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Synthesis and Structure of Triarylantimony Dioximates

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Abstract—The reaction of triphenylantimony, hydrogen peroxide and 5-bromo-2-hydroxybenzaldoxime in a 1 : 1 : 2 molar ratio in ether gives triphenylantimony bis(5-bromo-2-hydroxybenzaldoximate). The reaction of penta-*p*-tolylantimony with the same oxime in toluene yields tri-*p*-tolylantimony bis(cyclohexanone oximate). According to X-ray data, the Sb atoms in the products have a distorted trigonal bipyramidal coordination with the oximate ligands in axial positions. In triphenylantimony bis(5-bromo-2-hydroxybenzaldoximate), the O–Sb–O angle is 175.49(6)°, and the interatomic distances are as follows, Å: Sb–C 2.095–2.103; Sb–O 2.069(2) and 2.083(2); and Sb···N (intermolecular) 2.896(2) and 2.832(2). The respective geometric parameters of tri-*p*-tolylantimony bis(cyclohexanone oximate) are 174.25(6)°; 2.107–2.117; 2.049(2) and 2.057(2); and 2.890(2) and 2.861(2) Å.

Trialkylantimony dioximates $R_3Sb(ON{=}CR'R'')$ (R=Me, Et; R' and R'' are alkyl and aryl groups) have been prepared either by reactions of trialkylantimony dibromides with sodium oximates in boiling benzene [1] or THF [2] or with oximes in the presence of triethylamine as hydrogen bromide acceptor [3]. Triphenylantimony dioximates have also been prepared by reactions of triphenylantimony dimethoxide and oximes [4]. It is known that triorganylantimony dihalides are prepared by halogenation of triorganylantimony, whereas triorganylantimony dialkoxides, by alcoholysis of organylantimony dihalides. The syntheses of triorganylantimony dioximates described in [1–4] all are multistage.

We have been the first to synthesize triarylammonium dioximates by an oxidative addition procedure based on the reaction of triarylantimony with hydrogen peroxide in the presence of an oxime at a 1 : 1 : 2 molar reagent ratio [5].

$$Ar_3Sb + H_2O_2 + 2HON{=}CRR' \longrightarrow Ar_3Sb(ON{=}CRR')_2 + 2H_2O. \quad (1)$$

Using this procedure we have prepared a series of triarylantimony dioximates, including new and previously described compounds [6–8]. Proceeding with the research into the synthesis of compounds of the Ar_3SbX_2 type, we focused on the reaction of triarylantimony, hydrogen peroxide, and 5-bromo-2-hydroxybenzaldoxime. The hydrogen atoms in the two hydroxy groups in the latter differ from each other in mobility, and, therefore, their involvement in reaction might serve as a kind of activity test. It was established that the reaction results in formation of triphenylantimony bis(5-bromo-2-hydroxybenzaldoximate) (**I**).

$$Ar_3Sb + H_2O_2 + 2HON{=}C(H)C_6H_3(OH\text{-}2)(Br\text{-}5) \rightarrow Ar_3Sb[ON{=}C(H)C_6H_3(OH\text{-}2)(Br\text{-}5)]_2 + 2H_2O. \quad (2)$$

The reaction was carried out at room temperature. The yield of compound **I** was 82%.

We established that reaction (1) not always provides a high yield of triarylantimony dioximates, because in some cases one more reaction product of the general formula $(Ar_3SbON{=}CRR')_2O$ is formed. Hence, the reactions of triphenyl- and tri-*p*-tolylantimony with hydrogen peroxide and benzophenone (1 : 1 : 2 molar ratio) resulted in isolation, along with triphenylantimony bis(benzophenone oximate) (72%) and tri-*p*-tolylantimony bis(benzophenone oximate) (21%), of μ-oxobis[(benzophenone oximato)triphenylantimony] (26%) and μ-oxobis[(benzophenone oximato)tri-*p*-tolylantimony] (30%) [6].

According to [9–12], hydrogen peroxide oxidizes triarylantimony to Ar_3SbO or $Ar_3Sb(OH)_2$, depending on the size of the organic radical. In the presence of HX, derivatives of the general formula Ar_3SbX_2 are formed [13]. We found that with keto- or aldoximes as hydrogen-containing reagents, a competing reaction pathway appears, leading to compounds of the $(Ar_3SbX)_2O$ type. This transformation probably occurs by schemes (3)–(5).

$$Ar_3Sb + H_2O_2 \longrightarrow Ar_3Sb(OH)_2, \quad (3)$$

$$Ar_3Sb(OH)_2 + HON{=}CRR' \longrightarrow Ar_3Sb(OH)ON{=}CRR' + 2H_2O, \qquad (4)$$

$$2Ar_3Sb(OH)ON{=}CRR' \longrightarrow (Ar_3SbON{=}CRR')_2O + H_2O. \qquad (5)$$

As shown in [14], unsymmetrical compounds $Ar_3Sb(OH)X$ are unstable and transform to products with an Sb–O–Sb bridging bond.

The formation of compounds $(Ar_3SbON{=}CRR')_2O$ might by explained in terms of hydrolytic instability of derivatives $Ar_3Sb(ON{=}CRR')_2$ and their hydrolysis under the reaction conditions. However, Bajpai and Srivastava [4] showed that triarylantimony dioximates are resistant to hydrolysis. We also confirmed it by special experiments. That means that the formation of two products in the oxidation of triarylstibine with hydrogen peroxide in the presence of oximes evidently arises from other reasons.

We previously found that at a 1 : 1 : 1 reagent molar ratio, oxidative addition (1) provides a single organoantimony product, μ-oxobis[(oximato)triarylantimony], in 90% yield [6, 15].

$$2Ar_3Sb + 2H_2O_2 + 2HON{=}CRR' \longrightarrow (Ar_3SbON{=}CRR')_2 + 3H_2O_2, \qquad (6)$$

Ar = Ph, *p*-Tol; R R' = Ph; R = H, R' = C_4H_3O.

Note that Dodonov *et al.* [16], using *tert*-butyl hydroperoxide as oxidative agent in the synthesis of triphenyl and trimethylantimony dioximates (R_3Sb: *t*-BuOOH : HON=CR'R" 1 : 1 : 2, hexane), obtained 87–96% of the target product and observed no formation of μ-oxobis[(oximato)triorganylantimony].

It is known that in reactions of pentaarylantimony with protic acids only one aryl group is easily substituted to form Ar_4SbX (where X is the acid residue) [14]. Further dearylation requires special conditions, which is explained by a high strength of the Sb–C bond. For example, dimethoxytriphenylantimony was prepared by boiling pentaphenylantimony in methanol for 5 weeks in 80% yield [17]. Reactions of pentaorganylantimony with excess carboxylic acids gives adducts like $R_4SbOC(O)R'HOC(O)R$ rather than triorganylantimony dicarboxylates [18].

We found that triarylantimony dioximates can be prepared by the reaction of pentaarylantimony and oximes in a 1 : 2 molar ratio (toluene, 90–100°C, 1–5 h).

$$Ar_5Sb + 2HON{=}CRR' \rightarrow Ar_3Sb(ON{=}CRR')_2 + 2ArH, \qquad (7)$$

Ar = *p*-Tol; R, R' = *cyclo*-$C_{60}H_{10}$ (**II**); Ar = Ph, R, R' = *cyclo*-C_6H_{10} (**III**); Ar = Ph; R = R' = Ph (**IV**); Ar = *p*-Tol; R = Me, R' = Ph (**V**).

Note that small amounts of tetraarylantimony oximates (up to 10%) were found among the reaction products. This fact suggests that not all pentaarylantimony reacts according to the above-presented scheme.

The reactions of equimolar amounts of pentaarylantimony with cyclohexanone oxime or acetophenone oxime at 90°C gave triarylantimony dioximates in yields of up to 89%. If the reactions were carried out at room temperature or under short heating, tetraarylantimony oximates formed in yields of up to 93% [19].

The reaction of pentaarylantimony with oximes evidently involves several stages, the first afording tetraarylantimony oximate. However, in spite of the fairly high strength of the Sb–C bond, elimination of the second aryl group and formation of triarylantimony doximates occur under sufficiently mild conditions. Evidently, triarylantimony dioximates are more preferred by energy than tetraarylantimony oximate.

By special experiment it was established that the reaction of tetraphenylantimony benzophenone oximate with benzophenone oxime (toluene, 90°C, 5 h) gives rise to triphenylantimony bis(benzophenone oximate) (76%).

$$Ph_4SbON{=}CPh_2 + HON{=}CPh_2 \longrightarrow Ph_3Sb(ON{=}CPh_2)_2 + PhH. \qquad (8)$$

To gain insight into structural features of triarylantimony dioximates, we performed an X-ray diffraction analysis of triphenylantimony bis(5-bromo-2-hydroxybenzaldoximate) (**I**) and tri-*p*-tolylantimony bis(cyclohexanone oximate) (**II**) (Figs. 1 and 2). According to these data, the antimony atoms in compounds **I** and **II** have an almost undistorted trigonal bipyramidal coordination. The axial positions are occupied by the O atoms of the oximate ligands. The axial OSbO angle in compound **I** is 175.49(6)°, and in product **II** it is 174.25(6)° (Table 2). The $O^{1,2}SbC$ bond angles in structures **I** and **II** vary within 83.88(8)–93.23(9) and 84.65(7)–93.07(7)°, respectively. The deviation of antimony atoms from the equatorial plane in structure **I** is 0.0184 Å, and in the structure **II** the antimony atom locates exactly in the equatorial plane. The sum of CSbC angles in the equatorial plane practically does not differ from 360°C. The angles between equatorial aryl ligands are unequal: 115.4(9), 118.62(9) and 125.87(9)° in **I** and 117.65(7), 120.94(7), and 121.40(7)° in **II**. The Sb–C bond lengths are 2.095(2)–2.103(2)Å in **I** and 2.107(2)–2.117(2) Å in **II**. The $Sb–O^{1,2}$ bonds [2.069(2) and 2.083(2) Å in **I** and 2.049(2) and 2.057(2) Å in **II**] are shorter than equatorial Sb–C bonds. These results contradict one of the rules of the valence shell elec-

Table 1. Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic thermal parameters ($\times 10^{3}$) in **I** and **II**

Compound **I**					Compound **II**				
atom	x	y	z	U_{eq}, Å	atom	x	y	z	U_{eq}, Å
Sb	2979.0(1)	4824.4(1)	8550.31(8)	43.79(4)	Sb	7244.7(1)	7148.9(1)	6530.5(1)	52.21(4)
Br^1	655.5(3)	8431.2(3)	11813.1(2)	91.1(1)	O^1	6750(1)	6068(1)	5771(1)	59.4(4)
Br^2	5982.4(3)	2021.3(4)	5324.5(2)	115.1(2)	O^2	7872(1)	8105(1)	7324(1)	72.4(5)
O^1	2995(1)	5003(1)	9547(1)	55.0(5)	N^1	6717(2)	6600(2)	4709(1)	62.9(5)
O^2	2935(1)	4515(1)	7566(1)	53.7(5)	N^2	6877(2)	8193(2)	8354(2)	77.4(6)
O^3	2824(2)	8316(2)	9603(1)	71.4(6)	C^{11}	6787(2)	5918(2)	4093(2)	63.0(6)
O^4	6130(2)	4139(2)	7966(1)	74.4(6)	C^{12}	6761(3)	6380(2)	2965(2)	87.9(9)
N^1	2787(2)	6109(2)	9692(1)	51.5(6)	C^{13}	7977(3)	5928(2)	2085(2)	101.6(10)
N^2	3987(2)	4243(2)	7550(1)	50.8(6)	C^{14}	8083(3)	4689(2)	2345(2)	83.5(8)
C^{11}	1309(2)	5200(2)	8187(1)	49.6(7)	C^{15}	8162(3)	4285(2)	3475(2)	85.0(8)
C^{12}	613(2)	4954(2)	8567(2)	67(1)	C^{16}	6957(3)	4691(2)	4383(2)	76.8(7)
C^{13}	–507(2)	5152(2)	8299(2)	83(1)	C^{21}	7336(3)	8450(3)	9024(2)	101.1(9)
C^{14}	–906(2)	5586(2)	7673(2)	82(1)	C^{22}	8798(3)	8616(3)	8800(3)	156(1)
C^{15}	–228(2)	5854(2)	7304(2)	75(1)	C^{23}	8980(4)	9391(5)	9278(4)	264(2)
C^{16}	883(2)	5665(2)	7550(1)	61.5(8)	C^{24}	8061(4)	9432(4)	10458(3)	180(2)
C^{21}	3355(2)	3135(2)	8821(1)	44.7(6)	C^{25}	6576(4)	9467(3)	10508(3)	166(2)
C^{22}	2506(2)	2400(2)	8745(1)	61.0(8)	C^{26}	6368(3)	8550(3)	10150(2)	118(1)
C^{23}	2692(2)	1283(2)	8917(2)	73(1)	C^{31}	5582(2)	8229(2)	6481(2)	50.2(5)
C^{24}	3724(3)	895(2)	9169(1)	73(1)	C^{32}	5588(2)	9330(2)	6537(2)	59.6(6)
C^{25}	4575(2)	1604(2)	9243(2)	75(1)	C^{33}	4484(2)	10032(2)	6520(2)	65.7(7)
C^{26}	4395(2)	2748(2)	9067(1)	63.1(8)	C^{34}	3338(2)	9653(2)	6492(2)	60.0(7)
C^{31}	4111(2)	6132(2)	8639(1)	44.1(6)	C^{35}	3335(2)	8556(2)	6441(2)	67.7(7)
C^{32}	5027(2)	6217(2)	9172(1)	63.0(8)	C^{36}	4440(2)	7856(2)	6424(2)	62.0(6)
C^{33}	5706(2)	7135(3)	9240(2)	74(1)	C^{37}	2130(3)	10411(2)	6494(2)	86.2(9)
C^{34}	5457(2)	7988(3)	8790(2)	77(1)	C^{41}	9185(2)	7413(2)	5275(2)	47.8(5)
C^{35}	4552(3)	7908(3)	8250(2)	100(1)	C^{42}	9769(2)	6669(2)	4585(2)	61.9(6)
C^{36}	3881(3)	6978(2)	8173(2)	77(1)	C^{43}	11037(2)	6838(2)	3777(2)	78.2(8)
C^{41}	2212(2)	7310(2)	10435(1)	52.0(7)	C^{44}	11754(2)	7755(2)	3635(2)	72.1(7)
C^{42}	2365(2)	8307(2)	10123(1)	58.8(8)	C^{45}	11161(2)	8492(2)	4334(2)	70.1(7)
C^{43}	2050(3)	9328(2)	10329(2)	82(1)	C^{46}	9909(2)	8313(2)	5148(2)	60.8(6)
C^{44}	1547(3)	9355(3)	10826(2)	83(1)	C^{47}	13161(3)	7946(3)	2743(3)	121(1)
C^{45}	1386(2)	8400(2)	11137(1)	65.2(8)	C^{51}	7035(2)	5771(2)	7856(2)	56.4(6)
C^{46}	1722(2)	7376(2)	10951(1)	59.5(8)	C^{52}	5999(2)	5045(2)	8215(2)	66.6(7)
C^{47}	2486(2)	6212(2)	10223(1)	54.0(7)	C^{53}	5910(2)	4146(2)	9046(2)	75.0(8)
C^{51}	5052(2)	3479(2)	6889(1)	48.5(7)	C^{54}	6865(3)	3923(2)	9553(2)	74.8(8)
C^{52}	6052(2)	3651(2)	7374(1)	55.4(8)	C^{55}	7891(3)	4656(2)	9202(2)	83.0(9)
C^{53}	7014(2)	3314(2)	7237(2)	70(1)	C^{56}	7967(2)	5570(2)	8378(2)	73.8(8)
C^{54}	6988(2)	2823(3)	6632(2)	71(1)	C^{57}	6782(4)	2888(3)	10457(2)	118(1)
C^{55}	5997(2)	2675(2)	6159(1)	66.2(8)					
C^{56}	5042(2)	2990(2)	6278(1)	57.2(8)					
C^{57}	4013(2)	3798(2)	6996(1)	48.9(7)					
H^1	299(2)	768(2)	953.1(1)	85(1)					
H^2	535(2)	437(2)	799.6(1)	85(1)					

tron pair repulsion theory which states that in molecules with a trigonal bipyramidal configuration axial ligands are more remote from the central atom than equatorial [20]. In other structurally characterized triarylantimony dioximates, the Sb–C and Sb–O bond lengths span the ranges 2.097–2.120 and 2.044–2.080 Å [7, 8, 16], i.e. here, too, violation of the above-mentioned rule takes place. Note that the Sb–O bond

Table 2. Principal bond lengths (*d*) and bond angles (ω) in **I** and **II**

Compound **I**				Compound **II**			
bond	*d*, Å	angle	ω, deg	bond	*d*, Å	angle	ω, deg
$Sb–N^1$	2.896(2)	O^2SbO^1	175.49(6)	$Sb–O^2$	2.049(2)	O^2SbO^1	174.25(6)
$Sb–N^2$	2.832(2)	O^2SbC^{31}	92.33(8)	$Sb–O^1$	2.057(2)	O^2SbC^{31}	92.56(7)
$Sb–O^2$	2.069(2)	O^1SbC^{31}	91.61(8)	$Sb–C^{31}$	2.107(2)	O^1SbC^{31}	93.07(7)
$Sb–O^1$	2.083(2)	O^2SbC^{11}	86.80(8)	$Sb–C^{51}$	2.116(2)	O^2SbC^{51}	91.43(7)
$Sb–C^{31}$	2.095(2)	O^1SbC^{11}	93.23(9)	$Sb–C^{41}$	2.117(2)	O^1SbC^{51}	84.65(7)
$Sb–C^{11}$	2.096(2)	$C^{31}SbC^{11}$	118.62(9)	$Sb–N^2$	2.861(2)	$C^{31}SbC^{51}$	120.94(7)
$Sb–C^{21}$	2.103(2)	O^2SbC^{21}	92.04(8)	$Sb–N^1$	2.890(2)	O^2SbC^{41}	85.15(7)
$Br^1–C^{45}$	1.901(3)	O^1SbC^{21}	83.88(8)	$O^1–N^1$	1.418(2)	O^1SbC^{41}	92.92(7)
$Br^2–C^{55}$	1.899(3)	$C^{31}SbC^{21}$	125.87(9)	$O^2–N^2$	1.396(2)	$C^{31}SbC^{41}$	121.40(7)
$O^1–N^1$	1.391(2)	$C^{11}SbC^{21}$	115.49(9)	$N^1–C^{11}$	1.276(3)	$C^{51}SbC^{41}$	117.65(7)
$O^{-}N^2$	1.392(2)	N^1O^1Sb	111.4(1)	$N^2–C^{21}$	1.264(4)	O^2SbN^2	27.14(5)
$O^3–C^{42}$	1.374(3)	N^2O^2Sb	108.2(1)	$C^{11}–C^{12}$	1.476(3)	O^1SbN^2	154.02(5)
$O^4–C^{52}$	1.339(3)	$C^{47}N^1O^1$	113.8(2)	$C^{11}–C^{16}$	1.493(3)	$C^{31}SbN^2$	79.49(7)
$N^1–C^{47}$	1.277(3)	$C^{57}N^2O^2$	113.2(2)	$C^{12}–C^{13}$	1.532(4)	$C^{51}SbN^2$	78.22(7)
$N^2–C^{57}$	1.280(3)			$C^{13}–C^{14}$	1.500(4)	$C^{41}SbN^2$	112.27(7)
				$C^{14}–C^{15}$	1.490(4)	N^1O^1Sb	111.2(1)
				$C^{15}–C^{16}$	1.522(3)	N^2O^2Sb	110.8(1)
				$C^{21}–C^{26}$	1.483(4)	$C^{11}N^1O^1$	112.8(2)
				$C^{21}–C^{22}$	1.500(4)	$C^{21}N^2O^2$	113.4(2)

length in triarylantimony dioximates is close to the sum of the covalent radii of antimony and oxygen (2.07 Å [21]), being considerably smaller than in triarylantimony dicarboxylates (2.109–2.155 Å) [22–28] and triarylantimony bis(arenesulfonates) (2.105–2.133 Å) [29–31] but greater than in triphenylantimony dimethoxide (2.033 Å) [32]. In the latter compound, axial Sb–O bonds are shorter than equatorial Sb–C bonds.

The $O^{1,2}–N^{1,2}$ in compounds **I** and **II** are 1.391(2), 1.392(2) and 1.277(3), 1.280(3) Å, respectively, and

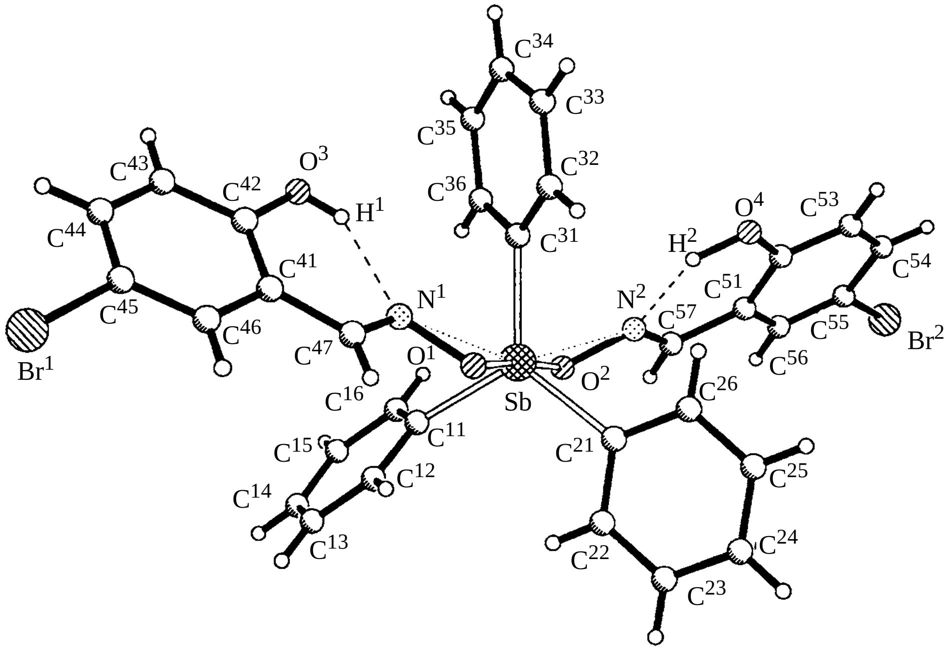

Fig. 1. Molecular structure of triphenylantimony bis(5-bromo-2-hydroxybenzaldoximate) (**I**).

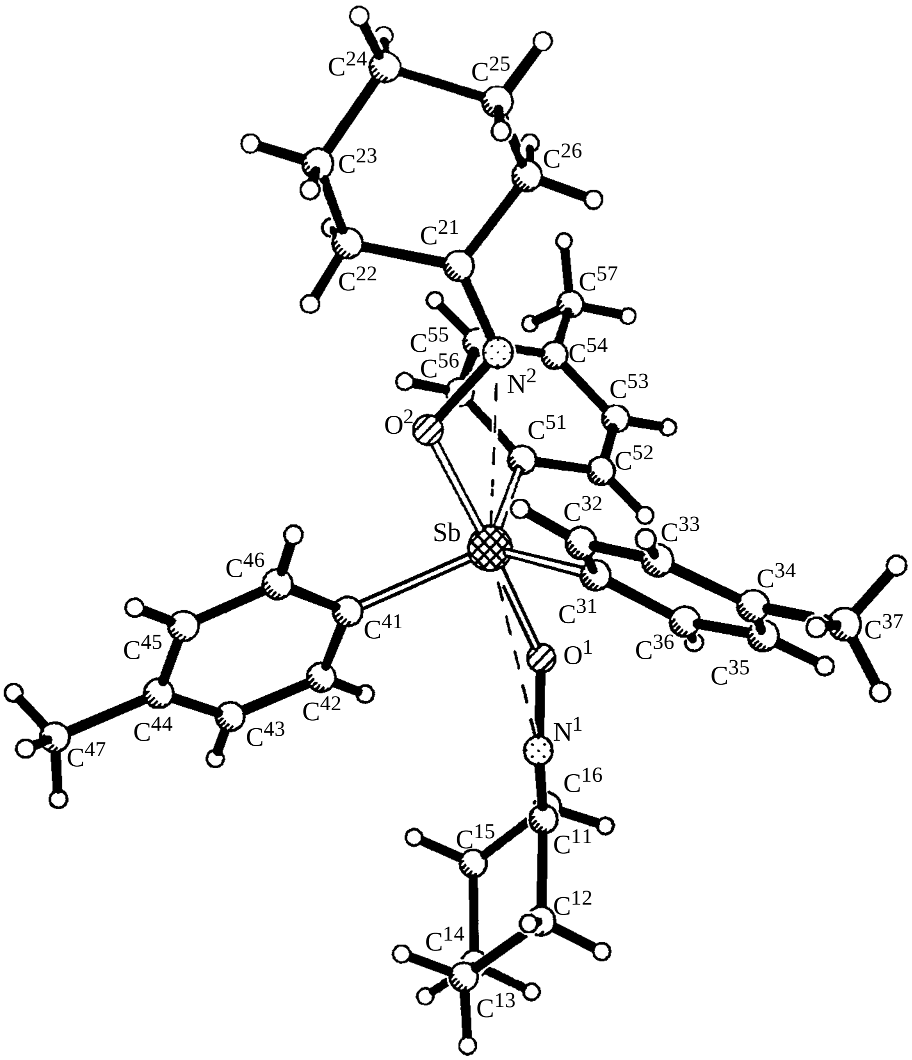

Fig. 2. Molecular structure of tri-*p*-tolylantimony bis(cyclohexanone oximate) (**II**).

the respective $N^{1,2}$–C distances are 1.418(2), 1.396(2), and 1.276(3), 1.264(4) Å; these values practically coincide with analogous interatomic distances in other triarylantimony dioximates [7, 8, 16]. The $SbO^{1,2}N^{1,2}$ angles are 111.4(1)° and 108.2(1)° in structure **I** and 111.2(1)° and 110.8(1)° in structure **II**.

Compound **I** contains $O^3H^1\cdots N^1$ and $O^4H^2\cdots N^2$ hydrogen bonds: The $O^{3,4}$–$H^{1,2}$ and $H^{1,2}\cdots N^{1,2}$ distances are 0.81(3), 1.05(3), 1.93(3), and 1.73(3) Å, respectively. The $O^{3.4}H^{1,2}N^{1,2}$ angles are 140° and 144°. The rings formed hydrogen bonds are not fully planar. The dihedral angle between the $N^1C^{47}C^{41}$ and $C^{42}O^3H^1$ planes is 8.0°, and the angle between the $N^2C^{57}C^{51}$ and $C^{52}O^4H^2$ planes is 2.3°. The lower mobility of the hydroxyl hydrogen atoms in 5-bromo-2-hydroxybenzaldoxime compared to the hydrogen atoms of the oxime groups is probably explained by involvement of the first ones in hydrogen-bond formation.

Note that the geometric parameters of tri-*p*-tolylantimony bis(cyclohexanone oximate) (**II**) and triphenylantimony bis(cyclohexanone oximate) [8], as well as of tri-*p*-tolylantimony bis(acetophenone oximate) [8] and its phenyl analog [7] practically do not differ from each other, implying a weak effect the electron-donor methyl groups in the aryl ligands on the antimony atom exert on the geometry of these molecules.

The distances between the Sb atom and the oximate nitrogen atoms Sb···N [2.832(2) and 2.895(2) Å in **I** and 2.861(2) and 2.890(2) Å in **II**] are shorter than the sum of the van der Waals radii of Sb and N (3.8 Å). The presence of an intramolecular Sb···N contact in compounds **I** and **II** does not significantly affect the equatorial angles which only slightly differ from the theoretical value of 120°, unlike what is observed in triarylantimony dicarboxylates, where intramolecular Sb···O=C contacts much increase one of the equatorial angles (143.8–151.7°) [22–28]. Bidentate ligation of the oximate ligand was observed in all previously structurally characterized tri- and tetraarylantimony oximates [5, 7, 8, 15, 19].

Additional coordination of a ligand with the antimony atom is determined by the presence of atoms with lone electron pairs and by geometric factors, specifically by the distances of the central atom to the ligand and electron-pair donor. The Sb–O bond length in triarylantimony dioximates [7, 8] is close to the sum of the covalent radii of Sb and O, which ensures interaction between Sb and the oximate nitrogen. The fact that the Sb···N distances in triarylantimony dioximates are much shorter than those expected by the van der Waals radii points to strong intramolecular donor–acceptor interactions in these compounds, which may be one of the reasons for their stability.

EXPERIMENTAL

X-ray diffraction analysis of crystals of triphenylantimony bis(5-bromo-2-hydroxybenzaldoxime) $C_{32}H_{25}Br_2N_2O_4Sb$ (I) was carried out on a Bruker SMART-1000CCD diffractometer (λMoK_α 0.71073 Å, graphite monochromator). Monoclinic crystals; at 24°C, a 12.774(2), b 11.837(3) Å; β 106.683(3)°, V 3030.2(7) Å^3, Z 4, d_{calc} 1.717 g cm^{-3}, space group $P2_1/n$. Intensities of 20219 reflections were measured, 4277 of which had $I > 2\sigma(I)$. Final divergence factors: R 0.036 and R_W 0.0787 [on 4277 reflections with $F^2 > 2\sigma(F^2)$].

X-ray diffraction analysis of crystals of tri-*p*-tolylantimony bis(cyclohexanone oximate) $C_{33}H_{41}\cdot N_2O_2Sb$ (II) was carried out on a Bruker SMART-1000CCD diffractometer (λMoK_α 0.71073 Å, graphite monochromator). Triclinic crystals; at 20°C, a 10.632(1), b 12.415(2), c 13.166(2) Å; α 77.023(2), β 68.288, γ 83.509(2)°, V 1572.4(3) Å^3, Z 2, d_{calc} 1.308 g cm^{-3}, space group P-1. Intensities of 20143 reflections were measured, 4959 of which had $I > 2\sigma(I)$. Final divergence factors: R 0.0368 and R_W 0.0792 [on 4959 reflections with $F^2 > 2\sigma(F^2)$].

Absorption was included by equivalent reflections. The structures were solved by the direct method and refined by the least-squares method anisotropically for non-hydrogen atoms. Hydrogen atoms were located geometrically and included in the refinement by means of the rider model. Data collection and edition and refinement of unit cell parameters were carried out using the SMART and SAINT Plus programs [33]. All calculations on structure determination and refinement were carried out using the SHELXTL/PC program [34]. The coordinates of non-hydrogen atoms are listed in Table 1, and the interatomic distances and bond angles, in Table 2.

Triphenylantimony bis(5-bromo-2-hydroxybenzaldoximate (I). To a solution of 0.50 g of triphenylantimony and 0.61 g of 5-bromo-2-hydroxybenzaldoxime in 20 ml of diethyl ether, 0.16 ml of 30% aqueous hydrogen peroxide was added. The resulting mixture was kept for 12 h at 20°C. Colorless crystals formed and were filtered off and dried to give 0.91 g (82%) of compound **I**, mp 203°C (decomp.).

Tri-*p*-tolylantimony bis(cyclohexanone oximate) (II). A mixture of 0.50 g of penta-*p*-tolylantimony and 0.19 g of cyclohexanone oxime in 10 ml of toluene was heated for 1 h at 90°C. After cooling, the solvent was removed, and the residue was crystallized from toluene–petroleum ether, 1 : 3 v/v. Yield 0.46 g (86%), mp 160°C (145°C [4]).

Similarly we obtained **triphenylantimony bis(cyclohexanone oximate) (III),** 67%, mp 124°C (116°C [4]); **triphenylantimony bis(benzophenone oximate) (IV),** 82%, mp 118°C (117°C [5]); and **tri-*p*-tolylantimony bis(acetophenone oximate) (V),** 91%, mp 125°C (126°C [8]).

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