

Synthesis and Structure of Triarylantimony Bis(arenesulfonates)

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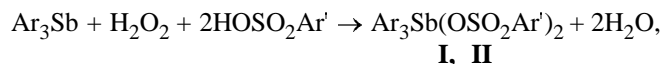
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Abstract—Triarylantimony bis(arenesulfonates) were prepared by reaction of triarylantimonies with hydrogen peroxide in the presence of arenesulfonic acids. The steric structure of the products was assessed. Triarylantimony bis(arenesulfonates) were reacted with sodium salts to obtain sodium arenesulfonates and the corresponding triarylantimony derivatives.

Antimony(V) compounds of the general formula Ph_3SbX_2 (X is an electronegative substituent) feature a trigonal-bipyramidal coordination of the central atom. However, the coordination of Sb may be distorted by intramolecular interactions with ligands X, as, for instance, in triphenylantimony diarene- and dialkanecarboxylates [1–3]. In triphenylantimony bis(benzenesulfonates), too, decreased distances between the antimony atom and the oxygen atoms of the sulfo groups, which are formally not bound with each other [the $\text{Sb}\cdots\text{O}=\text{S}$ distances are 3.274(4) and 3.445(4) Å] are observed, implying weak intramolecular interaction between these atoms [4]. However, in triphenylantimony bis(4-methylbenzenesulfonate) [5] and triphenylantimony bis(2,4-dimethylbenzenesulfonate) [6] no such interaction was revealed.

We performed an X-ray diffraction study of tri-*m*-tolylantimony bis(benzenesulfonate) (**I**) and tri-*p*-tolylantimony bis(2,5-dimethylbenzenesulfonate) (**II**), prepared by an oxidative addition reaction from triarylantimonies and hydrogen peroxide in the presence of arenesulfonic acids.



$\text{Ar} = m\text{-Tol}$, $\text{Ar}' = \text{Ph}$ (**I**); $\text{Ar} = p\text{-Tol}$, $\text{Ar}' = \text{C}_6\text{H}_3\text{Me}_2\text{-2,5}$ (**II**).

Compounds **I** and **II** have a trigonal-bipyramidal arrangement of the substituents at the central atom (Figs. 1 and 2). The sums of equatorial CSbC angles are 360 (**I**) and 359.82(12)° (**II**). The antimony atoms scarcely deviate from the equatorial plane: The deviations of Sb from the $\text{C}^1\text{C}^8\text{C}^{15}$ plane are 0.0090 (**I**) and 0.0391 Å (**II**). Axial angles are 170.6(2) (**I**) and 174.33(8)° (**II**). The respective angle in triphenylantimony bis(benzenesulfonate) is 178.3(1)°, and in

triphenylantimony bis(4-methylbenzenesulfonate) and bis(2,4-dimethylbenzenesulfonate), 176.1(2) and 176.8(1)°, respectively.

The mean $\text{Sb}-\text{C}_e$ bond lengths in disulfonates **I** and **II** are close to each other, 2.098(9) and 2.089(3) Å, respectively. The $\text{Sb}-\text{O}$ bond lengths are 2.124(5) and 2.107(5) Å (**I**) and 2.124(2), and 2.158(2) Å (**II**). The $\text{Sb}-\text{O}$ distances in triphenylantimony bis(benzenesulfonate) {2.128(2) and 2.106(3) Å [4]} are close to each other and almost coincide with analogous distances in compound **I**. In compounds **I** and **II**, shortened $\text{Sb}\cdots\text{O}=\text{S}$ contacts are revealed. The $\text{Sb}\cdots\text{O}^6$ and $\text{Sb}\cdots\text{O}^{3,6}$ distances are 3.427 (**I**) and 3.438, and 3.334 Å (**II**), which is smaller than the sum of the Van der Waals radii of these atoms (3.7 Å [7]). Note that the $\text{Sb}\cdots\text{O}=\text{S}$ intramolecular interactions result in lengthening of the corresponding $\text{S}=\text{O}$ distances. The S^2-O^6 [1.423(6) Å] (**I**) and S^1-O^3 [1.436(2) Å] and S^2-O^6 distances [1.440(3) Å] (**II**) almost coincide with the $\text{S}=\text{O}$ distances [1.412(7)–1.434(3) Å], where the O atoms are not involved in additional interactions with Sb. Moreover, equatorial CSbC angles in **I** and **II** are slightly enlarged from the side of the intramolecular contact. On this basis we can propose that the $\text{Sb}\cdots\text{O}$ interactions in disulfonates **I** and **II** are weak.

The fact that compound **II** contains two intramolecular contacts, whereas compound **I** contains one such contact appears to be a consequence of the steric situation in the coordination sphere of the Sb atoms. In compound **II**, the methyl substituents in the aryl rings are in the *para* positions, while in disulfonate **I**, in the *meta* positions. Thus, in the latter compound, stronger steric hindrances to additional coordination of Sb take place. This is indirectly evidenced by the magnitudes of the SbOS angles: 136.2(4) and 131.5(3)° in **I** and 129.82(13) and 127.57(14)° in **II**.

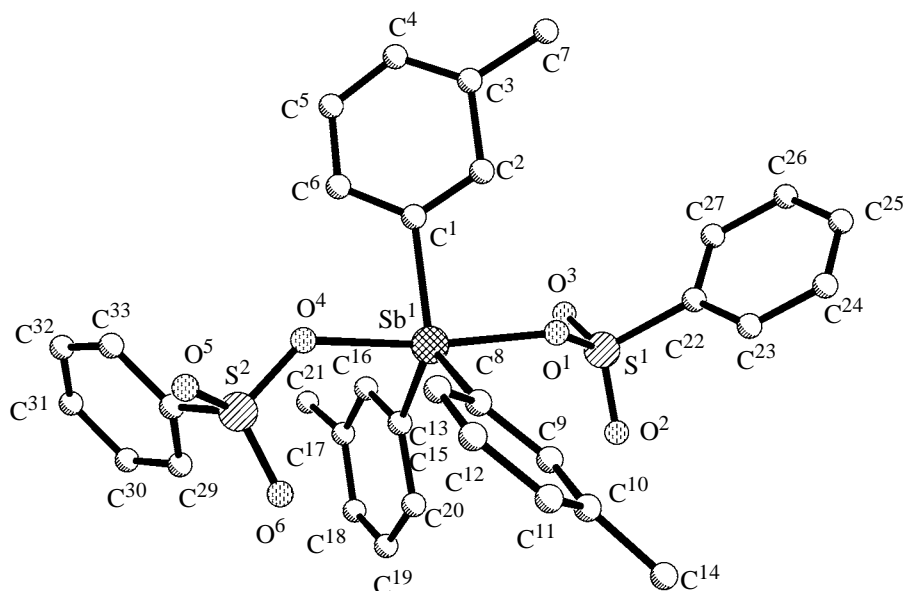


Fig. 1. General view of the molecule of tri-*m*-tolylantimony bis(benzenesulfonate) (I).

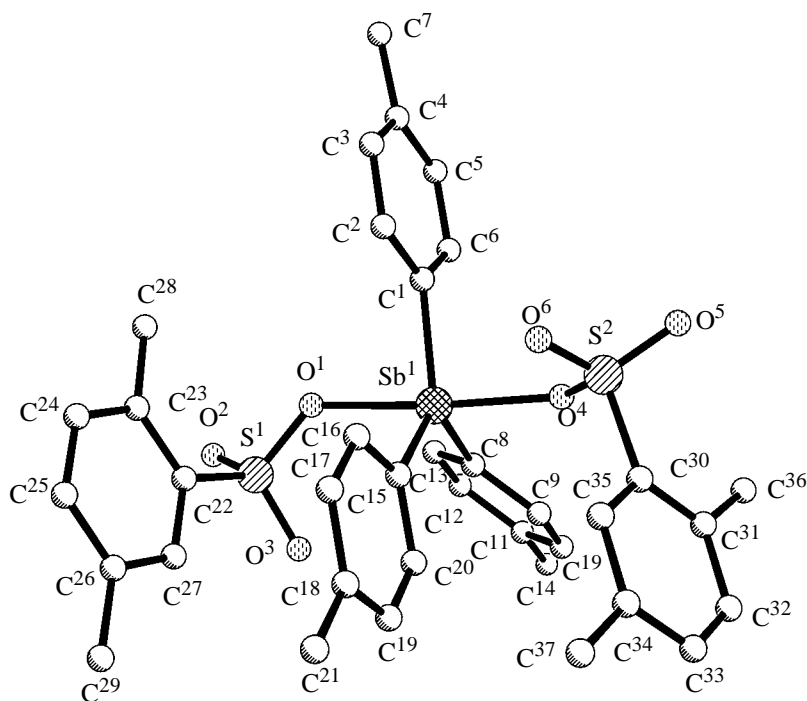
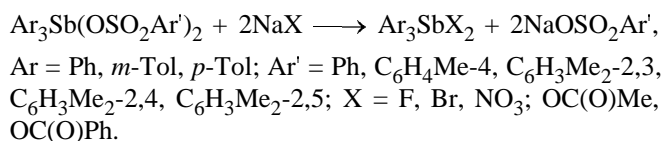


Fig. 2. General view of the molecule of tri-*p*-tolylantimony bis(2,5-dimethylbenzenesulfonate) (II).

Molecules of compound I in crystal form a complex system of weak intermolecular O...H interactions (Fig. 3). The O...H distances are 2.429–2.543 Å, and the angle at the H atom is 154.1–166.0°, which much exceeds the geometrical criterion for H bond { $d(\text{O}\cdots\text{H}) < 2.1$ Å [8]}, but is much smaller than the sum of the Van der Waals radii of O and H (2.7 Å [7]).

Reactions of triphenylantimony bis(benzenesul-

fonate) with metal chlorides, as shown in [4], involve substitution of the benzenesulfonate moieties by chlorine. We found that triarylantimony bis(arenesulfonates) react with sodium fluoride, bromide, nitrate, and acylates in a similar way.



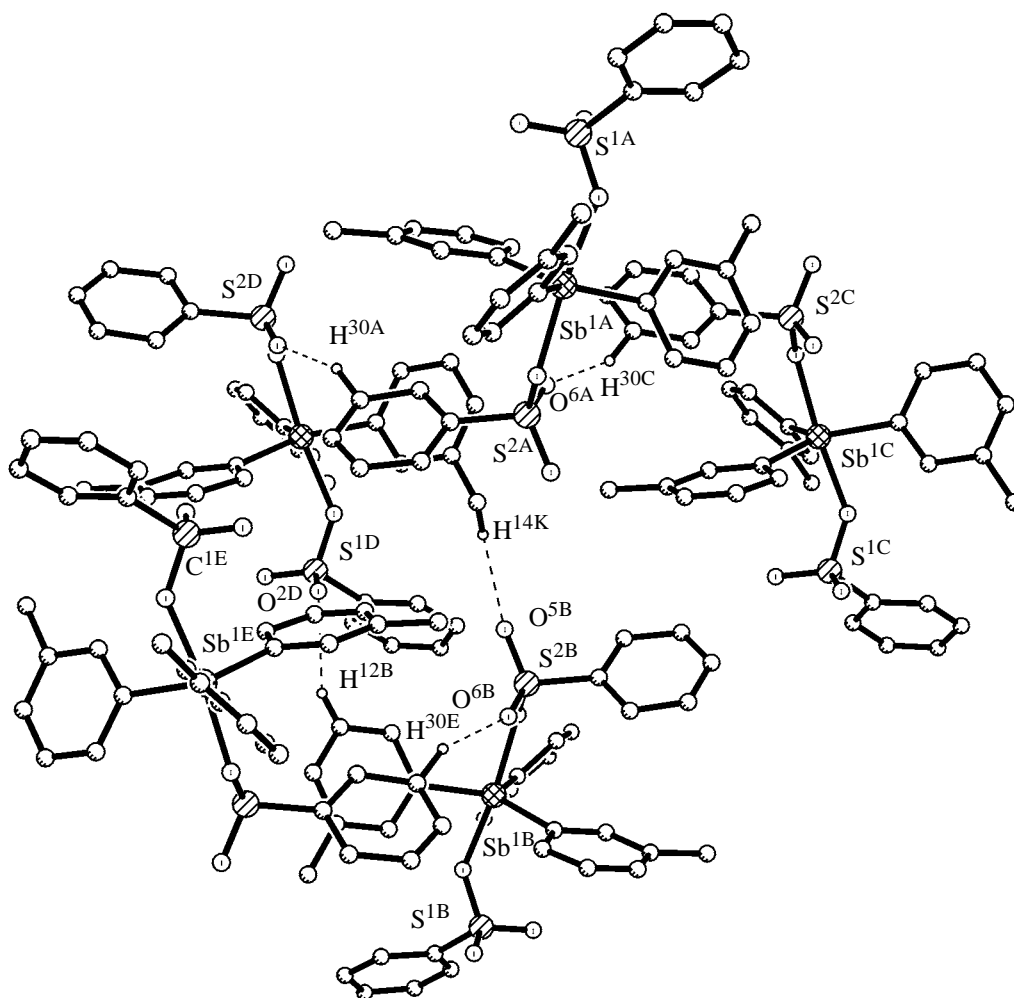


Fig. 3. System of intermolecular bonds in the crystal of tri-*m*-tolylantimony bis(benzenesulfonate) (I).

The reactions of triarylantimony bis(arenesulfonates) with sodium halides were performed in aqueous alcohols, while those with sodium acetate, benzoate, and nitrate, in toluene with heating. The yields of the target products reached 70–90%.

EXPERIMENTAL

The IR spectra were measured on a Hitachi-215 spectrometer in mineral oil.

Single-crystal X-ray diffraction analysis of compounds I and II was performed on a Siemens P3/PC automatic four-circle diffractometer (λ MoK α radiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta \leq 26.06^\circ$ for **I** and $2\theta \leq 27.54^\circ$ for **II**). Crystal data for **I**, C₃₃H₃₁O₆S₂Sb, monoclinic; at 20°C, *a* 14.495(3), *b* 12.773(3), *c* 17.680(4) Å; β 99.54(3)°, *V* 3228.1(11) Å³; space group *P*2(1)/*c*, *Z* 4, d_{calc} 1.460 g/cm³. Crystal data for **II**, C₃₇H₃₉O₆S₂Sb, triclinic; at 20°C, *a* 11.928(2), *b* 12.453(2), *c*

14.045(3) Å; α 100.450(4), β 110.345(4), γ 112.706(3)°; *V* 1680.0(5) Å³; space group *P*-1, *Z* 2, d_{calc} 1.513 g/cm³. The structures were solved by the direct method and refined by full-matrix least squares anisotropically for all non-hydrogen atoms to *R* 0.0802, *R_w* [on 6327 reflections with *I* > 2σ(*I*)] for **I** and to *R* 0.0551 and *R_w* 0.1127 [on 7718 reflections with *I* > 2σ(*I*)] for **II**. Substituent hydrogen atoms in **I** and **II** were located by Fourier synthesis and refined isotropically.

Data collection and treatment, as well as refinement of unit cell parameters were performed using the SMART and SAINT Plus programs [9]. All structural calculations were performed using SHELXTL/PC programs [10]. The principal bond lengths and bond angles are listed in the table.

Triarylantimony bis(arenesulfonates) I, II. To a mixture of 2.53 mmol of triarylantimony and 5.06 mmol of arenesulfonic acid in 20 ml of diethyl

Principal bond lengths (d) and bond angles (ω) in compounds **I** and **II**

Compound I		Compound II	
bond	d , Å	bond	d , Å
Sb–C ¹	2.112(9)	Sb–C ¹	2.087(3)
Sb–C ⁸	2.084(8)	Sb–C ⁸	2.092(3)
Sb–C ¹⁵	2.097(9)	Sb–C ¹⁵	2.087(3)
Sb–O ¹	2.124(5)	Sb–O ¹	2.158(2)
Sb–O ⁴	2.107(5)	Sb–O ⁴	2.124(2)
S ¹ –O ¹	1.492(6)	S ¹ –O ¹	1.522(2)
S ¹ –O ²	1.412(7)	S ¹ –O ²	1.434(3)
S ¹ –O ³	1.424(8)	S ¹ –O ³	1.436(2)
S ¹ –C ²²	1.766(9)	S ¹ –C ²²	1.775(3)
S ² –O ⁴	1.522(5)	S ² –O ⁴	1.525(2)
S ² –O ⁵	1.430(6)	S ² –O ⁵	1.432(3)
S ² –O ⁶	1.423(6)	S ² –O ⁶	1.440(3)
S ² –C ²⁸	1.757(9)	S ² –C ³⁰	1.777(3)
angle	ω , deg	angle	ω , deg
C ⁸ SbC ¹⁵	116.7(4)	C ⁸ SbC ¹⁵	119.96(12)
C ⁸ SbC ¹	126.7(3)	C ⁸ SbC ¹	115.24(12)
C ¹⁵ SbC ¹	116.6(4)	C ¹⁵ SbC ¹	124.62(12)
O ⁴ SbO ¹	170.6(2)	O ⁴ SbO ¹	174.33(8)
S ¹ O ¹ Sb	136.2(4)	S ¹ O ¹ Sb	129.82(13)
S ¹ O ⁴ Sb	131.5(3)	S ¹ O ⁴ Sb	127.57(14)

ether at 20°C we added 2.53 mmol of hydrogen peroxide as a 27% aqueous solution. After 12 h, the solvent was removed, and the residue was recrystallized from toluene to obtain compound **I**, yield 87%, mp 145°C. IR spectrum, ν , cm^{−1}: 1320 s, 1140 s, 1140 s (SO₂). Found, %: C 55.23; H 4.34. C₃₃H₃₁·O₆S₂Sb. Calculated, %: C 55.85; H 4.37.

Tri-*p*-tolylantimony bis(2,5-dimethylbenzenesulfonate) (**II**) was obtained in a similar way, yield 88%, mp 182°C. IR spectrum, ν , cm^{−1}: 1320 s, 1170 v.s., 1080 s (SO₂). Found, %: C 57.77; H 5.32. C₃₇H₃₉·O₆S₂Sb. Calculated, %: C 58.04; H 5.10.

Reaction of triphenylantimony bis(2,4-dimethylbenzenesulfonate) with sodium fluoride. To a solution of 1 g of triphenylantimony bis(2,4-dimethylbenzenesulfonate) in 15 ml of ethanol we added a solution of 0.12 g of sodium fluoride in 5 ml of water. After 1 h, the solvent was removed, and the residue was recrystallized from toluene to obtain 0.42 g (74%) of triphenylantimony difluoride, mp 99°C. The weight of the toluene-insoluble sodium 2,4-dimethylbenzenesulfonate (mp >250°C) was 0.50 g (88%).

The reaction with sodium bromide was performed in a similar way to obtain 71% of triphenylantimony

dibromide, mp 215°C, and 87% of sodium 2,4-dimethylbenzenesulfonate, mp >250°C. The IR spectra of the resulting compounds are identical to those of authentic samples.

Reaction of tri-*p*-tolylantimony bis(2,3-dimethylbenzenesulfonate) with sodium nitrate. A mixture of 0.5 g of tri-*p*-tolylantimony bis(2,3-dimethylbenzenesulfonate) and 0.1 g of sodium nitrate in 30 ml of toluene was heated for 6 h at 90°C. Fine crystals precipitated and were filtered off. The toluene was removed to obtain 0.3 g (90%) of tri-*p*-tolylantimony dinitrate, mp 172°C. The weight of the toluene-insoluble sodium 2,3-dimethylbenzenesulfonate was 0.21 g (79%), mp >250°C.

The reaction of triphenylantimony bis(2,4-dimethylbenzenesulfonate) with sodium benzoate was performed in a similar way to obtain 75% of triphenylantimony dibenzoate, mp 171°C, and 89 % of sodium 2,4-dimethylbenzenesulfonate, mp >250°C. The IR spectra of the resulting compounds are identical to those of authentic samples.

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