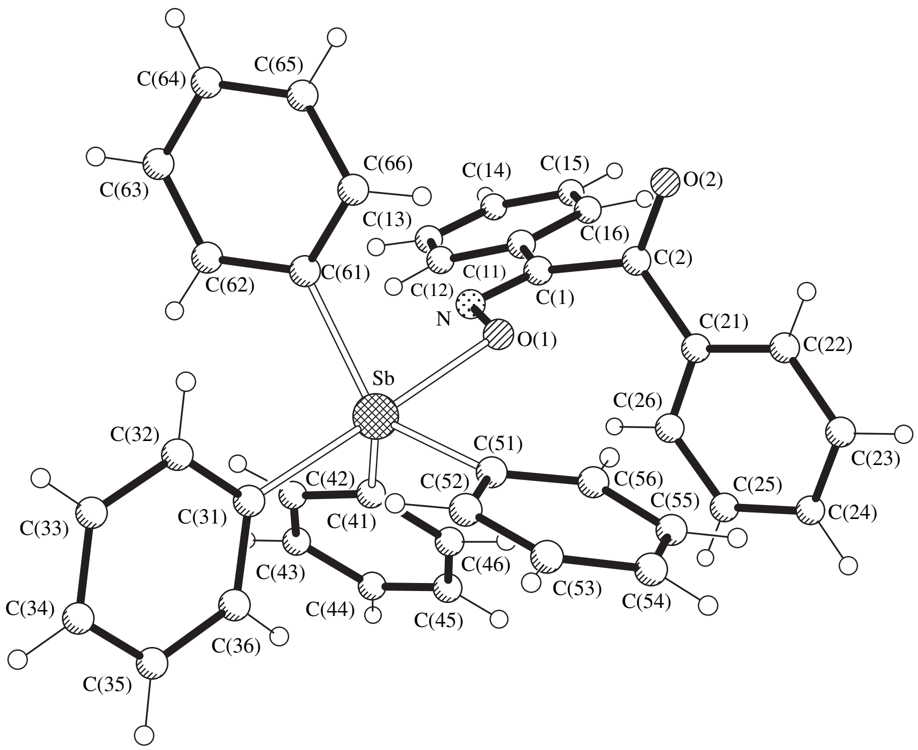

Fig. 2. Structure of molecule **II**.

angles in structures **I** and **II** lie in the ranges of 84.0(1)°–85.5(1)° and 82.71(6)°–87.60(6)°, respectively. The deviations of the Sb atoms from the equatorial plane are 0.189 and 0.178 Å in **I** and **II**, respectively. The sums of the CSbC angles in equatorial planes are 357.7° in **I** and 357.9° in **II**. The angles between the equatorial aryl ligands are nonequivalent, being equal to 111.4(2)°, 114.7(2)°, and 131.6(2)° in **I** and 113.68(7)°, 121.31(8)°, and 122.92(7)° in **II**. The Sb–C_{eq} bond lengths (2.120(4)–2.146(4) Å in **I** and 2.122(2)–2.125(2) Å in **II**) do not differ much from the Sb–O bond lengths (2.120(2) Å in **I** and 2.166(1) Å in **II**).

The O–N and N–C distances in compounds **I** and **II** are equal to 1.405(4), 1.256(4) and 1.382(2), 1.280(2) Å, respectively, which almost coincides with the lengths of similar bonds in other tetraarylantimony oximates [1–4]. The SbON angles are 103.6(2)° in **I** and 108.63(9)° in **II**.

It is noteworthy that the geometric parameters of the structures of **I** and **II** differ, which suggests the influence of the nature of organic groups present in the oximate ligands at the antimony atom.

The Sb···N distances in structures **I** and **II** (2.806(3) Å in **I** and 2.918(2) Å in **II**) are shortened as compared to the sum of the van de Waals radii of the Sb and N atoms (3.8 Å [5]). The intramolecular Sb···N contact in **II** only slightly affects the equatorial angles, which differ only slightly from the ideal value (120°). However, in the case of **I**, the difference between equatorial angles is substantial, being comparable to that observed in the structures of tetraarylantimony dicarboxylates in which the intramolecular Sb···O=C contacts result in an increase in one equatorial angle to 143.8°–151.7° [6–12].

EXPERIMENTAL

Synthesis of tetraphenylantimony 2-(cyclohexenyl-1)cyclohexanone oximate (I). A mixture of pentaphenylantimony (0.50 g) and 2-(cyclohexenyl-1)cyclohexanone oxime (0.19 g) in 15 ml of toluene was kept for 24 h at 20°C. The solvent was removed and the residue was recrystallized from a toluene–heptane (2 : 1 v/v) mixture. The yield of compound **I** was 0.61 g (99%), mp = 148°C.

Synthesis of tetraphenylantimony 1,2-diphenylethanedione monooximate (II). A mixture of pentaphenylantimony (0.50 g) and benzyl monooxime (0.22 g) in 15 ml of toluene was kept for 24 h at 20°C. The solvent was removed and the residue was recrystallized from a toluene–heptane (2 : 1 v/v) mixture. The yield of compound **II** was 0.50 g (78%), mp = 191°C.

X-Ray diffraction analysis of the crystals of compounds **I** and **II** was carried out on a SMART 1000 CCD diffractometer (graphite monochromator, MoK_α radiation, $\lambda = 0.71073$ Å). The structures were solved by the direct method and refined by least-squares calculations in the anisotropic approximation for non-hydro-

Table 1. Selected bond lengths and bond angles in structures **I** and **II**

Bond	*d*, Å	Angle	ω, deg
		I	
Sb–O	2.120(2)	OSbC(31)	85.4(1)
Sb–C(31)	2.120(4)	OSbC(51)	85.5(1)
Sb–C(51)	2.142(4)	C(31)SbC(51)	114.7(2)
Sb–C(41)	2.146(4)	OSbC(41)	84.0(1)
Sb–C(21)	2.203(4)	C(31)SbC(41)	111.4(2)
Sb–N	2.806(3)	C(51)SbC(41)	131.6(2)
O–N	1.405(4)	OSbC(21)	177.6(1)
N–C(1)	1.256(4)	C(31)SbC(21)	97.0(2)
C(1)–C(2)	1.506(7)	C(51)SbC(21)	93.2(1)
C(1)–C(6)	1.546(7)	C(41)SbC(21)	95.4(2)
C(2)–C(3)	1.502(7)	NOSb	103.6(2)
C(2)–C(7)	1.535(6)	C(1)NO	115.8(3)
C(3)–C(4)	1.548(7)	NC(1)C(2)	122.8(5)
C(4)–C(5)	1.517(7)	NC(1)C(6)	123.5(4)
		II	
Sb–C(61)	2.122(2)	C(61)SbC(41)	121.31(8)
Sb–C(41)	2.124(2)	C(61)SbC(51)	122.92(7)
Sb–C(51)	2.125(2)	C(41)SbC(51)	113.68(7)
Sb–O(1)	2.166(1)	C(61)SbO(1)	85.32(6)
Sb–C(31)	2.181(2)	C(41)SbO(1)	87.60(6)
Sb–N	2.918(2)	C(51)SbO(1)	82.71(6)
N–C(1)	1.280(2)	C(61)SbC(31)	94.07(7)
N–O(1)	1.382(2)	C(41)SbC(31)	95.58(7)
O(2)–C(2)	1.214(2)	C(51)SbC(31)	94.83(7)
C(1)–C(11)	1.486(2)	O(1)SbC(31)	176.58(6)
C(1)–C(2)	1.517(3)	C(61)SbN	77.87(6)
C(2)–C(21)	1.476(3)	C(41)SbN	70.83(6)
C(11)–C(12)	1.373(3)	C(51)SbN	108.31(6)
C(11)–C(16)	1.381(3)	O(1)SbN	26.67(4)
C(12)–C(13)	1.383(3)	C(31)SbN	156.30(6)
C(13)–C(14)	1.361(3)	C(1)NO(1)	112.5(1)
C(14)–C(15)	1.365(3)	C(1)NSb	155.9(1)
C(15)–C(16)	1.386(3)	O(1)NSb	44.71(7)
C(21)–C(26)	1.372(3)	NO(1)Sb	108.63(9)
C(21)–C(22)	1.388(3)	NC(1)C(11)	120.2(2)
C(22)–C(23)	1.387(4)	NC(1)C(2)	120.0(2)

Table 2. Crystal data and structure refinement results for **I** and **II**

Characteristics	**I**	**II**
Empirical formula	$C_{36}H_{38}NOSb$	$C_{38}H_{30}NO_2Sb$
M	622.42	654.38
Crystal system	Orthorhombic	Monoclinic
T, K	173(1)	298(2)
Space group	$Pna2_1$	$P2_1/n$
Unit cell parameters:		
a, Å	21.599(3)	10.247(2)
b, Å	13.634(2)	24.380(5)
c, Å	10.137(2)	12.543(2)
β, deg		90.109(4)
V, Å^3	2985.0(8)	3134(1)
Z	4	4
ρcalcd, g/cm^3	1.385	1.387
μ_{Mo}, mm^{-1}	0.953	0.914
$F(000)$	1280	1328
Crystal shape (size), mm	Prism (0.06 × 0.08 × 0.40)	Prism (0.07 × 0.24 × 0.26)
θ, deg	2.99–24.04	2.99–27.50
Ranges of reflection indices	$-24 \le h \le 23$	$-13 \le h \le 13$
	$-15 \le k \le 15$	$-31 \le k \le 27$
	$-10 \le l \le 11$	$-13 \le l \le 16$
The total number of reflections	13943	20163
The number of independent reflections	4563 ($R_{int} = 0.0631$)	7170 ($R_{int} = 0.0449$)
The number of reflections with $I > 2\sigma(I)$	3846	5349
The number of refined parameters	352	379
GOOF	1.067	1.034
R-factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0414$, $wR_2 = 0.0750$	$R_1 = 0.0345$, $wR_2 = 0.0797$
R-factors for all reflections	$R_1 = 0.0556$, $wR_2 = 0.0791$	$R_1 = 0.0535$, $wR_2 = 0.0876$
The residual electron density (min/max), e/Å^3	−0.956/0.735	−0.378/0.502

gen atoms. The H atoms were located geometrically and included in the refinement according to the rider model. The data collection and editing and the refinement of unit cell parameters were carried out using SMART and SAINT *Plus* program packages [13]. All calculations for the structure solution and refinement were carried out using the SHELXTL/PC program package [14].

The crystal data and the results of refinement for structures **I** and **II** are listed in Table 2 and the coordi-

Table 3. Atomic coordinates ($\times 10^4$) and isotropic equivalent thermal parameters U_{eq} ($\times 10^3$) for structures **I** and **II**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		I		
Sb	6640.34(9)	9496.4(1)	7903.0(5)	20.72(5)
O	6639(1)	8037(2)	8624(3)	25.6(7)
N	6429(1)	7483(2)	7544(3)	23(1)
C(1)	6246(2)	6630(2)	7804(6)	29.6(9)
C(2)	5975(2)	5957(4)	6777(5)	43(1)
C(3)	5364(2)	5544(4)	7214(5)	51(2)
C(4)	5401(3)	5058(4)	8592(6)	62(2)
C(5)	5637(2)	5801(4)	9585(5)	57(2)
C(6)	6257(2)	6184(3)	9206(5)	39(1)
C(7)	5943(2)	6449(3)	5416(4)	33(1)
C(8)	6310(2)	6141(3)	4451(5)	38(1)
C(9)	6320(2)	6581(4)	3102(5)	49(1)
C(10)	5763(2)	7219(3)	2791(6)	49(1)
C(11)	5616(2)	7850(4)	3976(5)	50(2)
C(12)	5472(2)	7239(3)	5198(5)	41(1)
C(21)	6626(2)	10990(3)	7077(4)	24(1)
C(22)	7080(2)	11308(3)	6189(4)	31(1)
C(23)	7051(2)	12244(3)	5640(5)	39(1)
C(24)	6572(2)	12858(3)	5991(5)	47(2)
C(25)	6128(2)	12550(3)	6868(5)	39(1)
C(26)	6152(2)	11629(3)	7393(4)	31(1)
C(31)	6885(2)	9896(3)	9857(4)	22(1)
C(32)	6829(2)	9244(3)	10879(4)	34(1)
C(33)	7004(2)	9513(3)	12151(4)	41(1)
C(34)	7232(2)	10414(3)	12392(4)	42(1)
C(35)	7290(2)	11091(4)	11381(5)	39(1)
C(36)	7122(2)	10825(3)	10116(4)	33(1)
C(41)	7433(2)	9018(3)	6802(4)	23(1)
C(42)	7982(2)	8917(3)	7472(4)	37(1)
C(43)	8503(2)	8585(4)	6839(6)	52(2)
C(44)	8479(2)	8357(3)	5510(6)	47(2)
C(45)	7933(2)	8463(3)	4837(5)	43(1)
C(46)	7411(2)	8781(3)	5485(4)	38(1)
C(51)	5669(2)	9282(2)	7590(4)	28(1)
C(52)	5373(2)	9688(3)	6496(5)	39(1)
C(53)	4747(2)	9526(4)	6319(6)	54(2)
C(54)	4413(2)	8995(4)	7212(6)	63(2)
C(55)	4707(2)	8606(3)	8319(5)	51(2)
C(56)	5340(2)	8744(3)	8489(5)	36(1)

Table 3. (Contd.)

Atom	x	y	z	U_{eq}, Å^2
II				
Sb	8441.9(1)	837.68(5)	7836.3(1)	43.61(3)
N	9860(1)	1511(1)	6303(1)	48.0(4)
O(1)	9382(1)	1588(1)	7322(1)	50.3(3)
O(2)	10197(2)	2823(1)	6543(1)	66.5(4)
C(1)	10591(2)	1907(1)	5999(1)	40.1(4)
C(2)	10790(2)	2401(1)	6715(1)	46.0(5)
C(11)	11268(2)	1878(1)	4953(1)	41.9(4)
C(12)	11183(2)	1412(1)	4343(2)	77.5(7)
C(13)	11822(3)	1380(1)	3375(2)	94.6(8)
C(14)	12589(2)	1799(1)	3026(2)	69.8(7)
C(15)	12700(2)	2261(1)	3635(2)	57.6(6)
C(16)	12038(2)	2304(1)	4594(2)	51.0(5)
C(21)	11728(2)	2352(1)	7605(2)	52.5(5)
C(22)	11776(2)	2754(1)	8388(2)	78.1(7)
C(23)	12658(3)	2700(1)	9221(2)	105.0(10)
C(24)	13476(3)	2264(2)	9272(2)	111.5(11)
C(25)	13441(3)	1873(1)	8502(2)	100.2(10)
C(26)	12573(2)	1917(1)	7662(2)	73.2(7)
C(31)	7420(2)	112(1)	8415(2)	48.0(5)
C(32)	6079(2)	66(1)	8356(2)	98.7(9)
C(33)	5431(2)	–386(1)	8753(3)	118.4(11)
C(34)	6094(3)	–803(1)	9210(2)	78.7(8)
C(35)	7405(2)	–765(1)	9301(2)	67.3(7)
C(36)	8072(2)	–314(1)	8905(2)	57.1(6)
C(41)	10148(2)	413(1)	7345(2)	47.0(5)
C(42)	10123(2)	0(1)	6608(2)	76.9(8)
C(43)	11262(2)	–262(1)	6310(2)	92.7(9)
C(44)	12406(2)	–115(1)	6770(2)	90.6(9)
C(45)	12442(3)	284(1)	7504(3)	110.9(11)
C(46)	11314(2)	552(1)	7788(2)	87.0(8)
C(51)	8615(2)	1208(1)	9363(2)	47.5(5)
C(52)	7742(2)	1073(1)	10164(2)	73.4(7)
C(53)	7900(3)	1285(1)	11179(2)	87.6(8)
C(54)	8936(3)	1613(1)	11418(2)	77.0(8)
C(55)	9806(2)	1751(1)	10632(2)	65.4(6)
C(56)	9644(2)	1562(1)	9614(2)	54.4(5)
C(61)	6955(2)	1050(1)	6731(2)	49.1(5)
C(62)	6451(2)	667(1)	6025(2)	77.0(8)
C(63)	5433(3)	801(1)	5345(3)	95.3(10)
C(64)	4893(3)	1314(1)	5384(2)	95.8(9)
C(65)	5361(3)	1681(1)	6082(3)	106.3(11)
C(66)	6402(2)	1560(1)	6755(2)	80.2(8)

nates and thermal factors of the atoms are given in Table 3.

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