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# Syntheses and Structures of Tetraphenylantimony Oximates: $Ph_4SbON{=}CHR$ ($R = C_6H_4Br$-2, $C_6H_4NO_2$-2, $C_4H_3S$)

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**Abstract**—The reactions of pentaphenylantimony with oximes or triphenylantimony dioximates in toluene afford tetraphenylantimony oximates $Ph_4SbON{=}CHR$ ($R = C_6H_4Br$-2 (**I**), $C_6H_4NO_2$-2 (**II**), and $C_4H_3S$-2 (**III**)). Triphenylantimony dioximates are synthesized by oxidative addition from triphenylantimony and oxime in diethyl ether in the presence of *tert*-butyl hydroperoxide. According to the X-ray diffraction data (CIF files CCDC no. 1055414 (**I**), 1055634 (**II**), and 1061727 (**III**)), the coordination mode of the antimony atoms in the molecules of compounds **I**–**III** is a distorted trigonal bipyramid with the oxygen atom of the oximate ligand in the axial position. The structural organization of the crystals is caused by weak hydrogen bonds.

**Keywords:** oximate, tetraphenylantimony, synthesis, structure, X-ray diffraction analysis

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## INTRODUCTION

On the one hand, organic antimony derivatives containing oximate ligands are interesting as compounds exhibiting biological activity [1–6]. On the other hand, oximes are ampolydentate ligands and, hence, attract attention as objects of coordination chemistry. An analysis of literature data shows that the publications are mainly devoted to the study of triarylantimony dioximates, whereas tetraarylantimony oximates can be considered as poorly studied compounds. Three methods for their synthesis were proposed: via substitution from tetraphenylantimony bromide and silver salts of oximes [7], by the dephenylation of pentaphenylantimony with oximes [8, 9], and via the ligand redistribution reaction from pentaphenylantimony and triphenylantimony dioximates [9]. Undoubtedly, the second method is attractive, since the synthesis proceeds in one step and affords only one solid product. However, it is established that the dephenylation of pentaphenylantimony by ketoximes sometimes includes the elimination of two phenyl groups, which is not characteristic of this reaction, and the formation of triphenylantimony dioximates [10].

In order to further study the methods for synthesis of tetraphenylantimony oximates, in this work we carried out the reactions of pentaphenylantimony with oximes containing various functional groups and with triphenylantimony dioximates and also established the structures of the obtained products $Ph_4SbON{=}CHR$ ($R = C_6H_4Br$-2 (**I**), $C_6H_4NO_2$-2 (**II**), and $C_4H_3S$-2 (**III**)).

## EXPERIMENTAL

**Synthesis of compound I.** A mixture of pentaphenylantimony (0.15 g, 0.30 mmol), 2-bromobenzaldoxime (0.06 g, 0.30 mmol), and toluene (4 mL) was heated in a boiling water bath for 15 min and cooled. Yellow transparent crystals were formed on concentrating the solution. The yield of compound **I** was 0.16 g (86%), mp = 175°C.

IR, ν, $cm^{-1}$: 3553, 3476, 3416, 1616, 1589, 1574, 1549, 1477, 1433, 1398, 1364, 1061, 1020, 972, 943, 750, 729, 694, 636, 446.

For $C_{31}H_{25}NOBrSb$

| | | |
|---|---|---|
| anal. calcd., %: | C, 59.14; | H, 3.97. |
| Found, %: | C, 59.07; | H, 4.06. |

Compounds **II** and **III** were synthesized using a similar procedure.

Compound **II**: light brown transparent crystals, 90% yield, mp = 162°C. IR, ν, $cm^{-1}$: 3552, 3478, 3456, 3415, 1618, 1595, 1541, 1506, 1479, 1433, 1342, 1327, 1280, 1109, 1064, 1013, 997, 966, 908, 881, 841, 729, 690, 528, 507, 482, 469, 446.

For $C_{31}H_{25}N_2O_3Sb$

| | | |
|---|---|---|
| anal. calcd., %: | C, 62.52; | H, 4.20. |
| Found, %: | C, 62.37; | H, 4.37. |

Compound **III**: brown transparent crystals, 91% yield, mp = 113°C. IR, ν, $cm^{-1}$: 3547, 3415, 1630, 1591, 1574, 1474, 1433, 1418, 1364, 1352, 1333, 1302, 1229, 1063, 1020, 997, 933, 882, 820, 729, 692,455, 447.

For $C_{36}H_{32}NOSSb$

| | | |
|---|---|---|
| anal. calcd., %: | C, 66.66; | H, 4.94. |
| Found, %: | C, 66.48; | H, 5.18. |

**Synthesis of $Ph_3Sb(ON{=}CHC_6H_4Br\text{-}2)_2$ (IV).** A mixture of triphenylantimony (0.15 g, 0.43 mmol), 2-bromobenzaldoxime (0.17 g, 0.86 mmol), and a 70% aqueous solution of *tert*-butyl hydroperoxide (0.055 g, 0.43 mmol) in diethyl ether (30 mL) was kept at room temperature for 24 h. The formed colorless crystals were filtered off and dried. The yield of compound **IV** was 0.30 g (94%), mp = 183°C.

IR, ν, $cm^{-1}$: 3521, 3479, 3416, 1616, 1580, 1553, 1465, 1435, 1385, 1362, 1328, 1020, 997, 943, 874, 752, 735, 711, 640, 552, 474, 457, 444.

For $C_{32}H_{25}Br_2N_2O_2Sb$

| | | |
|---|---|---|
| anal. calcd., %: | C, 51.13; | H, 3.33. |
| Found, %: | C, 51.02; | H, 3.47. |

Compounds $Ph_3Sb(ON{=}CHC_6H_4NO_2\text{-}2)_2$ (**V**) and $Ph_3Sb(ON{=}CHC_4H_3S\text{-}2)_2$ (**VI**) were synthesized using a similar procedure.

Compound **V**: yellow crystals, 97% yield, mp = 173°C). IR, ν, $cm^{-1}$: 3551, 3476, 3446, 1636, 1616, 1582, 1518, 1477, 1343, 1298, 997, 952, 920, 883, 847, 785, 735, 691, 642, 577, 546, 517, 459.

For $C_{32}H_{25}N_4O_6Sb$

| | | |
|---|---|---|
| anal. calcd., %: | C, 56.22; | H, 3.66. |
| Found, %: | C, 56.14; | H, 3.87. |

Compound **VI**: light brown crystals, 97% yield, mp = 157°C.

IR, ν, $cm^{-1}$: 1630, 1587, 1477, 1437, 1418, 1362, 1302, 1232, 1067, 997, 932, 885, 860, 823, 733, 690, 455.

For $C_{28}H_{23}N_2O_2S_2Sb$

| | | |
|---|---|---|
| anal. calcd., %: | C, 55.54; | H, 3.80. |
| Found, %: | C, 55.27; | H, 3.97. |

**Reaction of pentaphenylantimony with triphenylantimony bis(2-bromobenzaldoximate).** A mixture of pentaphenylantimony (0.25 g, 0.50 mmol), 2-bromobenzaldoximate (0.37 g, 1.00 mmol), and toluene (10 mL) was kept at 23°C for 24 h. The solution was concentrated to a volume of 3 mL and cooled. The formed colorless crystals were filtered off and dried. The yield of compound **I** was 0.62 g (98%), mp = 175°C.

Compounds **II** (97% yield, mp = 162°C) and **III** (96% yield, mp = 113°C) were synthesized using a similar procedure.

The IR spectra of compounds **I–III** were recorded on a Shimadzu IRAffinity-1S IR spectrometer in a range of 4000–400 $cm^{-1}$ (KBr pellets).

**X-ray diffraction analyses** of the crystals of compounds **I–III** were carried out on a D8 QUEST automated four-circle diffractometer (Bruker) ($MoK_\alpha$ radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 296(2) K. The data were collected and edited, the unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [11]. All calculations on structure determination and refinement were performed using the SHELXL/PC [12] and OLEX2 programs [13]. The structures of compounds **I–III** were determined by a direct method and refined using least squares in the anisotropic approximation for non-hydrogen atoms.

The main crystallographic data and the structure refinement results are presented in Table 1. Selected bond lengths and bond angles are given in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

We found that pentaphenylantimony interacted with aldoximes containing various functional groups in a toluene solution at room temperature to form the single organoantimony product, tetraphenylantimony oximate, in the yield up to 91%

$$Ph_5Sb + HON{=}CHR \rightarrow Ph_4SbON{=}CHR + PhH$$

$$R = C_6H_4Br\text{-}2\ (\mathbf{I}),\ C_6H_4NO_2\text{-}2\ (\mathbf{II}),\ C_4H_3S\text{-}2\ (\mathbf{III}).$$

The reactions of pentaphenylantimony and triphenylantimony dioximates $Ph_3Sb(ON{=}CHR)_2$ (R = $C_6H_4Br$-2, $C_6H_4NO_2$-2, $C_4H_3S$-2) proceed in toluene via the ligand redistribution scheme

$$Ph_5Sb + Ph_3Sb(ON{=}CHR)_2 \rightarrow 2Ph_4SbON{=}CHR.$$

At room temperature the reactions occurred within days, whereas on heating (90–100°C) the complete conversion was achieved within 1 h. The melting points and IR spectra of tetraphenylantimony oxi-

**Table 1.** Crystallographic data and experimental and refinement parameters for the structures of compounds **I–III**

| Parameter | Value | | |
|---|---|---|---|
| | **I** | **II** | **III** |
| *FW* | 1258.36 | 595.28 | 648.44 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P1$ | $P2_1/c$ | $P2_1/c$ |
| $a$, Å | 10.5648(4) | 21.4509(8) | 10.3584(4) |
| $b$, Å | 11.5829(4) | 8.1827(3) | 16.1689(7) |
| $c$, Å | 12.1428(4) | 17.8601(7) | 18.5943(7) |
| α, deg | 77.163(2) | 90 | 90 |
| β, deg | 64.716(2) | 106.242(2) | 96.858(2) |
| γ, deg | 78.633(2) | 90 | 90 |
| $V$, Å$^3$ | 1301.17(8) | 3009.8(2) | 3092.0(2) |
| $Z$ | 1 | 4 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 1.606 | 1.314 | 1.393 |
| μ, mm$^{-1}$ | 2.620 | 0.947 | 0.988 |
| $F$(000) | 624.0 | 1200.0 | 1320.0 |
| Crystal size, mm | 0.28 × 0.11 × 0.1 | 0.16 × 0.12 × 0.1 | 0.58 × 0.38 × 0.36 |
| Range of data collection over 2θ, deg | 3.76–64.18 | 5.36–46.62 | 6.62–59.24 |
| Ranges of reflection indices | $-15 \leq h \leq 15$,<br>$-17 \leq k \leq 17$,<br>$-18 \leq l \leq 18$ | $-23 \leq h \leq 23$,<br>$-9 \leq k \leq 9$,<br>$-19 \leq l \leq 19$ | $-14 \leq h \leq 14$,<br>$-22 \leq k \leq 22$,<br>$-23 \leq l \leq 25$ |
| Measured reflections | 69260 | 19099 | 81499 |
| Independent reflections | 18048 | 4304 | 8690 |
| Reflections with $I \geq 2\sigma(I)$ | 13148 | 3658 | 7200 |
| Refinement variables | 631 | 334 | 362 |
| GOOF | 1.019 | 1.078 | 1.058 |
| $R$ factors for $F^2 > 2\sigma(F^2)$ | $R_1 = 0.0348$<br>$wR_2 = 0.0623$ | $R_1 = 0.0621$<br>$wR_2 = 0.1860$ | $R_1 = 0.0375$<br>$wR_2 = 0.0883$ |
| $R$ factors for all reflections | $R_1 = 0.0647$<br>$wR_2 = 0.0701$ | $R_1 = 0.0718$<br>$wR_2 = 0.1962$ | $R_1 = 0.0491$<br>$wR_2 = 0.0957$ |
| Residual electron density (min/max), $e$/Å$^3$ | 0.85/–0.87 | 2.83/–0.67 | 0.85/–0.75 |

mates synthesized by two methods were completely identical.

Triphenylantimony dioximates were synthesized by oxidative addition from triphenylantimony, oxime, and *tert*-butyl hydroperoxide in ether [14]. The yields of the products were not lower than 94%.

$$Ph_3Sb + 2HON{=}CHR + t\text{-}BuOOH$$
$$\rightarrow Ph_3Sb(ON{=}CHR)_2 + H_2O + t\text{-}BuOH$$

$R = C_6H_4Br$-2 (**IV**), $C_6H_4NO_2$-2 (**V**), $C_4H_3S$-2 (**VI**).

According to the X-ray diffraction analysis data, the antimony atoms in compounds **I–III** have a distorted trigonal bipyramidal coordination mode with the axially arranged iminoxy groups (figure). The crystal of compound **I** contains two types of crystallographically independent molecules (**a** and **b**). Compound **III** crystallizes as a solvate with toluene.

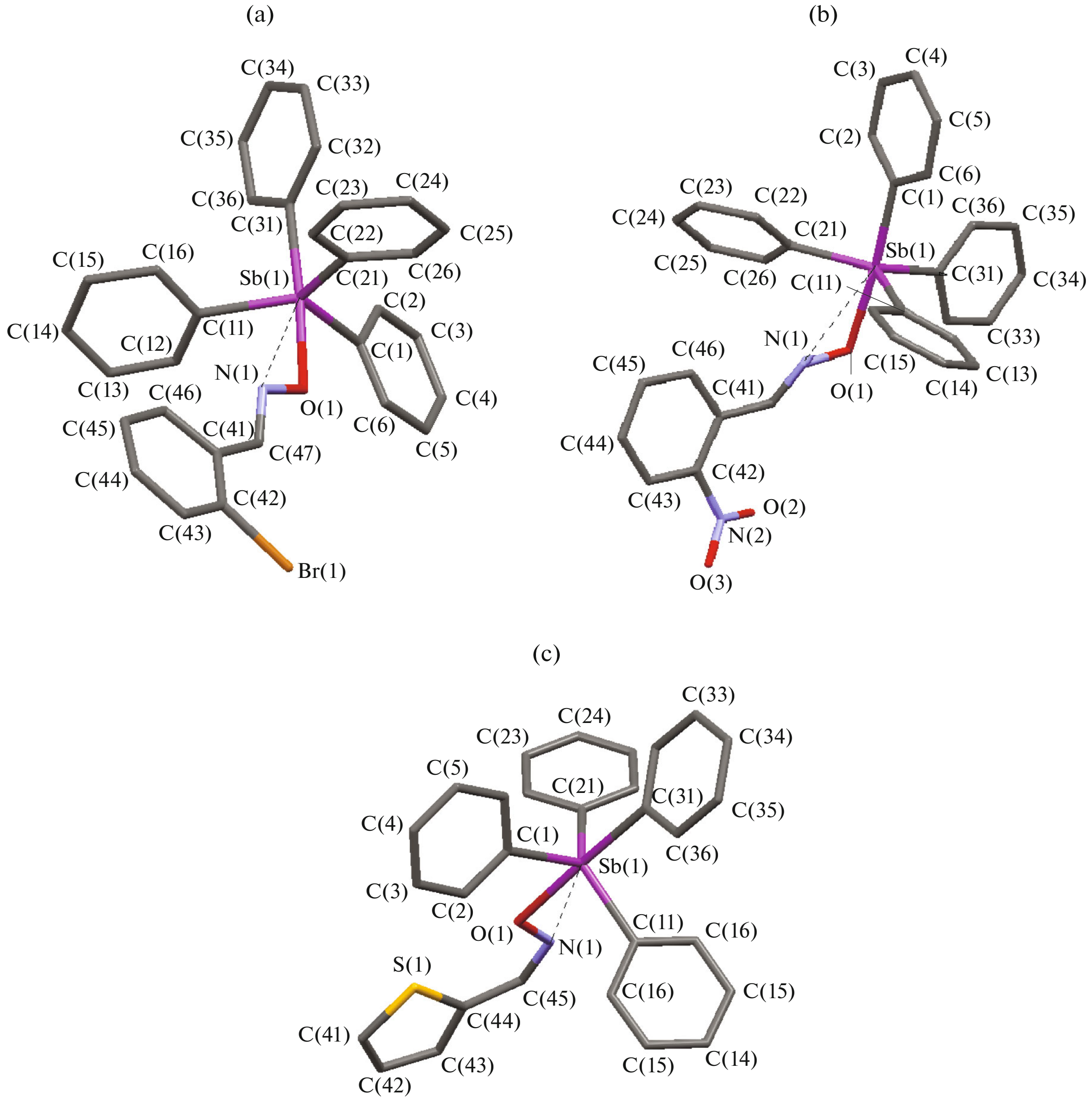
The $SbC_3$ fragments are nonplanar, and the shifts of the Sb atom from the plane [$C_3$] to the axial carbon atom are 0.159 (**Ia**), 0.147 (**Ib**), 0.188 (**II**), and 0.187 Å (**III**). The sums of the equatorial CSbC bond angles (358.3°, 358.7°, 357.7°, and 357.71° in **Ia**, **Ib**, **II**, and **III**, respectively) are less than 360°. The equatorial angles in compounds **I–III** differ from the theoretical value not more than by 6°. The equatorial Sb–C bonds in compounds **I–III** vary in a narrow range: 2.135(8)–

**Table 2.** Selected bond lengths (*d*) and bond angles (ω) in the structures of compounds **I–III**

| Bond | *d*, Å | Angle | ω, deg |
|---|---|---|---|
| **I** | | | |
| Sb(1)–O(1) | 2.138(6) | O(1)Sb(1)C(31) | 176.2(3) |
| Sb(1)–C(21) | 2.147(7) | C(1)Sb(1)O(1) | 83.6(3) |
| Sb(1)–C(1) | 2.137(9) | C(1)Sb(1)C(21) | 117.7(3) |
| Sb(1)–C(11) | 2.135(8) | C(1)Sb(1)C(31) | 97.3(3) |
| Sb(1)–C(31) | 2.216(7) | C(11)Sb(1)C(21) | 122.8(3) |
| Sb(2)–O(2) | 2.145(6) | C(11)Sb(1)C(1) | 117.8(3) |
| Sb(2)–C(81) | 2.167(8) | C(11)Sb(1)C(31) | 90.9(3) |
| Sb(2)–C(61) | 2.096(8) | O(2)Sb(2)C(81) | 176.4(3) |
| Sb(2)–C(51) | 2.117(9) | C(61)Sb(2)O(2) | 88.1(3) |
| Sb(2)–C(71) | 2.128(8) | C(61)Sb(2)C(51) | 124.2(3) |
| Br(1)–C(42) | 1.913(9) | C(61)Sb(2)C(71) | 115.0(3) |
| Br(2)–C(92) | 1.902(9) | C(51)Sb(2)C(81) | 90.6(3) |
| N(1)–O(1) | 1.392(9) | C(51)Sb(2)C(71) | 119.5(3) |
| N(1)–C(47) | 1.235(11) | C(71)Sb(2)O(2) | 84.5(3) |
| O(2)–N(2) | 1.379(10) | C(71)Sb(2)C(81) | 97.0(3) |
| Sb(1)···N(1) | 2.908(9) | | |
| Sb(2)···N(2) | 2.895(11) | | |
| **II** | | | |
| Sb(1)–O(1) | 2.178(5) | O(1)Sb(1)C(1) | 175.5(2) |
| Sb(1)–C(1) | 2.191(8) | C(21)Sb(1)O(1) | 83.5(3) |
| Sb(1)–C(21) | 2.133(8) | C(21)Sb(1)C(1) | 92.1(3) |
| Sb(1)–C(31) | 2.122(8) | C(31)Sb(1)C(1) | 98.0(3) |
| Sb(1)–C(11) | 2.090(8) | C(31)Sb(1)C(21) | 120.8(3) |
| O(1)–N(1) | 1.374(8) | C(11)Sb(1)O(1) | 86.4(3) |
| N(1)–C(47) | 1.265(10) | C(11)Sb(1)C(1) | 95.7(3) |
| O(3)–N(2) | 1.156(12) | C(11)Sb(1)C(21) | 125.9(3) |
| Sb(1)···N(1) | 2.819(9) | C(11)Sb(1)C(31) | 111.0(3) |
| **III** | | | |
| Sb(1)–C(1) | 2.126(3) | O(1)Sb(1)C(31) | 177.47(9) |
| Sb(1)–C(21) | 2.123(3) | C(1)Sb(1)O(1) | 83.63(9) |
| Sb(1)–C(31) | 2.187(2) | C(21)Sb(1)C(1) | 116.34(10) |
| Sb(1)–C(11) | 2.123(3) | C(11)Sb(1)C(1) | 118.99(11) |
| Sb(1)–O(1) | 2.1787(17) | C(11)Sb(1)C(21) | 122.38(10) |

2.147(8), 2.096(8)–2.128(8) (**Ia**, **Ib**), 2.090(8)–2.133(8) (**II**), and 2.123(3)–2.126(3) Å (**III**). The axial Sb–C bonds (2.216(7), 2.167(8), 2.191(8), 2.187(2) Å in compounds **Ia**, **Ib**, **II**, and **III**, respectively) are longer than the equatorial bonds. The Sb–O distances exceed the sum of covalent radii of the Sb and O atoms (2.07 Å [15]): 2.138(6) (**Ia**), 2.145(6) (**Ib**), 2.178(5) (**II**), and 2.1787(17) Å (**III**).

The molecules of compounds **I–III** contain intramolecular contacts between the metal and nitrogen atoms of the iminoxy groups. The Sb···N distances (2.908(9) Å (**Ia**), 2.895(11) Å (**Ib**), 2.819(9) Å (**II**), and 2.853(4) Å (**III**)) are by ~1 Å shorter than the sum of the van der Waals radii of Sb and N (3.8 Å [13]), being 74–76.5% of this value. Note that no substantial distortions of the equatorial angles are observed (120 ± 6°). However, the following relationship is observed: the shortening of the Sb···N distance is accompanied by a decrease in the SbON bond angle (109.1(5)°, 108.6(5)°, 102.7(4)°, and 104.4(1)° in compounds **Ia**, **Ib**, **II**, and **III**, respectively). The ONC angles in three



General view of the molecules: (a) **Ia**, (b) **II**, and (c) **III**.

structures have close values (113.9(2)°–114.8(6)°). No regular change in the O–N (1.392(9), 1.379(10), 1.374(8), 1.377(3) Å in compounds **Ia**, **Ib**, **II**, and **III**) and N–C (1.235(11), 1.283(10), 1.265(10), 1.273(4) Å) bond lengths is observed.

The crystal structures of compounds **I–III** are determined by weak hydrogen bonds C···H (2.69 Å) (**I**), O···H (2.65–2.68 Å) (**II**), and N···H (2.72 Å) (**III**).

Thus, the reactions of pentaphenylantimony with aldoximes containing functional groups in the organic radical make it possible to synthesize tetraphenylantimony oximates in high yields. The reactions of ligand redistribution between pentaphenylantimony and triphenylantimony dioximates are also efficient.

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