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Synthesis and Structure of Tetra-*para*-tolylantimony Bromide

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Abstract—Reaction of penta-*para*-tolylantimony with tri-*para*-tolylantimony dibromide resulted in tetra-*para*-tolylantimony bromide in 97% yield. The structure of the obtained compound was proved by X-ray diffraction analysis.

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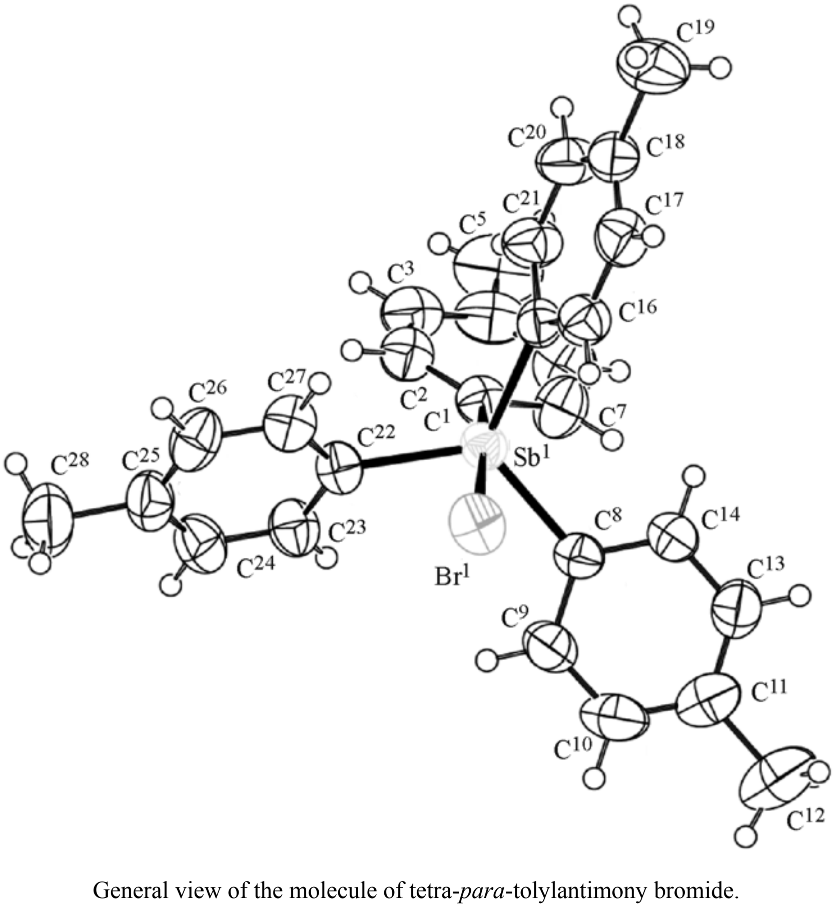
A known effective synthesis approach to antimony phenyl derivatives of general formula Ph_4SbX [X = Hlg, OC(O)R, OSO_2Ar, ON=CR_2] is based on the reaction of pentaphenylantimony with Ph_3SbX_2 [1–3], insufficiently studied with the other aryl derivatives of pentavalent antimony.

In the present work we obtained tetra-*para*-tolylantimony bromide by reacting equimolar amounts of penta-*para*-tolylantimony and tri-*para*-tolylantimony dibromide in toluene.

$$p\text{-Tol}_5\text{Sb} + p\text{-Tol}_3\text{SbBr}_2 \rightarrow 2p\text{-Tol}_4\text{SbBr}.$$



General view of the molecule of tetra-*para*-tolylantimony bromide.

Table 1. Crystal data and structure refinement for tetra-*para*-tolylantimony bromide

Parameter	Value
Formula	$C_{28}H_{28}BrSb$
M	566.16
T, K	273
Crystal system	Monoclinic
Space group	$P21/n$
a, Å	9.8565(3)
b, Å	23.2759(8)
c, Å	12.1005(4)
α, deg	90
β, deg	113.291(1)
γ, deg	90
V, Å^3	2549.86(14)
Z	4
d_{calc}, g cm^{-3}	1.475
μ, mm^{-1}	2.660
F(000)	1128.0
Crystal size, mm	0.48×0.26×0.22
Theta range for data collection, deg	4.54–55.16
Limiting indices	$-12 \le h \le 12$, $-30 \le k \le 15$, $-15 \le l \le 15$
Reflections collected	23616
Independent reflections	5879
R_{int}	0.0356
Refined parameters	275
GOOF	1.071
R-Factors on $F^2 > 2\sigma(F^2)$	R_1 0.0427 wR_2 0.0846
R-Indices (all data)	R_1 0.0623 wR_2 0.0911
Residual electron density (min/max), e Å^{-3}	0.95/–0.31

Table 2. Main bonds lengths and bond angles in the structure of tetra-*para*-tolylantimony bromide

Bond	d, Å	Angle	ω, deg
$Sb^1–Br^1$	2.9529(5)	$C^1Sb^1Br^1$	174.74(9)
$Sb^1–C^1$	2.143(4)	$C^8Sb^1C^1$	99.01(14)
$Sb^1–C^8$	2.101(4)	$C^9Sb^1C^{15}$	114.74(13)
$Sb^1–C^{15}$	2.117(3)	$C^8Sb^1C^{22}$	122.49(14)
$Sb^1–C^{22}$	2.109(3)	$C^{15}Sb^1Br^1$	88.33(10)

The reaction takes place in an aromatic hydrocarbon at room temperature within 1 day. Heating to 100°C allows achieving acomplete conversion in 1 h. After cooling the reaction product was isolated as crystalline substance. Melting point and IR spectral data were similar to those of the compound obtained by reaction of penta-*para*-tolylantimony and hydrobromic acid.

$$p\text{-Tol}_5\text{Sb} + \text{HBr} \rightarrow p\text{-Tol}_4\text{SbBr} + \text{TolH}.$$

According to X-ray diffraction (XRD) analysis, in the molecule the antimony atom has a distorted trigonal-bipyramidal coordination with the bromine atom in the axial position (see figure).

The aromatic rings in equatorial plane have a propeller conformation, wherein the angles between the plane of the rings and equatorial plane are 13.57°, 35.08°, 67.86°. High value of one of the angles causes probably intramolecular contact between the bromine atom and *ortho*-positioned hydrogen atom of the toluene ring $Br\cdots H^{16}–C^{16}$ ($Br\cdots H^{16}$ 2.71 Å,) with the sum of the van der Waals radii atoms of 3.1 Å [4]. The observed distortion of the axial angle C^1SbBr [174.74(9)°] can be ascrbed to the trend to increase the shortened distance. The fragment $Br–Sb–C^1$ is distorted due to the deviation of the Sb–Br bond towards tolyl ring ($C^8–C^{14}$) located in the equatorial plane.

The Sb atom is out-of-plane [C_3] towards the carbon atom of axial tolyl group by 0.284 Å, whereby the angles $BrSbC_{eq}$ [79.17(9)°–88.33(10)°] are less than the ideal value (90°), and values of the angles $C_{ax}SbC_{eq}$ [96.90(13)°–99.01(14)°] are larger. The sum of angles in the equatorial plane is 354.6°, and their values are different [114.7(1)°, 117.4(1)°, 122.5(1)°]. The ratio of the length of axial $Sb–C_{ax}$ bond [2.143(4) Å] to average value of the length of equatorial $Sb–C_{eq}$ bonds [2.101(4), 2.109(3), 2.117(3) Å] equals 1.016 (~1). All the observed parameters show a tendency of the C_4Sb fragment to transform into a tetrahedral structure. The distance Sb–Br [2.9529(5) Å] exceeds the sum of the covalent radii of the Sb and Br atoms (2.55 Å [4]), indicating the coordination nature of the bond. In sum, the resulting compound can be considered as a intimate ion pair of $[p\text{-Tol}_4\text{Sb}]^+$ and Br^-.

At the comparison of the geometric characteristics of Ph_4SbBr [5, 6] and $p\text{-Tol}_4\text{SbBr}$ it is seen that in the phenyl derivative the trigonal-bipyramidal coordination of the antimony atom is less distorted (the ratio of the axial Sb–C_{ax} bond to average value of the equatorial Sb–C_{eq} bonds equal to 1.023, the sum of the angles in the equatorial plane is 357.0°, average values of the angles BrSbC_{eq} and $\text{C}_{\text{ax}}\text{SbC}_{\text{eq}}$ constitute 84.09° and 96.01°. The distance Sb–Br (2.965 Å) in the phenyl derivative is more than in $p\text{-Tol}_4\text{SbBr}$. Note that in chlorides $[\text{Ar}_4\text{Sb}]^+\text{Cl}^-$ (Ar = Ph [7], *p*-Tol [8]) the contribution of the ionic form in the toluene derivative is also more than in tetraphenylantimony chloride.

EXPERIMENTAL

Single crystal XRD analysis was performed on an automatic four-circle diffractometer D8 QUEST Bruker ($\text{Mo}K_\alpha$-irradiation, λ 0.71073 Å, graphite monochromator). Data collection and refinement of the unit cell parameters were made using SMART and SAINT-Plus software [9]. The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms using SHELXL/PC software [10]. The main crystallographic data and structure refinement parameters are given in Table 1, the bond lengths and angles are listed in Table 2.

Tetra-*para*-tolylantimony bromide (I). A mixture of 0.20 g (0.35 mmol) of penta-*para*-tolylantimony and 0.19 g of tri-*para*-tolylantimony dibromide in 5 mL of toluene was heated at 100°C for 1 h. After cooling the solvent was removed. Yield 0.38 g (97%), mp 224°C. Found, %: C 59.48; H 5.07; Br 14.25. $\text{C}_{28}\text{H}_{28}\text{SbBr}$. Calculated, %: C 59.36; H 4.95; Br 14.13.

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