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Tetra(*para*-Tolyl)antimony Aroxides $(4\text{-}MeC_6H_4)_4SbOAr$ (Ar = $C_6H_3Cl_2$-2,6, $C_6H_3(NO_2)_2$-2,4, and $C_6H_2(NO_2)_3$-2,4,6): Syntheses and Structures

V. V. Sharutin[a], *, O. K. Sharutina[a], and P. V. Andreev[b]

[a] *National Research Southern Ural State University, Chelyabinsk, Russia*
[b] *Nizhni Novgorod State University, Nizhni Novgorod, Russia*
**e-mail: vvsharutin@rambler.ru*

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Abstract—Tetra(*para*-tolyl)antimony aroxides, $[(4\text{-}MeC_6H_4)_4SbOC_6H_3Cl_2\text{-}2,6] \cdot 1/2TolH$ (**IA**, **IB**), $(4\text{-}MeC_6H_4)_4SbOC_6H_3(NO_2)_2$-2,4 (**II**), and $(4\text{-}MeC_6H_4)_4SbOC_6H_2(NO_2)_3$-2,4,6 (**III**), are synthesized by the reactions of penta-*para*-tolylantimony with 2,6-dichlorophenol, 2,4-dinitrophenol, and 2,4,6-trinitrophenol, respectively, in toluene. The structures of the synthesized compounds are determined by X-ray diffraction analysis (CIF files CCDC 1050584 (**I**), 1433797 (**II**), and 999305 (**III**)). The Sb atoms in compounds **IA**, **IB**, and **II** have a distorted trigonal bipyramidal coordination with the aroxy groups in the axial positions (axial angles CSbO are 178.01(6)°, 177.74(7)°, and 174.42(11)° and Sb–O angles are 2.244(1), 2.230(2), and 2.507(3) Å). In crystal **III**, the CSbC angles in the tetrahedral cation $[(4\text{-}MeC_6H_4)_4Sb]^+$ are 103.6(2)°–116.22(2)°. A weak interaction is observed between the cation and picrate anion $[OC_6H_2(NO_2)_3\text{-}2,4,6]^-$ (Sb···O distance is 3.472(3) Å).

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INTRODUCTION

It is known that in the antimony derivatives of the general formula R_4SbX the coordination polyhedron of the central atom and the character of its binding with the electronegative ligand X are determined by the nature of the ligand and organic radicals R. For example, the coordination polyhedron of Sb in molecules of tetraphenylantimony methoxide [1] and tetraphenylantimony hydroxide [2] is an almost undistorted trigonal bipyramid and the Sb–O bonds can be characterized as covalent polar ones. The crystal of tetraphenylantimony perchlorate contains the tetraphenylstibonium cation (the antimony atom is tetracoordinate) and anions ClO_4^- [3]. However, in the predominant majority of compounds R_4SbX, the antimony atoms have a distorted trigonal bipyramidal coordination mode. These compounds are of doubtless interest, since they allow one to reveal the factors determining the degree of distortion.

An analysis of the published structural data for tetraphenylantimony aroxides Ph_4SbOAr shows an increase in the distortion of the coordination polyhedron of the central atom if the Ar group contains substituents exhibiting electron-withdrawing properties [4–9].

Continuing the study of the influence of the nature of phenol and aryl radicals at the antimony atom on the geometric characteristics of molecules of tetraarylantimony aroxides, we synthesized and structurally characterized three new tetra(*para*-tolyl)antimony aroxides: $[(4\text{-}MeC_6H_4)_4SbOC_6H_3Cl_2\text{-}2,6] \cdot 1/2TolH$ (**I**), $(4\text{-}MeC_6H_4)_4SbOC_6H_3(NO_2)_2$-2,4 (**II**), and $(4\text{-}MeC_6H_4)_4SbOC_6H_2(NO_2)_3$-2,4,6 (**III**).

EXPERIMENTAL

Synthesis of tetra(*para*-tolyl)antimony 2,6-dichlorophenoxide toluene solvate (I). A mixture of penta(*para*-tolyl)antimony (0.29 g, 0.5 mmol) and 2,6-dichlorophenol (0.08 g, 0.5 mmol) in toluene (3 mL) was kept for 24 h at room temperature, and the solvent was removed slowly. The yield of colorless crystals of compound **I** was 0.31 g (89%); T_m = 175°C. IR, ν, cm^{-1}: 1590, 1573, 1494, 1291, 1191, 1065, 1015, 851, 799, 776, 731, 698, 615, 579, 496.

For $C_{37.5}H_{35}OCl_2Sb$

anal. calcd., %:	C, 64.84;	H, 5.04;	Cl, 10.23.
Found, %:	C, 64.53;	H, 5.05;	Cl, 9.96.

Compounds **II** and **III** were synthesized similarly.

The yield of compound **II** was 93%, T_m = 167°C. IR, ν, cm^{-1}: 1598, 1575, 1521, 1496, 1326, 1264, 1191,

1133, 1121, 1069, 1017, 915, 836, 808, 754, 716, 698, 639, 579, 527, 488.

For $C_{34}H_{31}N_2O_5Sb$

anal. calcd., %:	C, 60.98;	H, 4.63;	N, 4.18.
Found, %:	C, 60.71;	H, 4.69;	N, 4.06.

The yield of compound **III** was 95%, T_m = 131°C. IR, ν, cm^{-1}: 1629, 1611, 1592, 1557, 1504, 1343, 1306, 1287, 1277, 1195, 1164, 1073, 1013, 916, 795, 749, 725, 712, 585, 482.

For $C_{34}H_{30}N_3O_7Sb$

anal. calcd., %:	C, 57.14;	H, 4.20;	N, 5.88.
Found, %:	C, 57.02;	H, 4.24;	N, 5.75.

The IR spectra of compounds **I**–**III** were recorded on a Bruker Tensor 27 spectrometer in Nujol in a range of 4000–400 cm^{-1}.

The X-ray diffraction analyses of crystals **I**–**III** were carried out on a D8 QUEST diffractometer (Bruker) at 296(2) K (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data collection and editing, the refinement of unit cell parameters, and the application of an absorption correction were carried out using the SMART and SAINT-Plus programs [10]. All calculations on the determination and refinement of structures **I**–**III** were performed using the SHELXL/PC [11] and OLEX2 programs [12]. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and results for the refinement of structures **I**–**III** 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 (CCDC 1050584 (**I**), 1433797 (**II**), and 999305 (**III**); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Tetra-*para*-tolylantimony aroxides **I**–**III** were synthesized by the dearylation of penta-*para*-tolylantimony with the corresponding phenol under mild conditions in yields close to the quantitative one.

$$(4\text{-}MeC_6H_4)_5Sb + ArOH \rightarrow (4\text{-}MeC_6H_4)_4SbOAr + MeC_6H_5$$

Ar = $C_6H_3Cl_2$-2,6 (**I**), $C_6H_3(NO_2)_2$-2,4 (**II**), $C_6H_2(NO_2)_3$-2,4,6 (**III**)

Compounds **I**–**III** were crystallized directly from a toluene solution upon its concentrating (compound **I** was obtained as a toluene solvate).

According to the X-ray diffraction analysis data, the antimony atoms in compounds **I** and **II** have a distorted trigonal bipyramidal coordination mode with the oxygen atoms of the aroxyl group in the axial position (Figs. 1a, 1b). The crystal of compound **I** contains two types of crystallographically independent molecules (**A** and **B**). The structure of molecule **A** is shown in Fig. 1.

The axial angles OSbC are 178.01(6)°, 177.74(7)° in **IA**, **IB** and 174.42(11)° in **II**. The sum of the CSbC angles in the equatorial plane is 357.6(3)°, 358.1(4)° in **IA**, **IB** and 354.4(7)° in **II**. The antimony atoms shift from the equatorial planes [C_3] to the axial carbon atoms by 0.189 Å in **IA**, 0.167 Å in **IB**, and 0.402 Å in **II**, resulting in a deviation of the values of angles between the axial and equatorial bonds from a theoretical value of 90°. The $OSbC_{eq}$ angles change in the ranges 83.07(6)°–86.07(7)°, 84.41(7)°–86.18(7)° in **IA**, **IB** and 75.31(12)°–82.97(12)° in **II**. The $C_{ax}SbC_{eq}$ angles change in the ranges 94.99(8)°–95.36(8)°, 93.34(9)°–95.48(9)° in **IA**, **IB** and 99.71(15)°–102.99(18)° in **II**. The Sb–C_{eq} bonds are 2.090(2)–2.133(2), 2.089(2)–2.130(2) Å in **IA**, **IB** and 2.105(4)–2.111(3) Å in **II**. The Sb–C_{ax} bonds (2.168(2), 2.178(2) (**IA**, **IB**) and 2.134(4) Å (**II**)) are longer than the equatorial bonds, which is characteristic of the trigonal bipyramidal coordination mode of the central atom. The ratios of the Sb–C_{ax} distances to the average values of the Sb–C_{eq} bonds are 1.026 (**IA**), 1.032 (**IB**), and 1.012 (**II**). The Sb–O distances (2.244(1), 2.230(2) Å in **IA**, **IB** and 2.507(3) Å in **II**) significantly exceed the sum of covalent radii of the antimony and oxygen atoms (2.07 Å [13]).

All observed geometric parameters for a molecule of compound **II** (a decrease in the sum of the equatorial angles, a significant shift of the antimony atom from the equatorial plane, and bringing together the values of lengths of the axial and equatorial bonds) indicate a tendency of the trigonal bipyramidal coordination mode of the antimony atom for the transition to the tetrahedral mode.

The introduction of an additional nitro group into the aroxyl ligand of compound **III** results in the formation of a ionic structure in which the $[OC_6H_2(NO_2)_3\text{-}2,4,6]^-$ anion is coordinated to the antimony atom of the tetrahedral cation $[(4\text{-}MeC_6H_4)_4Sb]^+$ (Fig. 1c). In the cation, the CSbC angles change in the range 103.6(2)°–116.2(2)°, whereas the Sb–C bonds vary from 2.074(4) to 2.103(4) Å. The Sb···O(1) distance (3.472(5) Å) is noticeably shorter than the sum of van der Waals radii of the Sb and O atoms (3.7 Å [13]). Due to this, evidently, the tetrahedral configuration of the cation is distorted.

Note that tetraphenylantimony picrate is also a ionic compound but, unlike compound **III**, the cation and anion in crystal are joined by hydrogen bonds

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

Parameter	Value		
	I	**II**	**III**
FW	1388.63	669.36	714.37
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*
a, Å	10.0012(5)	10.9836(5)	19.2536(9)
b, Å	13.6477(8)	11.3242(5)	17.0783(7)
c, Å	14.7814(8)	14.4420(6)	20.0744(9)
α, deg	63.577(2)	101.3850(10)	90
β, deg	72.949(2)	106.0690(10)	90
γ, deg	71.387(2)	106.3620(10)	90
V, Å^3	1684.90(16)	1580.62(12)	6600.8(5)
Z	1	2	8
ρ_{calcd}, g/cm^3	1.369	1.406	1.438
μ, mm^{-1}	1.004	0.915	0.887
F(000)	706	680	2896
Crystal size, mm	0.70 × 0.27 × 0.21	0.32 × 0.22 × 0.10	0.40 × 0.20 × 0.10
Data collection over θ range, deg	2.9–28.38	3.520–26.369	2.93–25.45
Ranges of reflection indices	$-13 \leqslant h \leqslant 13$, $-18 \leqslant k \leqslant 18$, $-19 \leqslant l \leqslant 19$	$-13 \leqslant h \leqslant 13$, $-11 \leqslant k \leqslant 13$, $-16 \leqslant l \leqslant 18$	$-23 \leqslant h \leqslant 23$, $-19 \leqslant k \leqslant 20$, $-24 \leqslant l \leqslant 24$
Measured reflections	107840	4733	62320 (0.0403)
Independent reflections (R_{int})	16627 (0.0262)	3886 (0.0152)	6007
Reflections with $F^2 > 2\sigma(F^2)$	14445	3570	4528
Refinement variables	757	383	410
GOOF	1.076	1.128	1.098
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0259$, $wR_2 = 0.0568$	$R_1 = 0.0303$, $wR_1 = 0.0746$	$R_1 = 0.0467$, $wR_2 = 0.1170$
R factors for all reflections	$R_1 = 0.0346$, $wR_2 = 0.0606$	$R_1 = 0.0345$, $wR_1 = 0.0786$	$R_1 = 0.0654$, $wR_2 = 0.1291$
Residual electron density (min/max), *e*/Å^3	0.59/–0.31	0.30/–0.38	1.31/–0.49

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

Bond	*d*, Å	Bond	*d*, Å
		I	
Sb(1)–O(1)	2.244(1)	Sb(2)–O(2)	2.230(2)
Sb(1)–C(11)	2.133(2)	Sb(2)–C(51)	2.089(2)
Sb(1)–C(1)	2.116(2)	Sb(2)–C(61)	2.130(2)
Sb(1)–C(21)	2.090(2)	Sb(2)–C(71)	2.112(2)
Sb(1)–C(31)	2.168(2)	Sb(2)–C(81)	2.178(2)
O(1)–C(41)	1.282(3)	O(2)–C(91)	1.338(3)
		II	
Sb(1)–O(1)	2.507(11)	Sb(1)–C(21)	2.105(4)
Sb(1)–C(1)	2.106(3)	Sb(1)–C(31)	2.134(4)
Sb(1)–C(11)	2.111(3)	O(1)–C(41)	1.270(5)
		III	
Sb(1)···O(1)	3.472(3)	Sb(1)–C(21)	2.103(4)
Sb(1)–C(1)	2.100(4)	Sb(1)–C(31)	2.099(4)
Sb(1)–C(11)	2.074(5)	O(1)–C(41)	1.230(6)
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Sb(1)C(31)	178.01(6)	O(2)Sb(2)C(81)	177.74(7)
C(1)Sb(1)C(11)	118.92(7)	C(51)Sb(2)C(61)	113.88(9)
C(21)Sb(1)C(11)	112.63(8)	C(51)Sb(2)C(71)	119.00(9)
C(21)Sb(1)C(1)	126.05(8)	C(61)Sb(2)C(71)	125.25(9)
C(11)Sb(1)C(31)	95.36(8)	C(81)Sb(2)C(51)	95.48(9)
C(1)Sb(1)C(31)	94.99(8)	C(81)Sb(2)C(61)	94.93(8)
C(21)Sb(1)C(31)	95.09(7)	C(81)Sb(2)C(71)	93.34(9)
O(1)Sb(1)C(21)	83.07(6)	O(2)Sb(2)C(51)	85.84(7)
O(1)Sb(1)C(11)	86.07(7)	O(2)Sb(2)C(61)	86.18(7)
O(1)Sb(1)C(1)	85.50(6)	O(2)Sb(2)C(71)	84.41(7)
		II	
O(1)Sb(1)C(31)	174.42(11)	C(11)Sb(1)C(31)	99.71(15)
C(1)Sb(1)C(11)	113.20(12)	C(21)Sb(1)C(31)	99.90(15)
C(21)Sb(1)C(11)	118.29(14)	O(1)Sb(1)C(1)	78.92(12)
C(21)Sb(1)C(1)	117.83(15)	O(1)Sb(1)C(11)	82.97(12)
C(1)Sb(1)C(31)	102.92(14)	O(1)Sb(1)C(21)	75.70(13)
		III	
O(1)Sb(1)C(11)	172.9(1)	C(11)Sb(1)C(21)	108.94(17)
C(1)Sb(1)C(11)	106.42(16)	C(21)Sb(1)C(31)	109.04(16)
C(1)Sb(1)C(21)	116.22(16)	O(1)Sb(1)C(1)	78.25(17)
C(1)Sb(1)C(31)	108.94(17)	O(1)Sb(1)C(21)	63.80(15)
C(11)Sb(1)C(31)	103.59(16)	O(1)Sb(1)C(31)	79.58(16)

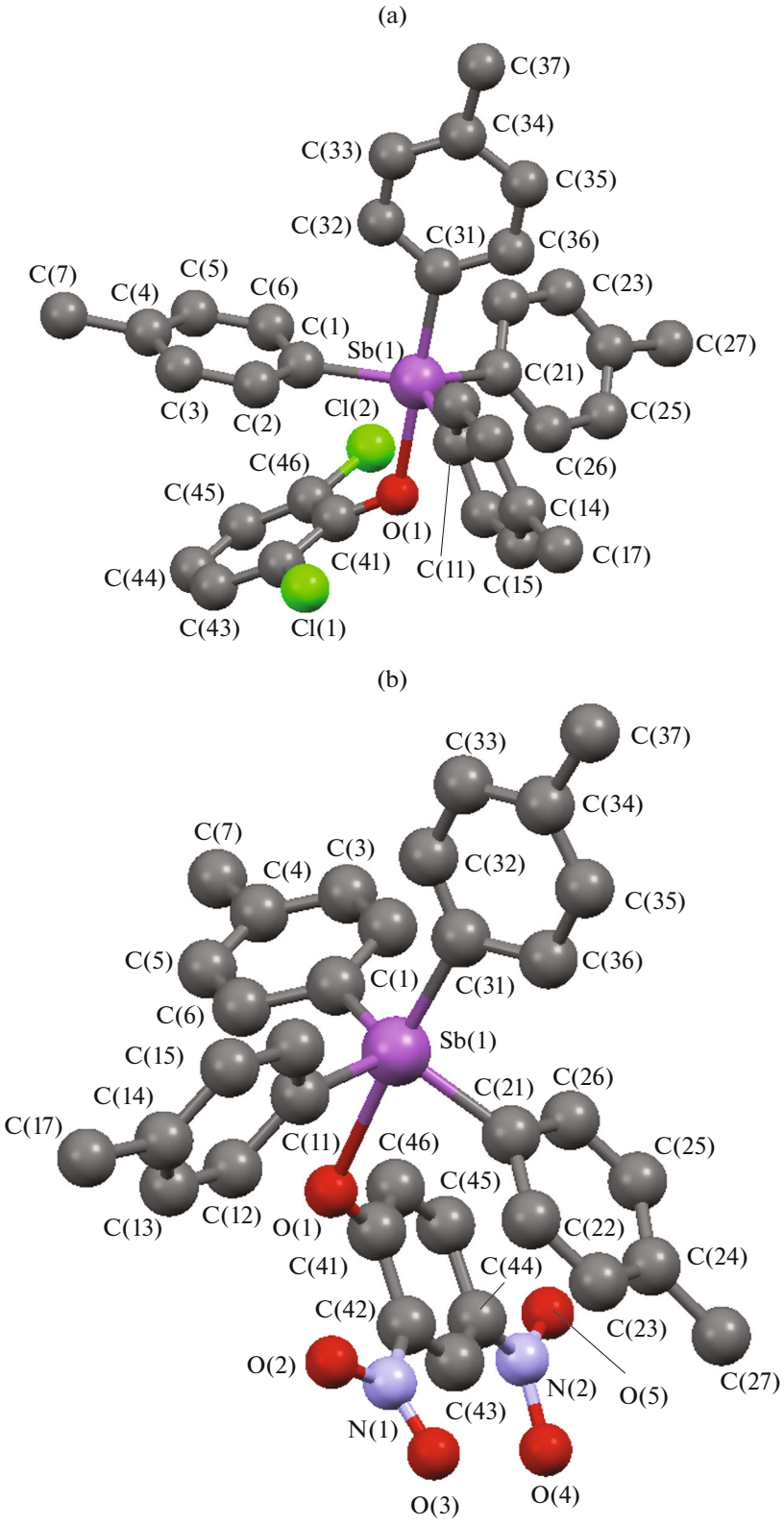

Fig. 1. Structures of compounds (a) **IA** (solvate toluene molecule is omitted), (b) **II**, and (c) **III**.

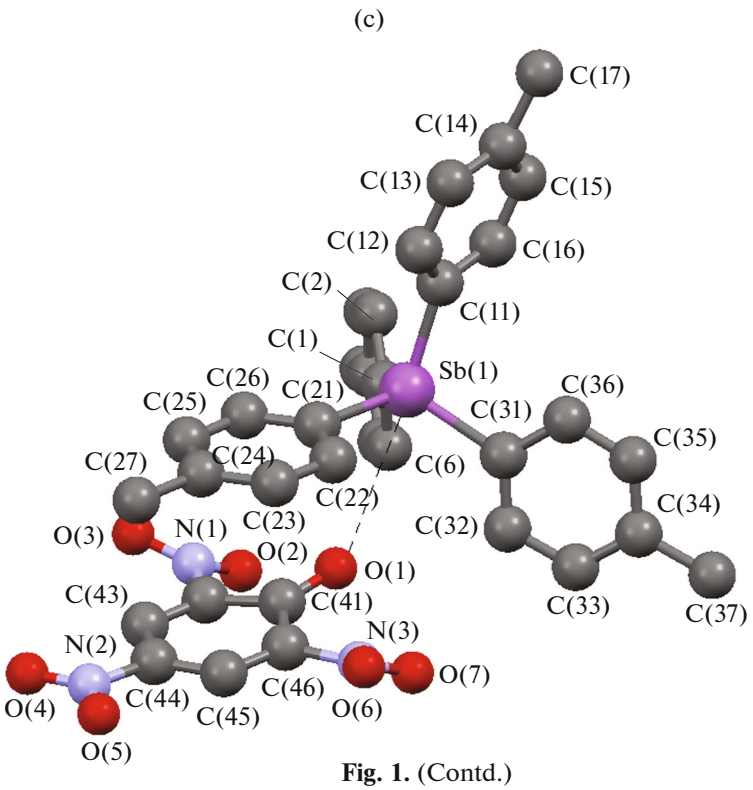

Fig. 1. (Contd.)

C_{Ph}–H···O_{Ar} only [14]. In the picrate anions of compound **III** and tetraphenylantimony picrate, the C–O bonds are equal within the experimental inaccuracy (1.230(6) and 1.232(4) Å, respectively).

The change in the coordination polyhedron of the antimony atom in the series of tetra(*para*-tolyl)antimony aroxides **I**–**III** can be explained from the viewpoint of basicity of the phenoxide anion: the lower the basicity of the latter, the weaker the Sb–O coordination bond and the more ionic the structure of compound $(4\text{-}MeC_6H_4)_4SbOAr$. As a result, three nitro groups in picrate having an inductive effect favor the stabilization of the phenoxide anion and decrease its basicity: the Ar_4Sb group is transformed into a stable tetrahedral cation.

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