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Synthesis and Structures of Tetra- and Triarylantimony Oximates

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Abstract—Tetraphenylantimony acetophenoneoximate (**I**) and tetra-*n*-tolylantimony 3-nitrobenzaloximate (**II**) were synthesized by reacting pentaarylantimony with oxime or triarylantimony dioximate in toluene. Tri-*n*-tolylantimony bis(acetophenoneoximate) (**III**) and triphenylantimony bis(cyclohexanoneoximate) (**IV**) were synthesized by reacting triarylantimony with oxime and hydrogen peroxide. The structures of compounds **I**–**IV** were determined using X-ray diffraction analysis. The antimony atoms in **I**–**IV** are coordinated to the axial oxime groups to form a distorted trigonal bipyramid. The Sb–C(Ph) and Sb–O bond lengths and Sb···N intramolecular contacts in structures **I** and **II** lie within 2.114–2.135, 2.137–2.154, and 2.857–2.871 Å, respectively; the respective values in structures **III** and **IV** are 2.097–2.112, 2.058–2.080, and 2.779–2.874 Å.

According to the valence shell electron pair repulsion theory (VSEPR), molecules whose central atoms contain five electron pairs on the valence shell preferably have trigonal-bipyramidal configuration with the axial ligands more removed father from the centre than the equatorial ligands [1]. In terms of the VSEPR theory, electronegative substituents in these molecules always occupy the axial positions. The higher the electronegativity of the ligand, the more remote it is from the central atom [2]. Molecules of organic antimony compounds with the general formulas Ar_4SbX and Ar_3SbX_2 (X is the electronegative ligand) usually have the form of a trigonal bipyramid with axial substituents X [3], which agrees with the VSEPR theory. However, some of the structurally characterized antimony(V) compounds are beyond the framework of this theory. Thus, in dimethoxytriphenylantimony, the axial (ax) Sb–O bonds are shorter than the equatorial (eq) Sb–C bonds [4]. Furthermore, in methoxytetraphenylantimony [4], aroxytetraarylantimony compounds containing electron-donating substutuents in the aroxy group [5–7] and in tetraphenylantimony oximates [8, 9], the $Sb–O_{ax}$ bonds are shorter than the $Sb–C_{ax}$ bonds. This contradicts the rule asserting that the distance between the ligand and the central atom increases with increasing electronegativity of the ligand. If ligand X contains potential coordination centers, then, similar to tetra- and triarylantimony acylates [10–17], trigonal-bipyramidal coordination of the Sb atom can be distorted and its coordination number can increase to six or seven.

With the purpose of studying the structures of aryl Sb(V) compounds in more detail, we carried out X-ray diffraction analysis of tetraphenylantimony acetophenoneoximate (**I**), tetra-*n*-tolylantimony 3-nitrobenzaloximate (**II**), tri-*n*-tolylantimony bis(acetophenoneoximate) (**III**), and triphenylantimony bis(cyclohexanoneoximate) (**IV**).

EXPERIMENTAL

Synthesis of tetraphenylantimony acetophenoneoximate (I). A mixture of 1.00 g (1.97 mmol) of Ph_5Sb and 0.27 g (1.97 mmol) of HON=CMePh in 10 ml of toluene was heated at 90°C for 1 h. After cooling, the solvent was removed; the residue was recrystallized from a toluene–heptane mixture (1 : 3). The yield was 1.05 g (94%), mp 126°C. Compound **I** was also obtained from Ph_5Sb and $Ph_3Sb(ON{=}CMePh)_2$ in a yield of 95% (toluene, 90°C, 1 h).

Tetra-*n*-tolylantimony 3-nitrobenzaloximate (II) was synthesized similar to **I**. The yield was 99%, mp 129°C.

Synthesis of tri-*n*-tolylantimony bis(acetophenoneoximate) (III). A solution of 1.00 g (2.53 mmol) of tri-*n*-tolylstibine and 0.69 g (5.03 mmol) of acetophenoneoxime in 20 ml of ether was mixed with 0.29 ml of 30% aqueous hydrogen peroxide. The mixture was allowed to stand at 20°C for 12 h. The colorless crystals that formed were filtered off and dried. The yield was 1.59 g (95%), mp 126°C.

Triphenylantimony bis(cyclohexanoneoximate) (IV) was synthesized similar to **III**. The yield was 92%, mp = 124°C (116°C [18]).

X-ray diffraction analysis of the natural-faceted single crystals of **I**–**IV** was carried out on a Bruker SMART-1000 CCD diffractometer. For compound **I**, the data were collected in sets of 606 frames at $\varphi = 0°$,

Table 1. Crystallographic data and details of data collection for structures **I**–**IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Empirical formula	$C_{67}H_{59}N_2O_2Sb_2$	$C_{35}H_{33}N_2O_3Sb$	$C_{37}H_{37}N_2O_2Sb$	$C_{30}H_{35}N_2O_2Sb$
M	1167.66	651.38	663.44	577.35
T, K	296(2)	296(2)	293(2)	295(2)
Radiation (λ, Å)	MoK_α (0.71073)	MoK_α (0.71073)	MoK_α (0.71073)	MoK_α (0.71073)
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
Unit cell parameters:				
a, Å	13.759(2)	10.5225(11)	11.925(1)	10.176(1)
b, Å	13.855(2)	15.9662(17)	14.806(1)	15.222(2)
c, Å	17.956(2)	19.027(2)	19.809(2)	17.839(2)
α, deg	72.260(2)	90	101.922(2)	90
β, deg	72.627(2)	93.847(2)	99.797(2)	95.716(3)
γ, deg	62.443(2)	90	95.974(2)	90
V, Å^3	2839.4(6)	3189.3(6)	3336.6(6)	2749.4(7)
Z	2	4	4	4
ρ (calcd), g/cm^3	1.366	1.357	1.321	1.395
μ_{Mo}, mm^{-1}	0.997	0.900	0.860	1.032
F(000)	1186	1328	1360	1184
Crystal shape and size, mm	Prism 0.20 × 0.23 × 0.33	Prism 0.12 × 0.19 × 0.33	Prism 0.20 × 0.23 × 0.25	Prism 0.06 × 0.10 × 0.20
θ, deg	1.89–30.03	2.50–23.28	1.97–26.10	2.41–28.01
Range of indices	$-19 \le h \le 19$, $-19 \le k \le 19$, $-25 \le l \le 25$	$-9 \le h \le 11$, $-16 \le k \le 17$, $-21 \le l \le 21$	$-14 \le h \le 14$, $-18 \le k \le 18$, $-24 \le l \le 24$	$-13 \le h \le 13$, $-16 \le k \le 20$, $-23 \le l \le 19$
Total number of reflections	41560	13309	36938	18013
Independent reflections	16370 (R_{int} = 0.0410)	4597 (R_{int} = 0.0369)	13192 (R_{int} = 0.0520)	6611 (R_{int} = 0.0547)
Reflections with $I > 2\sigma(I)$	10473	3581	7655	4087
Number of refined parameters	661	374	767	317
GOOF	0.926	0.940	0.824	0.829
Final R-factor ($I > 2\sigma(I)$)	$R_1 = 0.0294$, $wR_2 = 0.0671$	$R_1 = 0.0272$, $wR_2 = 0.0620$	$R_1 = 0.0356$, $wR_2 = 0.0701$	$R_1 = 0.0333$, $wR_2 = 0.0637$

90°, 180°, and 270°; for compounds **II**–**IV**, sets of 606, 435, and 230 frames were collected at $\varphi = 0°, 90°$, and 180° (ω-scan with an angle of 0.3° between the frames and 10 s exposition per frame (for compound **IV**, 20 s per frame); the crystal–detector distance was 45 mm). Correction for absorption of X-rays by the samples was applied using face indices.

The structures of compounds **I**–**IV** were solved by the direct methods and refined by the least-squares method in anisotropic approximation for non-hydrogen atoms. Positions of hydrogen atoms were calculated geometrically and refined in the rider model.

Data collection and processing and refinement of the unit cell parameters were performed using the SMART and SAINT *Plus* programs [19]. Structures **I**–**IV** were calculated and refined using the SHELXTL/PC programs [20].

Selected crystallographic parameters and the details of refinement of structures **I**–**IV** are presented in Table 1, coordinates and thermal parameters of atoms are given in Table 2, and their bond lengths and angles are listed in Table 3.

RESULTS AND DISCUSSION

Compounds **I** and **II** were synthesized from pentaarylantimony and oxime or triarylantimony dioximate:

$$Ar_5Sb + HON{=}CRR' \longrightarrow Ar_4SbON{=}CRR' + ArH,$$

Table 2. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic thermal parameters ($\times 10^3$) in structures **I–IV**

Atom	*x*	*y*	*z*	U_{eq}, Å^2	Atom	*x*	*y*	*z*	U_{eq}, Å^2
		I					**I**		
Sb(1)	5183.52(7)	2225.32(8)	2447.49(6)	43.57(3)	C(61)	561(1)	9738(1)	2495(1)	47.9(4)
Sb(2)	958.80(7)	7986.68(8)	3091.41(6)	44.88(3)	C(62)	–303(1)	10630(1)	2798(1)	61.4(5)
O(1)	4619(1)	3949(1)	1905(1)	61.2(3)	C(63)	–559(1)	11704(1)	2361(1)	79.4(6)
O(2)	1328(1)	6270(1)	3583(1)	58.3(3)	C(64)	43(2)	11886(2)	1615(1)	83.1(6)
N(1)	5559(1)	4183(1)	1605(1)	57.8(4)	C(65)	904(2)	11021(2)	1307(1)	76.6(6)
N(2)	1523(1)	6107(1)	4344(1)	59.5(4)	C(66)	1161(1)	9964(1)	1748(1)	62.3(5)
C(1)	5398(1)	5081(1)	1082(1)	53.4(4)	C(71)	2633(1)	7642(1)	3067(1)	46.9(4)
C(2)	4297(1)	5835(2)	832(1)	80.5(7)	C(72)	2881(1)	8438(1)	3180(1)	59.4(5)
C(3)	1569(1)	5178(1)	4794(1)	54.1(5)	C(73)	3979(1)	8222(2)	3164(1)	74.3(5)
C(4)	1485(2)	4286(1)	4545(1)	74.2(6)	C(74)	4825(1)	7222(2)	3007(1)	77.7(6)
C(5)	5970(2)	–609(2)	9642(2)	170(1)	C(75)	4578(1)	6446(2)	2878(1)	78.7(6)
C(6)	5784(3)	–1178(3)	10590(3)	271(2)	C(76)	3492(1)	6640(1)	2914(1)	65.1(5)
C(7)	4714(3)	–391(3)	10833(3)	233(2)	C(81)	–247(1)	8392(1)	4131(1)	51.1(4)
C(11)	5631(1)	479(1)	3040(1)	44.3(4)	C(82)	13(1)	8548(2)	4756(1)	81.1(6)
C(12)	6461(1)	–399(1)	2704(1)	57.1(5)	C(83)	–820(2)	8881(2)	5409(1)	95.1(7)
C(13)	6715(1)	–1475(1)	3106(1)	68.8(6)	C(84)	–1884(2)	9053(2)	5432(1)	82.8(7)
C(14)	6142(1)	–1702(1)	3860(1)	65.6(5)	C(85)	–2138(1)	8900(2)	4816(1)	77.1(6)
C(15)	5312(1)	–852(1)	4203(1)	62.4(5)	C(86)	–1327(1)	8567(1)	4169(1)	61.7(5)
C(16)	5059(1)	229(1)	3803(1)	54.8(4)	C(91)	535(1)	7655(1)	2175(1)	46.3(4)
C(21)	5525(1)	2617(1)	3370(1)	49.8(4)	C(92)	–369(1)	8437(1)	1832(1)	56.8(5)
C(22)	6434(1)	1896(1)	3715(1)	63.6(5)	C(93)	–642(1)	8229(2)	1238(1)	70.9(5)
C(23)	6608(2)	2127(2)	4356(1)	85.6(6)	C(94)	–5(2)	7256(2)	968(1)	78.1(5)
C(24)	5874(2)	3038(2)	4658(1)	92.0(6)	C(95)	909(2)	6469(2)	1299(1)	77.5(6)
C(25)	4959(2)	3750(2)	4325(1)	93.4(7)	C(96)	1173(1)	6668(1)	1904(1)	62.7(5)
C(26)	4793(2)	3553(1)	3671(1)	71.4(6)	C(101)	1712(1)	5025(1)	5613(1)	54.4(5)
C(31)	6388(1)	1846(1)	1405(1)	45.4(4)	C(102)	1289(1)	4374(1)	6252(1)	65.9(6)
C(32)	6177(1)	1513(1)	840(1)	59.3(5)	C(103)	1393(2)	4275(2)	7016(1)	81.8(8)
C(33)	6988(1)	1215(2)	171(1)	70.3(5)	C(104)	1943(2)	4791(2)	7155(1)	90.5(8)
C(34)	7999(2)	1221(2)	81(1)	73.3(6)	C(105)	2368(2)	5434(2)	6528(1)	88.7(7)
C(35)	8226(1)	1515(2)	648(1)	79.7(6)	C(106)	2245(2)	5557(2)	5772(1)	72.8(6)
C(36)	7426(1)	1838(2)	1303(1)	66.8(5)			**II**		
C(41)	3520(1)	2507(1)	2478(1)	45.0(4)	Sb	333.3(2)	5379.2(1)	2189.7(1)	47.62(9)
C(42)	3299(1)	1662(1)	2405(1)	52.6(4)	O(1)	1028(2)	6125(1)	1354(1)	59.5(6)
C(43)	2214(1)	1835(1)	2432(1)	63.3(5)	O(2)	5850(4)	4013(2)	1695(2)	134(1)
C(44)	1352(1)	2832(2)	2560(1)	69.1(6)	O(3)	7471(3)	4128(2)	1094(2)	140(1)
C(45)	1557(1)	3662(2)	2642(1)	71.0(6)	N(1)	2245(2)	5864(2)	1273(1)	59.0(7)
C(46)	2638(1)	3509(1)	2588(1)	60.0(5)	N(2)	6441(4)	4367(3)	1264(2)	90(1)
C(51)	6398(1)	5327(1)	710(1)	54.7(4)	C(1)	2821(3)	6266(2)	819(2)	61.6(9)
C(52)	6459(2)	6022(1)	–30(1)	74.6(6)	C(11)	4135(3)	6041(2)	699(2)	59.6(9)
C(53)	7400(2)	6224(2)	–395(1)	85.2(7)	C(12)	4844(4)	6501(2)	257(2)	75(1)
C(54)	8276(2)	5768(2)	–27(1)	86.6(7)	C(13)	6087(4)	6272(3)	137(2)	84(1)
C(55)	8253(2)	5065(2)	705(1)	87.8(7)	C(14)	6630(4)	5587(3)	460(2)	80(1)
C(56)	7310(1)	4854(2)	1061(1)	75.2(6)	C(15)	5909(4)	5129(3)	904(2)	71(1)

Table 2. (Contd.)

Atom	x	y	z	$U_{\rm eq}$, Å^2	Atom	x	y	z	$U_{\rm eq}$, Å^2
		II					**III**		
C(16)	4688(3)	5347(2)	1033(2)	63.4(9)	C(16)	1579(4)	8700(3)	–1467(3)	95(1)
C(21)	581(3)	4325(2)	1535(2)	47.1(8)	C(21)	6215(3)	8321(2)	1598(2)	56.2(9)
C(22)	289(3)	4356(2)	816(2)	53.7(8)	C(22)	5997(3)	9230(2)	1776(2)	64(1)
C(23)	423(3)	3657(2)	410(2)	57.5(9)	C(23)	6689(3)	9848(3)	2344(2)	73(1)
C(24)	864(3)	2908(2)	694(2)	56.0(8)	C(24)	7606(3)	9601(3)	2752(2)	67(1)
C(25)	1176(3)	2888(2)	1406(2)	65.0(9)	C(25)	7827(3)	8701(3)	2562(2)	69(1)
C(26)	1016(3)	3588(2)	1820(2)	62.9(9)	C(26)	7140(3)	8063(3)	1996(2)	65(1)
C(27)	1006(4)	2149(2)	241(2)	85(1)	C(27)	8315(4)	10282(3)	3391(2)	104(2)
C(31)	–488(3)	4689(2)	3043(2)	49.9(8)	C(31)	5872(3)	6894(3)	–137(2)	64(1)
C(32)	–434(3)	5050(2)	3704(2)	63.0(9)	C(32)	6068(4)	5993(3)	–347(2)	101(2)
C(33)	–1123(4)	4727(2)	4235(2)	73(1)	C(33)	6619(4)	5735(3)	–903(2)	109(2)
C(34)	–1872(3)	4023(2)	4123(2)	68(1)	C(34)	6996(4)	6361(4)	–1252(2)	85(1)
C(35)	–1891(3)	3652(2)	3471(2)	72(1)	C(35)	6815(3)	7260(4)	–1035(2)	81(1)
C(36)	–1228(3)	3982(2)	2943(2)	62.4(9)	C(36)	6252(3)	7535(3)	–493(2)	73(1)
C(37)	–2641(4)	3696(3)	4710(2)	108(2)	C(37)	7603(4)	6067(4)	–1857(2)	136(2)
C(41)	–1254(3)	6210(2)	2053(2)	47.9(8)	C(41)	3460(3)	6943(3)	870(2)	67(1)
C(42)	–2398(3)	6002(2)	2318(2)	57.1(9)	C(42)	3134(4)	7314(3)	1487(3)	100(1)
C(43)	–3429(3)	6539(3)	2238(2)	65(1)	C(43)	2023(5)	7112(4)	1587(3)	120(2)
C(44)	–3360(3)	7291(2)	1898(2)	62.7(9)	C(44)	1214(5)	6502(4)	1066(4)	111(2)
C(45)	–2210(3)	7500(2)	1635(2)	60.7(9)	C(45)	1559(5)	6121(4)	464(3)	131(2)
C(46)	–1167(3)	6972(2)	1704(2)	54.7(8)	C(46)	2663(4)	6336(3)	365(2)	108(2)
C(47)	–4489(4)	7877(3)	1821(2)	96(1)	C(47)	–21(5)	6295(5)	1182(4)	173(3)
C(51)	1969(3)	5774(2)	2820(2)	53.5(8)	C(51)	5466(3)	5503(3)	2694(2)	69(1)
C(52)	2234(4)	6593(3)	2953(2)	83(1)	C(52)	5805(4)	4842(3)	3050(3)	101(2)
C(53)	3327(5)	6819(3)	3355(2)	97(1)	C(53)	5477(5)	4786(4)	3679(3)	117(2)
C(54)	4174(4)	6248(4)	3608(2)	83(1)	C(54)	4791(5)	5377(4)	3954(3)	108(2)
C(55)	3902(4)	5436(3)	3474(3)	111(2)	C(55)	4443(4)	6041(4)	3609(3)	110(2)
C(56)	2811(4)	5197(3)	3086(2)	97(1)	C(56)	4768(4)	6091(3)	2993(2)	97(1)
C(57)	5409(4)	6493(4)	4037(2)	130(2)	Sb(2)	7608.8(2)	9700.9(2)	6951.8(1)	52.61(8)
		III			O(3)	6392(2)	9100(2)	7417(1)	61.5(6)
Sb(1)	5139.5(2)	7346.0(2)	747.2(1)	61.99(9)	O(4)	8840(2)	10258(1)	6468(1)	57.4(6)
O(1)	4606(2)	8468(2)	362(1)	67.9(7)	N(3)	5461(2)	8648(2)	6884(2)	59.8(7)
O(2)	5743(2)	6233(2)	1099(1)	73.4(7)	N(4)	8956(2)	11240(2)	6661(1)	56.0(7)
N(1)	3734(3)	8053(2)	–227(2)	63.6(8)	C(3)	4694(3)	8152(2)	7084.0(2)	57.0(9)
N(2)	5403(3)	6203(2)	1738(2)	67.3(8)	C(4)	9422(3)	11637(2)	6246(2)	54.8(9)
C(1)	3180(3)	8621(3)	–500(2)	60.0(9)	C(5)	9773(4)	11134(3)	5600(2)	91(1)
C(2)	5809(3)	5578(3)	2025(2)	71(1)	C(6)	4769(3)	8075(3)	7834(2)	89(1)
C(7)	3425(3)	9658(2)	–229(2)	88(1)	C(61)	9575(4)	12662(3)	6423(2)	65(1)
C(8)	6585(4)	4947(3)	1713(2)	119(2)	C(62)	10557(4)	13181(3)	6364(2)	101(2)
C(11)	2228(3)	8186(3)	–1102(2)	62.2(9)	C(63)	10681(7)	14161(5)	6537(3)	138(3)
C(12)	1956(4)	7241(3)	–1310(2)	94(1)	C(64)	9826(9)	14582(5)	6759(4)	157(4)
C(13)	1043(4)	6827(4)	–1853(3)	110(2)	C(65)	8849(6)	14095(4)	6815(3)	139(2)
C(14)	398(4)	7347(4)	–2199(3)	99(1)	C(66)	8725(4)	13123(3)	6652(2)	97(1)
C(15)	665(4)	8271(4)	–2020(3)	109(2)	C(71)	3695(3)	7667(2)	6532(2)	58.1(9)

Table 2. (Contd.)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		III		
C(72)	2681(3)	7314(3)	6691(2)	78(1)
C(73)	1744(4)	6892(3)	6165(3)	92(1)
C(74)	1813(4)	6810(3)	5480(3)	92(1)
C(75)	2811(4)	7142(3)	5319(2)	100(1)
C(76)	3746(4)	7562(3)	5832(2)	88(1)
C(81)	8543(3)	10311(2)	7970(2)	59.2(9)
C(82)	9695(3)	10608(3)	8092(2)	69(1)
C(83)	10305(3)	11016(3)	8757(2)	85(1)
C(84)	9780(4)	11182(4)	9314(2)	119(2)
C(85)	8620(5)	10934(5)	9186(2)	153(3)
C(86)	7994(4)	10491(4)	8527(2)	121(2)
C(87)	10441(5)	11682(5)	10044(2)	196(4)
C(91)	7927(3)	8379(2)	6442(2)	49.8(8)
C(92)	7485(3)	7577(3)	6622(2)	68(1)
C(93)	7643(3)	6711(3)	6268(2)	73(1)
C(94)	8233(3)	6603(2)	5725(2)	65(1)
C(95)	8698(3)	7405(3)	5559(2)	68(1)
C(96)	8545(3)	8270(2)	5912(2)	62.0(9)
C(97)	8367(4)	5652(3)	5318(2)	97(1)
C(101)	6402(3)	10432(2)	6469(2)	56.0(9)
C(102)	6418(3)	10586(3)	5809(2)	71(1)
C(103)	5601(4)	11042(3)	5499(2)	84(1)
C(104)	4761(4)	11371(3)	5843(3)	85(1)
C(105)	4774(3)	11233(3)	6501(3)	87(1)
C(106)	5579(3)	10767(3)	6818(2)	71(1)
C(107)	3827(4)	11844(4)	5490(3)	131(2)
		IV		
Sb	7571.2(2)	756.2(1)	8591.0(1)	38.9(1)
O(1)	6546(2)	1897(1)	8322(1)	46.6(5)
O(2)	8656(2)	–384(1)	8766(1)	47.3(5)
N(1)	7040(3)	2581(2)	8810(1)	51.8(7)
N(2)	7947(3)	–999(2)	9168(2)	53.4(7)
C(11)	6182(3)	3177(2)	8895(2)	50.3(8)
C(12)	6578(4)	3925(2)	9417(2)	77(1)
C(13)	6156(5)	4807(3)	9073(2)	83(1)
C(14)	4699(5)	4808(3)	8761(2)	86(1)
C(15)	4428(4)	4092(3)	8200(2)	82(1)
C(16)	4790(3)	3190(2)	8528(2)	70(1)
C(21)	8300(3)	–1794(2)	9091(2)	49(1)
C(22)	7591(4)	–2480(2)	9501(2)	69(1)
C(23)	8517(5)	–3127(3)	9921(2)	85(1)
C(24)	9477(4)	–3505(3)	9417(3)	89(1)
C(25)	10250(4)	–2786(3)	9073(3)	88(1)
C(26)	9333(3)	–2131(2)	8631(2)	62(1)
C(31)	9296(3)	1291(2)	8203(2)	43(1)
C(32)	10518(3)	1214(3)	8604(2)	65(1)
C(33)	11616(4)	1567(3)	8319(3)	81(1)
C(34)	11505(4)	1987(3)	7645(3)	74(1)
C(35)	10313(5)	2056(3)	7245(2)	83(1)
C(36)	9205(4)	1723(2)	7528(2)	65(1)
C(41)	7133(3)	841(2)	9713(2)	44(1)
C(42)	8071(3)	673(2)	10308(2)	55(1)
C(43)	7755(4)	728(3)	11043(2)	69(1)
C(44)	6494(4)	934(2)	11182(2)	68(1)
C(45)	5547(4)	1080(3)	10601(2)	74(1)
C(46)	5861(3)	1046(2)	9869(2)	62(1)
C(51)	6195(3)	162(2)	7776(2)	40(1)
C(52)	4985(3)	554(2)	7579(2)	50(1)
C(53)	4091(3)	170(2)	7040(2)	59(1)
C(54)	4410(4)	–590(2)	6695(2)	64(1)
C(55)	5605(4)	–980(2)	6883(2)	64(1)
C(56)	6485(3)	–614(2)	7431(2)	54(1)

$$Ar_5Sb + Ar_3Sb(ON{=}CRR')_2 \longrightarrow 2Ar_4SbON{=}CRR'.$$

Triarylantimony dioximates were synthesized from triarylstibine, oxime, and hydrogen peroxide (molar ratio of 1 : 2 : 1) via the reaction of oxidative addition:

$$Ar_3Sb + 2HON{=}CRR' + H_2O_2$$
$$\longrightarrow Ar_3Sb(ON{=}CRR')_2 + 2H_2O.$$

According to X-ray diffraction data, crystals **I** consist of two individual molecules (**a** and **b**) with close parameters. The antimony atoms in compounds **I** and **II** have virtually undistorted trigonal-bipyramidal coordination with the axial O atoms (Fig. 1, 2). The sums of the $C_{eq}SbC_{eq}$ bond angles are equal to 359.05(6)° (**Ia**), 359.12(6)° (**Ib**), and 358.1(1)° (**II**); the axial angles OSbC are equal to 175.72(4)°, 175.31(5)°, and 175.7(1)° for molecules **Ia**, **Ib**, and **II**, respectively. The $O_{ax}SbC_{eq}$ and $C_{ax}SbC_{eq}$ bond angles in structures **I** and **II** lie within the range of 82.4(1)°–89.40(5)° and 92.24(5)°–96.1(1)°, respectively. The Sb–C_{eq} bond lengths lie within the range of 2.114(1)–2.131(2) Å for compound **I** and 2.121(3)–2.135(3) Å for compound **II**. The axial Sb–C_{ax} bonds (2.193(1) (**Ia**), 2.207(1) (**Ib**), and 2.187(3) (**II**) Å) are noticeably longer than the equatorial bonds. The Sb–O_{ax} bonds (2.138(1), 2.137(2), and 2.154(2) Å in **Ia**, **Ib**, and **II**, respectively) are noticeably shorter than the Sb–C_{ax} bonds. The Sb–O_{ax} distance in compound **II** agrees with the analogous

Table 3. Bond lengths and angles in structures **I–IV**

Bond	*d*, Å	Angle	ω, deg
		I	
Sb(1)–C(31)	2.114(1)	C(31)Sb(1)C(41)	118.89(6)
Sb(1)–C(41)	2.122(2)	C(31)Sb(1)C(21)	121.19(6)
Sb(1)–C(21)	2.123(2)	C(41)Sb(1)C(21)	118.97(5)
Sb(1)–O(1)	2.138(1)	C(31)Sb(1)O(1)	89.40(5)
Sb(1)–C(11)	2.193(1)	C(41)Sb(1)O(1)	82.85(5)
O(1)–N(1)	1.390(2)	C(21)Sb(1)O(1)	87.92(5)
N(1)–C(1)	1.278(2)	C(31)Sb(1)C(11)	93.87(5)
Sb(2)–C(71)	2.114(2)	C(41)Sb(1)C(11)	93.14(5)
Sb(2)–C(81)	2.117(1)	C(21)Sb(1)C(11)	92.74(6)
Sb(2)–C(91)	2.131(2)	O(1)Sb(1)C(11)	175.72(4)
Sb(2)–O(2)	2.137(1)	N(1)O(1)Sb(1)	106.97(7)
Sb(2)–C(61)	2.207(1)	C(1)N(1)O(1)	113.6(1)
O(2)–N(2)	1.402(2)	N(1)C(1)C(51)	115.4(1)
N(2)–C(3)	1.279(2)	N(1)C(1)C(2)	123.7(2)
		C(71)Sb(2)C(81)	119.17(6)
		C(71)Sb(2)C(91)	120.55(5)
		C(81)Sb(2)C(91)	119.40(6)
		C(71)Sb(2)O(2)	88.44(5)
		C(81)Sb(2)O(2)	89.10(5)
		C(91)Sb(2)O(2)	83.12(5)
		C(71)Sb(2)C(61)	93.34(5)
		C(81)Sb(2)C(61)	93.81(6)
		C(91)Sb(2)C(61)	92.24(6)
		O(2)Sb(2)C(61)	175.31(5)
		N(2)O(2)Sb(2)	104.62(8)
		C(3)N(2)O(2)	114.4(2)
		N(2)C(3)C(101)	114.8(2)
		N(2)C(3)C(4)	124.8(2)
		II	
Sb–C(21)	2.121(3)	C(21)SbC(51)	116.1(1)
Sb–C(51)	2.127(3)	C(21)SbC(41)	123.2(1)
Sb–C(41)	2.135(3)	C(51)SbC(41)	118.8(1)
Sb–O(1)	2.154(2)	C(21)SbO(1)	86.8(1)
Sb–C(31)	2.187(3)	C(51)SbO(1)	87.2(1)
O(1)–N(1)	1.365(3)	C(41)SbO(1)	82.4(1)
O(2)–N(2)	1.203(4)	C(21)SbC(31)	96.1(1)
O(3)–N(2)	1.213(4)	C(51)SbC(31)	94.4(1)
N(1)–C(1)	1.263(4)	C(41)SbC(31)	93.3(1)
N(2)–C(15)	1.486(5)	O(1)SbC(31)	175.7(1)
		C(42)C(41)Sb	120.1(2)
		C(46)C(41)Sb	121.6(2)
		C(56)C(51)Sb	119.6(3)
		C(52)C(51)Sb	122.6(3)
		N(1)O(1)Sb	106.4(2)
		C(1)N(1)O(1)	114.7(3)
		O(2)N(2)O(3)	123.0(5)
		O(2)N(2)C(15)	120.2(4)
		O(3)N(2)C(15)	116.8(4)
		N(1)C(1)C(11)	118.9(3)
		III	
Sb(1)–O(2)	2.067(2)	O(2)Sb(1)O(1)	176.81(9)
Sb(1)–O(1)	2.080(2)	O(2)Sb(1)C(41)	92.8(1)
Sb(1)–C(41)	2.099(4)	O(1)Sb(1)C(41)	90.1(1)
Sb(1)–C(31)	2.106(4)	O(2)Sb(1)C(31)	85.8(1)
Sb(1)–C(21)	2.107(3)	O(1)Sb(1)C(31)	91.4(1)
O(1)–N(1)	1.406(3)	C(41)Sb(1)C(31)	127.3(1)
O(2)–N(2)	1.401(3)	O(2)Sb(1)C(21)	92.2(1)
N(1)–C(1)	1.272(4)	O(1)Sb(1)C(21)	87.8(1)
N(2)–C(2)	1.277(4)	C(41)Sb(1)C(21)	116.7(1)
C(1)–C(11)	1.481(5)	C(31)Sb(1)C(21)	116.1(1)
C(1)–C(7)	1.499(5)	N(1)O(1)Sb(1)	104.0(2)
C(2)–C(51)	1.473(5)	N(2)O(2)Sb(1)	108.7(2)
C(2)–C(8)	1.499(5)	C(1)N(1)O(1)	115.0(3)
C(11)–C(12)	1.363(5)	C(2)N(2)O(2)	113.4(3)
C(11)–C(16)	1.364(5)	N(1)C(1)C(11)	115.3(3)
C(12)–C(13)	1.381(5)	N(1)C(1)C(7)	123.6(3)
C(13)–C(14)	1.348(6)	C(32)C(31)Sb(1)	122.6(3)
C(14)–C(15)	1.329(6)	C(36)C(31)Sb(1)	119.5(3)
C(15)–C(16)	1.397(6)	C(46)C(41)Sb(1)	123.5(3)
C(21)–C(26)	1.380(4)	C(42)C(41)Sb(1)	119.0(3)
Sb(2)–O(3)	2.066(2)	O(3)Sb(2)O(4)	177.99(8)
Sb(2)–O(4)	2.075(2)	O(3)Sb(2)C(81)	87.4(1)
Sb(2)–C(81)	2.097(3)	O(4)Sb(2)C(81)	93.6(1)
Sb(2)–C(101)	2.108(3)	O(3)Sb(2)C(101)	91.6(1)
Sb(2)–C(91)	2.112(3)	O(4)Sb(2)C(101)	89.5(1)
O(3)–N(3)	1.396(3)	C(81)Sb(2)C(101)	119.0(1)
O(4)–N(4)	1.410(3)	O(3)Sb(2)C(91)	91.6(1)
N(3)–C(3)	1.278(4)	O(4)Sb(2)C(91)	86.4(1)
N(4)–C(4)	1.271(4)	C(81)Sb(2)C(91)	118.7(1)
C(3)–C(71)	1.479(5)	C(101)Sb(2)C(91)	122.3(1)
C(3)–C(6)	1.502(5)	N(3)O(3)Sb(2)	107.7(2)
C(4)–C(61)	1.471(5)	N(4)O(4)Sb(2)	109.0(2)
C(4)–C(5)	1.490(5)	C(3)N(3)O(3)	114.7(3)
C(61)–C(62)	1.367(5)	C(4)N(4)O(4)	113.3(3)
C(61)–C(66)	1.369(5)	N(3)C(3)C(71)	116.0(3)
C(62)–C(63)	1.407(7)	N(3)C(3)C(6)	123.0(3)
C(63)–C(64)	1.339(9)	C(71)C(3)C(6)	120.9(3)
C(64)–C(65)	1.338(8)	N(4)C(4)C(61)	115.9(3)
C(65)–C(66)	1.394(7)	N(4)C(4)C(5)	124.5(3)
C(71)–C(76)	1.377(5)	C(82)C(81)Sb(2)	121.3(3)
C(71)–C(72)	1.378(5)	C(86)C(81)Sb(2)	120.7(3)
C(72)–C(73)	1.383(5)	C(96)C(91)Sb(2)	122.2(2)
C(73)–C(74)	1.355(6)	C(92)C(91)Sb(2)	120.5(3)
C(74)–C(75)	1.354(6)	C(106)C(101)Sb(2)	119.5(3)
C(75)–C(76)	1.369(5)	C(102)C(101)Sb(2)	121.7(3)
		IV	
Sb–O(1)	2.058(2)	O(1)–Sb–O(2)	174.89(8)
Sb–O(2)	2.064(2)	O(1)–Sb–C(41)	91.1(1)
Sb–C(41)	2.097(3)	O(2)–Sb–C(41)	93.9(1)
Sb–C(31)	2.113(3)	O(1)–Sb–C(31)	90.9(1)
Sb–C(51)	2.118(3)	O(2)–Sb–C(31)	85.7(1)
Sb–N(1)	2.864(3)	C(41)–Sb–C(31)	123.4(1)
Sb–N(2)	2.874(3)	O(1)–Sb–C(51)	85.1(1)
O(1)–N(1)	1.416(3)	O(2)–Sb–C(51)	93.0(1)
O(2)–N(2)	1.419(3)	C(41)–Sb–C(51)	119.5(1)
N(1)–C(11)	1.279(4)	C(31)–Sb–C(51)	117.0(1)
N(2)–C(21)	1.273(4)	C(11)–N(1)–O(1)	112.9(2)
C(51)–C(52)	1.382(4)	C(21)–N(2)–O(2)	114.2(3)
		N(1)–C(11)–C(16)	125.7(3)
		N(1)–C(11)–C(12)	117.9(3)
		N(2)–C(21)–C(26)	127.5(3)
		N(2)–C(21)–C(22)	117.1(3)

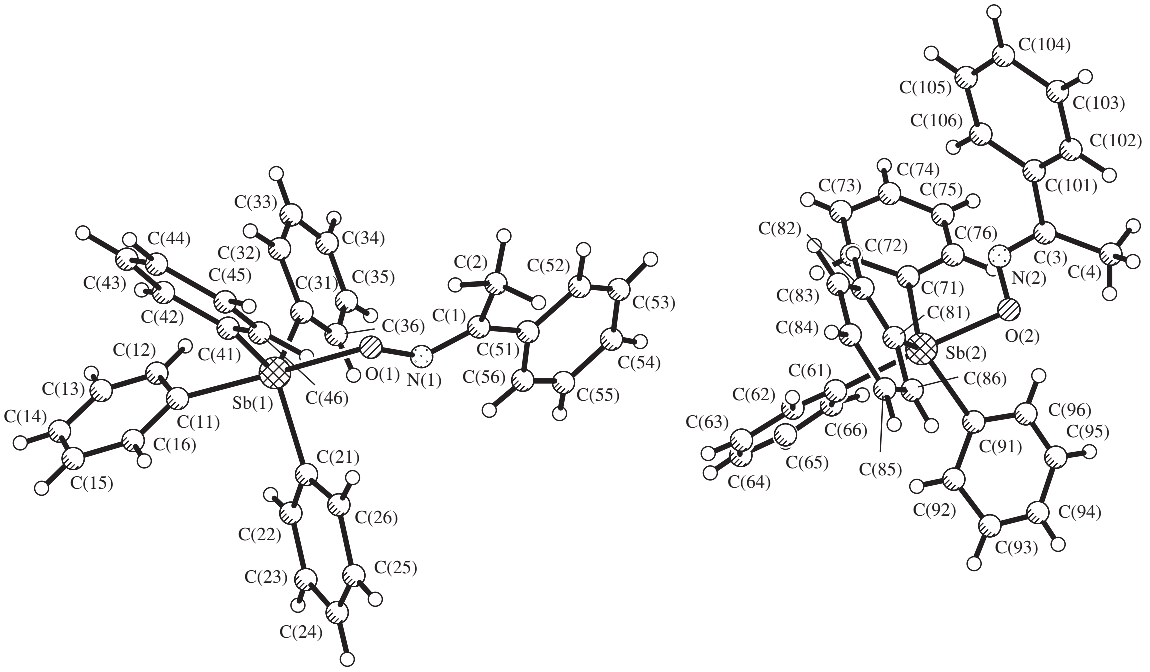

Fig. 1. Molecular structure of tetraphenylantimony acetophenoneoximate (**I**).

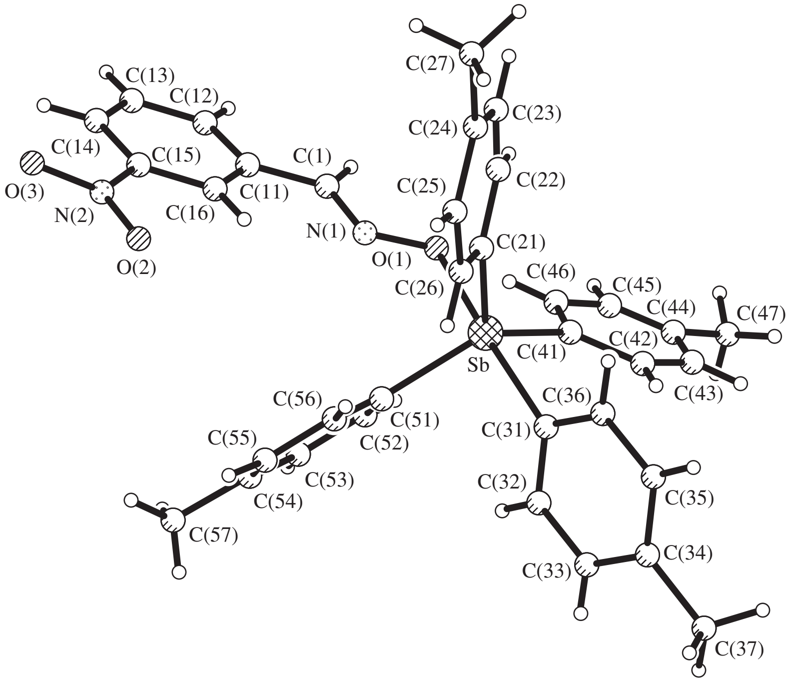

Fig. 2. Molecular structure of tetra-*n*-tolylantimony 3-nitrobenzaloximate (**II**).

distances in other structurally characterized tetraphenylantimony oximates (2.150(3)–2.146(4 [8, 9]) Å). Similar Sb–O distances (2.121(4)–2.143(4) Å) are observed in aroxytetraarylantimony compounds containing electron-donating substutuents in the aroxy group [6, 7], while in tetraarylantimony acylates, the Sb–O$_{ax}$ bonds are found to be noticeably longer (2.223–2.530 Å) [10–14].

In structures **I** and **II**, the Sb atom is involved in intramolecular contact with the N atom of the oxime group. The Sb··N distance (2.871(1) (**Ia**), 2.836(1) (**Ib**), and 2.857(3) (**II**) Å) is noticeably shorter than the

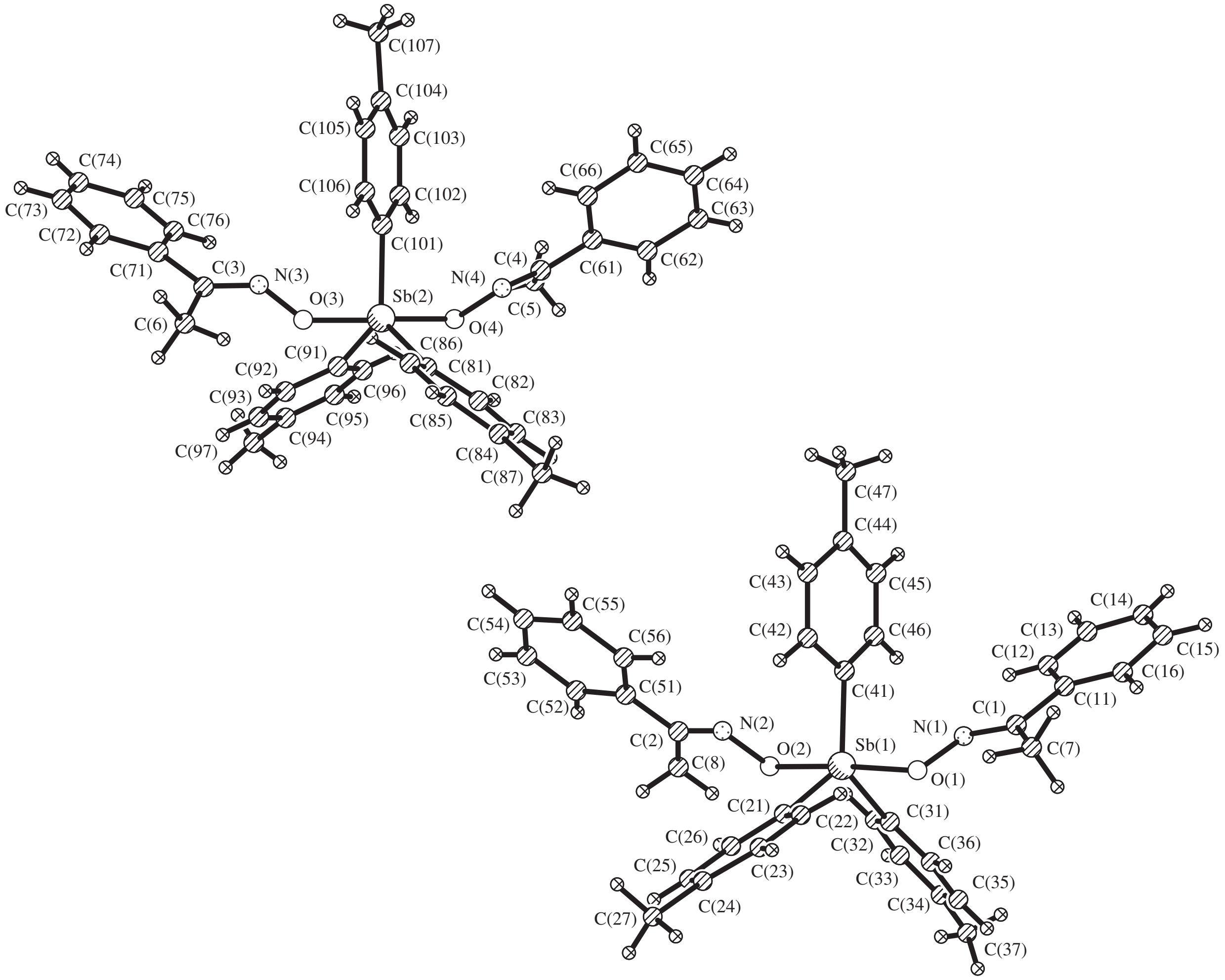

Fig. 3. Molecular structure of tri-*n*-tolylantimony bis(acetophenoneoximate) (**III**).

sum of the van der Waals radii of Sb and N atoms (3.8 Å [21]). In tetraarylantimony acylates, the intramolecular contact Sb··O=C is less pronounced (the Sb··O distances vary within range the 3.0–3.3 Å [10–12]). Closer contact of the central atom with the nitrogen atom is likely due to the Sb–O bond in tetraarylantimony oximates **I** and **II** being shorter than that in tetraarylantimony acylates. Bidentate coordination of the oximate ligand was also observed in μ-oxo-bis[(furfuroloximato)triphenylantimony] [17].

The intramolecular contact Sb··N in compound **I** does not influence the $C_{eq}SbC_{eq}$ angles, which are close to the ideal value of 120° (118.97(5)°–121.19(6)°). In compound **II**, one of the equatorial angles CSbC (from the side of the Sb··N contact) is slightly greater than the other two angles (123.2(1)°, 116.1(1)°, and 118.8(1)°). The intramolecular contacts Sb··N in two independent molecules of tetraphenylantimony furfuroloximate and in tetraphenylantimony benzophenoneoximate are equal to 2.841(5), 2.940(6), and 2.964(5) Å, respectively; the equatorial angles CSbC in these compounds also insignificantly change [8, 9]. Note that in tetraphenylantimony acylates, the intramolecular contact Sb··O=C more greatly influences the equatorial angles (129.3(1)°–143.3(2)°) [10–12].

The SbON angles in molecules **Ia**, **Ib**, and **II** are equal to 106.97(7)°, 104.62(7)°, and 106.4(2)°, respectively. The lengths of the O–N bonds (1.390(2), 1.402(2), and 1.365(3) Å) and of the N–C bonds (1.278(2), 1.279(2), and 1.263(4) Å) are similar to the lengths of the analogous bonds in other tetraphenylantimony oximates [8, 9]. In compound **II**, the lengths of the N–O bonds in the nitro group (1.203(4) and 1.213(4) Å) and the O(2)N(2)O(3) angle (123.0(5)°) show normal values [22].

The X-ray diffraction analysis of compounds **III** and **IV** indicates a trigonal-bipyramidal coordination of Sb atoms to O atoms of the axial oxime ligands (Fig. 3, 4). There are two individual molecules (**a** and **b**) in crystal **III**. The sums of the CSbC angles in the equatorial planes of structures **III** and **IV** differ from 360° by less than 0.1°. However, the individual angles $C_{eq}SbC_{eq}$ are different: 116.7(1)°, 116.1(1)°, and 127.3(1)° in **IIIa**; 118.7(1)°, 119.0(1)°, and 122.3(1)° in **IIIb**;

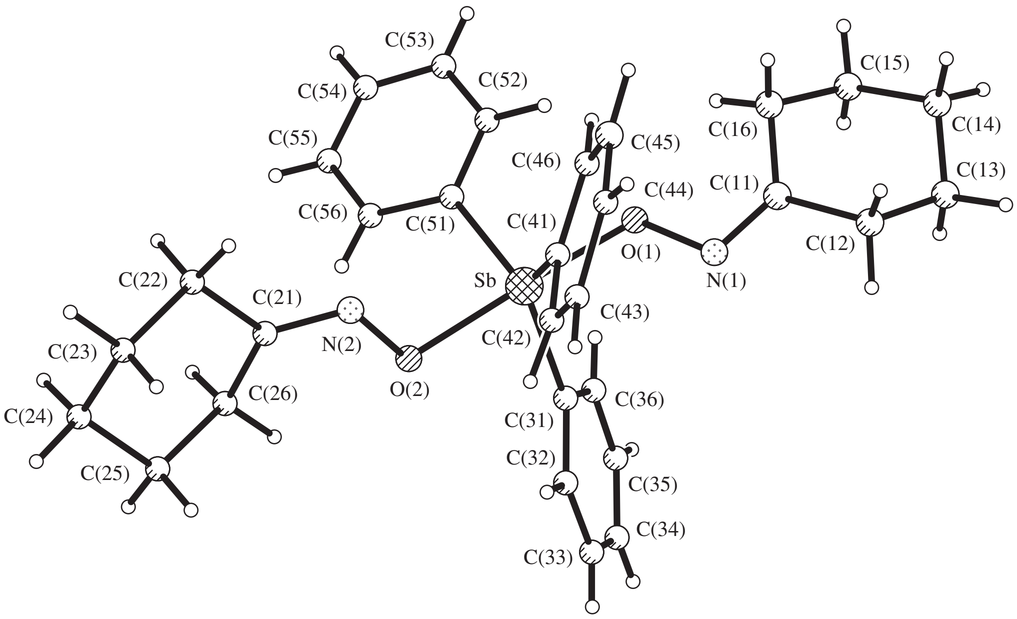

Fig. 4. Molecular structure of triphenylantimony bis(cyclohexanoneoximate) (**IV**).

117.0(1)°, 119.5(1)°, and 123.4(1)° in **IV**. The axial angles OSbO are equal to 176.81(9)° (**IIIa**), 177.99(8)° (**IIIb**), and 174.89(8)° (**IV**). The Sb–C bond lengths lie within the range of 2.099(4)–2.107(3) Å (**IIIa**), 2.097(3)–2.112(3) Å (**IIIb**), and 2.097(3)–2.118(3) (**IV**); the Sb–O_{ax} bonds (2.066(2)–2.080(1) Å in **III**; 2.058(2) and 2.064(2) Å in **IV**) are shorter than the Sb–C_{eq} bonds. It should be noted that in triarylantimony dioximates, the Sb–O bond length is close to the sum of the covalent radii of antimony and oxygen atoms (2.07 Å [21]); the corresponding bond in triarylantimony diacylates [14–17] and triarylantimony disulfonates [17, 23, 24] is noticeably shorter; while it is longer in triphenylantimony dimethoxide [4].

As in compounds **I** and **II**, the antimony atom and nitrogen atoms of oximate groups in compounds **III** and **IV** are involved in intramolecular contacts. The Sb··N distances (2.779(3), 2.844(3) Å (**IIIa**), 2.824(3), 2.864(3) Å (**IIIb**), and 2,864(3), 2.874(3) Å (**IV**)) are close to the analogous distances in **I** and **II**, in spite of the fact that the Sb–O bond lengths in these compounds are different. Thus, the coordination number of the antimony atom in **III** and **IV** is equal to 7 (5 + 2).

The geometrical parameters of the acetophenoneoxime group in compounds **I** and **III** are similar.

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