

# SYNTHESIS AND STRUCTURE OF TRI(META-TOLYL)ANTIMONY BIS(BENZENESULFONATE)

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Tri(*meta*-tolyl)antimony bis(benzenesulfonate) *m*-Tol<sub>3</sub>Sb(OSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (**1**) has been synthesized by interaction of tri(*meta*-tolyl)antimony with benzenesulfonic acid in the presence of *tert*-butyl hydroperoxide (mole ratio 1:2:1) in ether solution. Antimony atoms in **1** have trigonal-bipyramidal coordination with arenesulfonate substituents in axial positions (OSbO 171.05(11)°, CSbC 116.21(19)°, 117.38(18)°, 126.40(15)°). The Sb–C and Sb–O distances equal 2.091(4), 2.098(4), 2.115(4) и 2.105(2), 2.116(3) Å. Intermolecular contact (Sb⋯O 3.421(3) Å) occurs between the central atom and the oxygen atom of sulfonate group.

**Keywords:** tri(*meta*-tolyl)antimony, benzenesulfonic acid, *tert*-butyl hydroperoxide, molecular structure, X-ray diffraction analysis.

## Introduction

In the course of research on the synthesis and structure of quinquevalent antimony arenesulfonates [1–4] we have studied the reaction of tri(*meta*-tolyl)antimony with benzenesulfonic acid in the presence of *tert*-butyl hydroperoxide in ether. The structure of the obtained product has been established by X-ray diffraction analysis.

## Experimental

**Tri(*meta*-tolyl)antimony bis(benzenesulfonate) synthesis.** The mixture of 0.250 g (0.63 mmol) tri(*meta*-tolyl)antimony, 0.200 g (1.26 mmol) benzenesulfonic acid and 0.057 g 70% aqueous solution of *tert*-butyl hydroperoxide in 10 mL ether stood for 24 h at room temperature. The obtained crystals were recrystallized from toluene. The yield is 0.386 g (86%) of colorless crystals **1** with decomposition temperature 152 °C. Found, %: C 55.23, H 4.34. Calculated for C<sub>33</sub>H<sub>31</sub>O<sub>6</sub>S<sub>2</sub>Sb, %: C 55.87, H 4.37. IR spectrum, (ν, cm<sup>-1</sup>): 1320, 1140, 1140 (SO<sub>2</sub>).

**IR spectra** were recorded on the Fourier-transform spectrometer Bruker Tensor 27 in KBr pellets.

**The X-ray diffraction analyses** of crystal **1** were performed on the Bruker D8 Quest diffractometer (Mo K<sub>α</sub>-emission, λ = 0.71073 Å, graphite monochromator). The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [5]. All calculations for structure determination and refinement were performed using the SHELXL/PC [6] and OLEX2 programs [7]. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for the structures are listed in Table 1, the 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 1057589, [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk); <http://www.ccdc.cam.ac.uk>).

Table 1

Crystallographic data and the experimental and structure refinement parameters for compound **1**

Parameter	Value
Empirical formula	C <sub>33</sub> H <sub>31</sub> O <sub>6</sub> S <sub>2</sub> Sb
Formula weight	709.45
<i>T</i> , K	296
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
<i>a</i> , Å	14.4831(6)

Parameter	Value
$b$ , Å	12.7730(5)
$c$ , Å	17.7157(7)
$\alpha$ , deg	90.00
$\beta$ , deg	99.4680(10)
$\gamma$ , deg	90.00
$V$ , Å <sup>3</sup>	3232.6(2)
$Z$	4
$\rho$ (calcd.), g/cm <sup>3</sup>	1.458
$\mu$ , mm <sup>-1</sup>	1.024
$F(000)$	1440.0
Crystal size, mm	0.68 × 0.38 × 0.26
2 $\theta$ Range of data collection, deg	6.54 – 51.4°
Range of refraction indices	-17 ≤ $h$ ≤ 17, -15 ≤ $k$ ≤ 15, -21 ≤ $l$ ≤ 21
Measured reflections	40302
Independent reflections	6147
$R_{\text{int}}$	0.0288
Refinement variables	382
$GOOF$	1.081
$R$ factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0387$ , $wR_2 = 0.0866$
$R$ factors for all reflections	$R_1 = 0.0513$ , $wR_2 = 0.0973$
Residual electron density (min/max), e/Å <sup>3</sup>	0.80/-0.49

Table 2

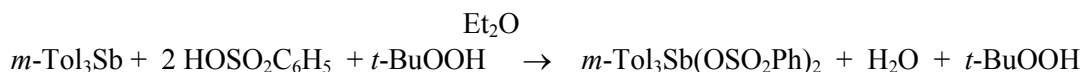
Selected bond lengths and bond angles in the structure of compound 1

Bond	$d$ , Å	Angle	$\omega$ , deg
Sb(1)–O(1)	2.116(3)	C(11)Sb(1)O(1)	94.96(14)
Sb(1)–C(11)	2.091(4)	C(11)Sb(1)C(1)	117.38(18)
Sb(1)–C(1)	2.098(4)	C(11)Sb(1)O(4)	93.68(14)
Sb(1)–O(4)	2.105(2)	C(11)Sb(1)C(21)	116.21(19)
Sb(1)–C(21)	2.115(4)	C(1)Sb(1)O(1)	85.33(13)
S(1)–O(1)	1.499(3)	C(1)Sb(1)O(4)	92.74(12)
S(1)–O(2)	1.402(4)	C(1)Sb(1)C(21)	126.40(15)
S(1)–O(3)	1.407(4)	O(4)Sb(1)O(1)	171.05(11)
S(1)–C(31)	1.772(4)	O(4)Sb(1)C(21)	85.13(14)
S(2)–O(5)	1.411(3)	C(21)Sb(1)O(1)	88.98(15)
S(2)–O(6)	1.425(3)	O(1)S(1)C(31)	100.53(19)
S(2)–O(4)	1.523(3)	O(2)S(1)O(1)	109.9(2)
S(2)–C(41)	1.765(4)	O(2)S(1)O(3)	118.3(3)
C(11)–C(12)	1.371(7)	O(2)S(1)C(31)	108.9(2)
C(11)–C(16)	1.377(7)	O(3)S(1)O(1)	109.1(2)
C(12)–C(13)	1.393(8)	O(3)S(1)C(31)	108.7(2)
C(13)–C(14)	1.394(14)	O(5)S(2)O(6)	118.2(2)
C(13)–C(17)	1.489(12)	O(5)S(2)O(4)	107.14(18)
C(14)–C(15)	1.339(14)	O(5)S(2)C(41)	108.9(2)
C(15)–C(16)	1.391(9)	O(6)S(2)O(4)	109.74(17)
C(31)–C(32)	1.362(6)	O(6)S(2)C(41)	108.1(2)
C(31)–C(36)	1.367(7)	O(4)S(2)C(41)	103.88(17)

### Results and Discussion

It is known that oxidation of tri(*meta*-tolyl)antimony by hydrogen peroxide in the presence of benzenesulfonic acid leads to formation of tri(*meta*-tolyl)antimony bis(benzenesulfonate) with 72% yield [4].

We have established that the oxidative addition reaction with the use of tri(*meta*-tolyl)antimony, benzenesulfonic acid and *tert*-butyl hydroperoxide leads to formation of the target product with 86% yield:



Note that compound **1**, obtained by this reaction, has higher melting point (152 °C), than that according to the procedure with the use of hydrogen peroxide (145 °C [4]).

From the X-ray analysis data it follows that the antimony atoms in tri(*meta*-tolyl)antimony bis(benzenesulfonate) have trigonal-bipyramidal coordination with arenesulfonate substituents in axial positions (Fig. 1).

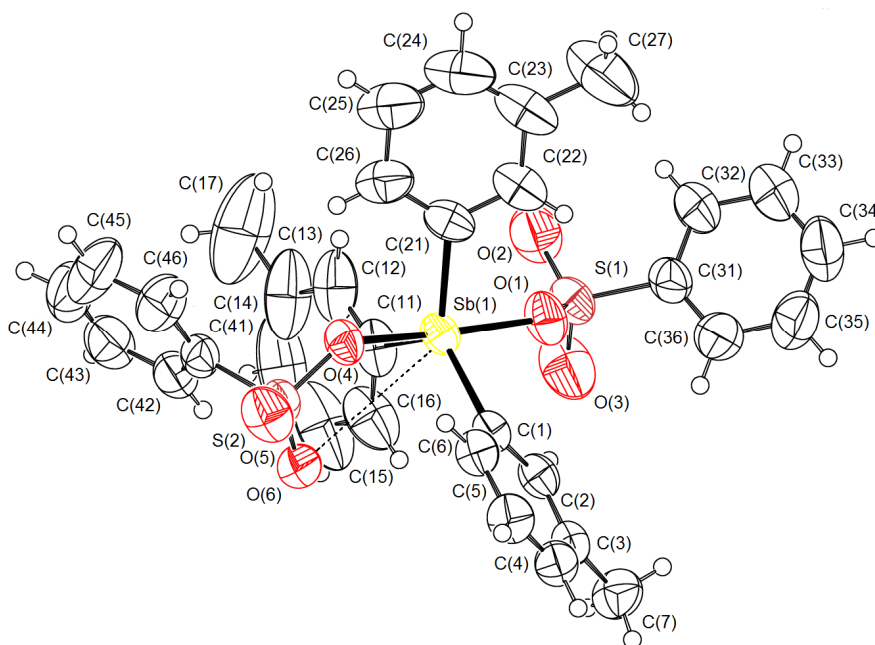


Fig. 1. The structure of compound **1**

The value of axial angle OSbO equals 171.05(11)°, the angles between equatorial phenyl substituents are unequal: 116.21(19)°, 117.38(18)°, 126.40(15)° (Table 2). Their sum (359.99°) is practically consistent with the theoretical value. This fact testifies that the antimony atoms and three carbon atoms, bonded to them, are coplanar. The distances Sb–C equal 2.091(4), 2.098(4), 2.115(4) Å, the bonds Sb–O (2.105(2), 2.116(3) Å) are of covalent character.

As viewed from the maximal equatorial angle CSbC the close intermolecular contact between the central atom and the oxygen atom O(6) of the sulfonate group is observed (Sb···O 3.421(3) Å), which is less than the sum of Van der Waals radii of antimony and oxygen atoms (3.7 Å [8]). The structural organization of the crystal is formed with the participation of weak hydrogen bonds of the type O···H (2.525, 2.650 Å).

### Conclusions

Thus, tri(*meta*-tolyl)antimony is oxidized by *tert*-butyl hydroperoxide in the presence of benzenesulfonic acid in ether to obtain tri(*meta*-tolyl)antimony bis(benzenesulfonate). In its molecule one sulfonate group is characterized by monodentate bonding type, the other one is of bidentate type.

### References

1. Sharutin V.V., Sharutina O.K., Panova L.P., Bel'skii V.K. [Tetraphenylstibonium Arenesulfonates. Synthesis and Structure]. *Russian Journal of Coordination Chemistry*, 1997, vol. 23, no. 7, pp. 513–519. (in Russ.)
2. Sharutin V.V., Sharutina O.K., Panova L.P., Bel'skii V.K. [Tetra- and Triphenylantimony Sulfonates]. *Russian Journal of General Chemistry*, 1997, vol. 67, no. 9, 1438–1442.
3. Sharutin V.V., Sharutina O.K., Panova L.P., Platonova T.P., Pakusina A.P., Bel'skii V.K. [Synthesis and Structure of Tri-*p*-Tolylantimony Ditosylate]. *Russian Journal of General Chemistry*, 2002, vol. 72, iss. 2, pp. 229–231. DOI: 10.1023/A:1015469517544
4. Sharutin V.V., Sharutina O.K., Platonova T.P., Pakusina A.P., Panova L.P., Fukin G.K., Zakharov L.N. [Synthesis and Structure of Triarylantimony Bis(arenesulfonates)]. *Russian Journal of General Chemistry*, 2003, vol. 73, iss. 3, pp. 354–357. DOI: 10.1023/A:1024945617228
5. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
6. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
7. Dolomanov O.V., Bourhis L.J., Gildea R.J., Howard J.A.K., Puschmann H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, vol. 42, pp. 339–341. DOI: 10.1107/S0021889808042726.
8. Batsanov S.S. [Atomic Radiuses of the Elements]. *Russian Journal of Inorganic Chemistry*, 1991, vol. 36, no. 12, pp. 3015–3037. (in Russ.)

Received 18 September 2015

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УДК 547.53.024+549.242+548.312.5

DOI: 10.14529/chem150412

## СИНТЕЗ И СТРОЕНИЕ БИС(БЕНЗОЛСУЛЬФОНАТА) ТРИ(МЕТА-ТОЛИЛ)СУРЬМЫ

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Взаимодействием три(*meta*-толил)сурьмы с бензолсульфоновой кислотой в присутствии *трет*бутилгидропероксида (1:2:1 мольн.) в растворе эфира синтезирован бис(бензолсульфонат) три(*meta*-толил)сурьмы (*m*-Tol<sub>3</sub>Sb(OSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>) (1). Атомы сурьмы в **1** имеют тригонально-бипирамидальную координацию с аренсульфонатными заместителями в аксиальных положениях (OSbO 171,05(11)°, CSbC 116,21(19)°, 117,38(18)°, 126,40(15)°). Расстояния Sb–C и Sb–O равны 2,091(4), 2,098(4), 2,115(4) и 2,105(2), 2,116(3) Å. Между центральным атомом и атомом кислорода сульфонатной группы имеет место внутримолекулярный контакт (Sb···O 3.421(3) Å).

Ключевые слова: три(*meta*-толил)сурьма, бензолсульфоновая кислота, *трет*-бутилгидропероксид, молекулярная структура, рентгеноструктурный анализ.

### Литература

1. Аренсульфонаты тетрафенилстибония. Синтез и строение / В.В. Шарутин, О.К. Шарутина, Л.П. Панова и др. // Журнал коорд. химии. – 1997. – Т. 23, № 7. – С. 513–519.

2. Сульфонаты тетра- и триарилсурьмы / В.В. Шарутин, О.К. Шарутина, Л.П. Панова, В.К. Бельский // Журн. общ. химии. – 1997. – Т. 67, № 9. – С. 1531–1535.
3. Синтез и строение дитозилата три-*n*-толилсурьмы / В.В. Шарутин, О.К. Шарутина, Л.П. Панова и др. // Журн. общ. химии. – 2002. – Т. 72, Вып. 2. – С. 249–251.
4. Синтез и строение бис(аренсульфонатов) триарилсурьмы / В.В. Шарутин, О.К. Шарутина, Т.П. Платонова и др. // Журн. общ. химии. – 2003. – Т. 73, Вып. 3. – С. 380–384.
5. Bruker (1998). SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System. Bruker AXS Inc., Madison, Wisconsin, USA.
6. Bruker (1998). SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data. Bruker AXS Inc., Madison, Wisconsin, USA.
7. OLEX2: a complete structure solution, refinement and analysis program / O.V. Dolomanov, L.J. Bourhis, R.J. Gildea et al. // J. Appl. Cryst. – 2009. – V. 42. – P. 339–341.
8. Бацанов, С.С. Атомные радиусы элементов / С.С. Бацанов // Журн. неорган. химии. – 1991. – Т. 36, Вып. 12. – С. 3015–3037.

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*Поступила в редакцию 18 сентября 2015 г.*

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**ОБРАЗЕЦ ЦИТИРОВАНИЯ**

Sharutin, V.V. Synthesis and structure of tri(meta-tolyl)antimony bis(benzenesulfonate) / V.V. Sharutin, O.K. Sharutina, V.S. Senchurin // Вестник ЮУрГУ. Серия «Химия». – 2015. – Т. 7, № 4. – С. 93–97. DOI: 10.14529/chem150412

**FOR CITATION**

Sharutin V.V., Sharutina O.K., Senchurin V.S. Synthesis and Structure of Tri(meta-tolyl)antimony Bis(Benzenesulfonate). *Bulletin of the South Ural State University. Ser. Chemistry*. 2015, vol. 7, no. 4, pp. 93–97. DOI: 10.14529/chem150412

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