Russian Journal of General Chemistry, Vol. 71, No. 1, 2001, pp. 79–82. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 1, 2001, pp. 87–90.

Reaction of Triphenylbismuth Bis(arenesulfonates) with Triphenylstibine

V. V. Sharutin, O. K. Sharutina, I. I. Pavlushkina, I. V. Egorova, A. P. Pakusina, D. B. Krivolapov, A. T. Gubaidullin, and I. A. Litvinov

Blagoveshchensk State Pedagogical University, Blagoveshchensk, Russia

Received November 9, 1999

Abstract—Tetraphenylantimony arenesulfonates and diphenylbismuth arenesulfonates were prepared by reaction of triphenylbismuth bis(arenesulfonates) with triphenylstibine in toluene at 25°C. The crystal and molecular structure of diphenylbismuth 2,4-dimethylbenzenesulfonate was studied by single crystal X-ray diffraction. The molecules of the compound in the crystal form chains of $Ph_2BiOSO_2C_6H_3Me_2$-2,4 fragments linked with oxygen atoms of the sulfo group of the bridging arenesulfonate ligand.

It is known that triphenylstibine reacts with triphenylbismuth dichloride with transfer of both phenyl groups and chlorine atoms to antimony, yielding tetraphenylantimony chloride and triphenylantimony dichloride [1]. In this work we studied the reaction of triphenylstibine with triphenylbismuth bis(arenesulfonates). We found that the reaction yields tetraphenylantimony arenesulfonate, with the second product being diphenylbismuth arenesulfonate.

$$Ph_3Bi(OSO_2Ar)_2 + Ph_3Sb \rightarrow Ph_2BiOSO_2Ar$$
$$+ Ph_4SbOSO_2Ar$$
$$Ar = 2,4\text{-}C_6H_3Me_2\ (\mathbf{I}),\ 2,5\text{-}C_6H_3Me_2\ (\mathbf{II}).$$

Table 1. Atomic coordinates, equivalenty isotropic thermal parameters $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å^2), and isotropic thermal parameters of H atoms (B_{iso}, Å^2) in the structure of **I**

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
Bi^1	0.42857(4)	0.27421(4)	0.27200(2)	2.992(7)	C^{25}	0.6008(9)	–0.1422(9)	0.2998(6)	3.3(2)
S^1	0.6775(2)	0.0844(2)	0.3205(2)	3.22(6)	C^{26}	0.494(1)	–0.355(1)	0.4515(8)	6.4(4)
O^{11}	0.5676(6)	0.1218(6)	0.2483(4)	3.6(2)	C^{27}	0.609(1)	–0.140(1)	0.2086(6)	5.1(3)
O^2	0.7018(7)	0.1620(7)	0.3923(4)	4.2(2)	H^2	0.69(1)	0.397(9)	0.359(6)	8(3)[a]
O^3	0.2895(6)	0.4380(6)	0.2849(4)	3.8(2)	H^3	0.850(9)	0.535(8)	0.335(5)	6(3)[a]
C^1	0.5636(9)	0.4044(9)	0.2439(6)	3.2(2)	H^4	0.81(1)	0.62(1)	0.197(8)	12(4)[a]
C^2	0.670(1)	0.4373(9)	0.3137(7)	4.0(3)	H^5	0.625(8)	0.562(7)	0.109(5)	3(2)[a]
C^3	0.759(1)	0.517(1)	0.2978(9)	6.2(4)	H^6	0.482(7)	0.449(6)	0.126(5)	3(2)[a]
C^4	0.743(1)	0.565(1)	0.2170(8)	6.1(4)	H^8	0.20(1)	0.371(9)	0.139(6)	8(3)[a]
C^5	0.641(1)	0.535(1)	0.1511(7)	5.9(4)	H^9	0.10(1)	0.33(1)	–0.022(7)	12(4)[a]
C^6	0.552(1)	0.456(1)	0.1648(7)	4.8(3)	H^{10}	0.148(8)	0.187(7)	–0.105(5)	4(2)[a]
C^7	0.3219(8)	0.2491(8)	0.1322(6)	2.6(2)	H^{11}	0.309(8)	0.102(7)	–0.038(5)	4(2)[a]
C^8	0.222(1)	0.317(1)	0.0906(7)	6.6(4)	H^{12}	0.39(1)	0.12(1)	0.098(8)	11(4)[a]
C^9	0.156(1)	0.294(1)	0.0073(8)	9.1(4)	H^{21}	0.641(9)	0.000(8)	0.452(5)	6(3)[a]
C^{10}	0.193(1)	0.212(1)	–0.0400(7)	5.1(3)	H^{22}	0.568(7)	–0.157(7)	0.517(4)	3(2)[a]
C^{11}	0.286(1)	0.146(1)	–0.0016(8)	8.5(4)	H^{24}	0.54(1)	–0.308(8)	0.301(6)	7(3)[a]
C^{12}	0.353(1)	0.166(1)	0.0827(8)	7.9(4)	H^{261}	0.42(1)	–0.326(9)	0.465(6)	7(3)[a]
C^{20}	0.6331(8)	–0.0490(8)	0.3569(6)	2.7(2)	H^{262}	0.54(1)	–0.416(9)	0.461(6)	7(3)[a]
C^{21}	0.621(1)	–0.0573(9)	0.4417(6)	3.5(3)	H^{263}	0.43(1)	–0.393(9)	0.390(6)	8(3)[a]
C^{22}	0.577(1)	–0.156(1)	0.4693(6)	4.4(3)	H^{271}	0.578(8)	–0.071(7)	0.166(5)	3(2)[a]
C^{23}	0.542(1)	–0.2487(9)	0.4159(7)	4.1(3)	H^{272}	0.578(9)	–0.205(8)	0.175(6)	6(3)[a]
C^{24}	0.555(1)	–0.240(1)	0.3324(6)	4.0(3)	H^{273}	0.687(8)	–0.121(7)	0.195(5)	4(2)[a]

[a] The atoms were refined isotropically.

1070-3632/01/7101-0079 $25.00 ©2001 MAIK "Nauka/Interperiodica"

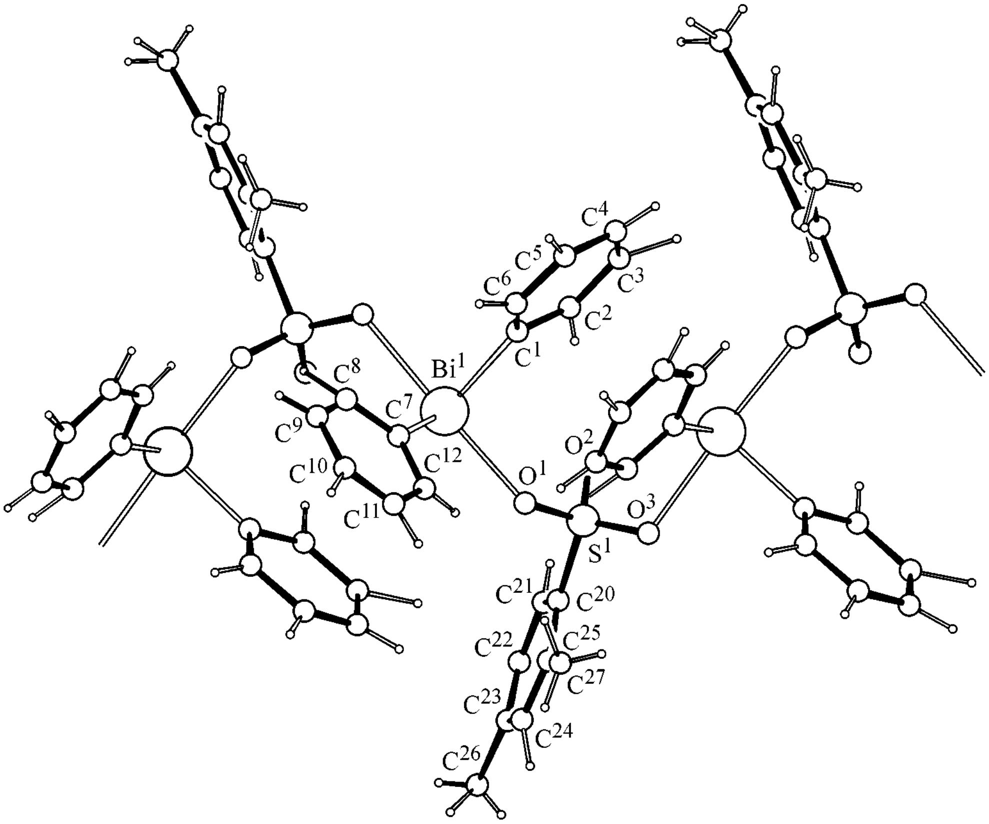


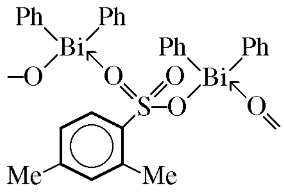
Fig. 1. Geometry of **I** in the crystal.

The reaction occurs in toluene at 25°C, and within 12–18 h coarse crystals of diphenylbismuth arenesulfonate grow on the ampule walls, and a finely crystalline precipitate of a mixture of diphenylbismuth and tetraphenylantimony arenesulfonates is formed on the bottom. Previously diarylbismuth arenesulfonates were prepared by dearylation of triarylbismuth with arenesulfonic acid [2].

Table 2. Selected bond lengths (*d*, Å) and bond angles (ω, deg) in the structure of **I**

Bond	*d*	Bond	*d*
Bi^1–O^1	2.406(7)	Bi^1–O^3	2.459(7)
Bi^1–C^1	2.22(1)	Bi^1–C^7	2.240(8)
S^1–O^1	1.481(6)	S^1–O^2	1.425(8)
S^1–O^3	1.475(8)	S^1–C^{20}	1.76(1)
Angle	ω	Angle	ω
O^{1}Bi^{1}O^3	175.1(2)	O^{1}Bi^{1}C^1	90.6(3)
O^{1}Bi^{1}C^7	85.8(3)	O^{3}Bi^{1}C^1	85.8(3)
O^{3}Bi^{1}C^7	91.1(3)	C^{1}Bi^{1}C^7	94.7(3)
O^{1}S^{1}O^2	112.2(4)	O^{1}S^{1}O^3	108.4(4)
O^{1}S^{1}C^{20}	106.6(4)	O^{2}S^{1}O^3	114.8(4)
O^{2}S^{1}C^{20}	107.7(5)	O^{3}S^{1}C^{20}	106.5(4)
Bi^{1}O^{1}S^1	119.7(4)	Bi^{1}O^{3}S^1	117.7(4)

The single crystal X-ray diffraction study of diphenylbismuth 2,4-dimethylbenzenesulfonate showed (Fig. 1, Table 1) that the crystalline compound has the polymeric structure.



The bismuth atom, with the stereochemically active lone electron pair considered as a phantom ligand, has a trigonal-bipyramidal configuration. The O^{1}BiO^3 angle is 175.1(2)°. The angles between the pseudo-axial oxygen atoms and the *ipso* carbon atoms of the phenyl rings vary from 85.8(3)° to 91.1(3)°. The Bi–C bond lengths are equal within the experimental error, whereas the Bi–O bond lengths differ noticeably (Table 2). The S–O bond lengths show an inverse correlation with the Bi–O bond lengths: The bond with the O atom forming the shorter bond with Bi is longer. Thus, there is no "leveling" of the Bi–O bonds

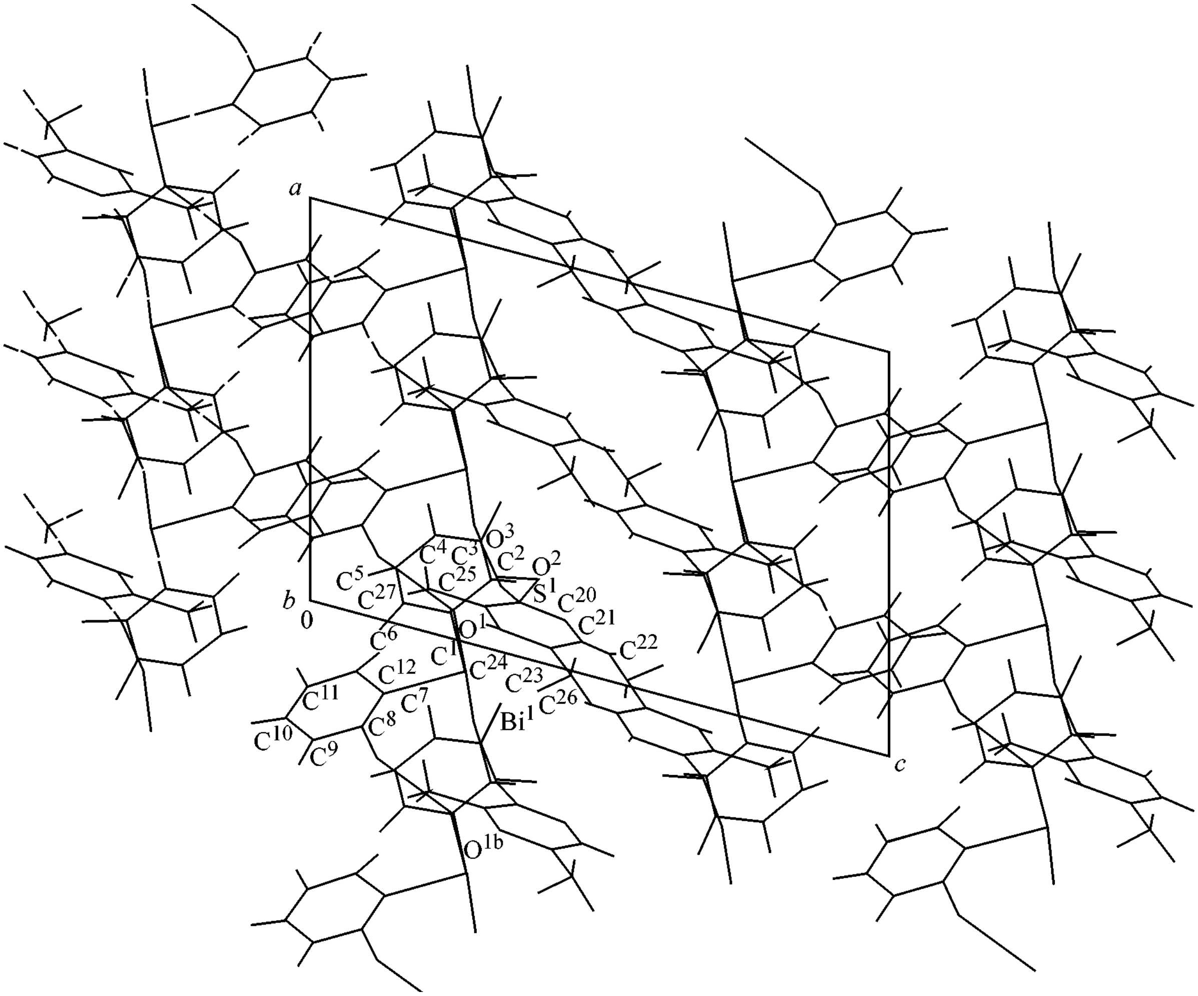


Fig. 2. Crystal packing of **I**. Projection along the 0*Y*-axis.

in the crystal, which allows the Bi–O^1 bond to be considered as mainly valence bond, and the Bi–O^3 bond, as a coordination bond.

The linear structure of the O–Bi–O group is favorable for the hyperconjugation between the O^3 lone electron pair and the Bi–O^1 antibonding orbital (n–σ^* interaction), which results in noticeable lengthening of the Bi–O^1 bond and formation of an $=O^3 \rightarrow Bi-O^1$ three-center bond.

The polymeric chains in the crystal are directed along the 0*X*-axis and have no short contacts corresponding to strong intermolecular interactions. The C–H···P and stacking interactions between parallel aromatic rings are observed only within the chain (Fig. 2).

EXPERIMENTAL

The IR spectra were taken on a Hitachi-215 spectrometer (mull in mineral oil between NaCl plates).

Single crystal X-ray diffraction study of $C_{20}H_{19}O_3SBi$ (I) was performed on an Enraf-Nonius CAD-4 automatic four-circle diffractometer. The crystals are monoclinic; at 20°C a 10.702(1), b 11.639(2), c 15.893(2) Å; β 104.94(1)°, V 1912.6(5) Å^3, Z 4, d_{calc} 1.90 g cm^{-3}, space group $P2_1/a$. The unit cell parameters and the intensities of 4285 reflections, 2072 of which were observed with $I \geq 3\sigma$, were measured at 20°C using MoK_α radiation (λMoK_α 0.71074 Å, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 29.96°$). The absorption was taken into account empirically (μMo 93.1 cm^{-1}). The structure was solved by the heavy atom method and refined first in the isotropic and then in the anisotropic approximation. All hydrogen atoms were revealed from the differential electron density series and refined isotropically in the final refinement cycles. The structure was refined to R 0.037 and R_W 0.038 for 2088 unique reflections with $F^2 \geq 3\sigma$. The atomic coordinates are given in Table 1, and the main geometric parameters, in Table 2. All calculations were performed with a

DEC AlphaStation 200 computer using the MolEN program package [3]. The intermolecular contacts were analyzed and the molecular drawings obtained using the WINPL98 program [4].

Diphenylbismuth 2,4-dimethylbenzenesulfonate. A mixture of 1.00 g of triphenylstibine, 2.29 g of triphenylbismuth bis(2,4-dimethylbenzenesulfonate), and 30 ml of toluene was allowed to stand at 25°C for 72 h. Coarse crystals that formed on the ampule wall were collected, dried, and weighed. Diphenylbismuth 2,4-dimethylbenzenesulfonate was obtained; yield 1.00 g (64%), mp 211°C. Found, %: C 43.75; H 3.53; S 5.67. $C_{20}H_{19}O_3SBi$. Calculated, %: C 43.80; H 3.47; S 5.84. The mother liquor was evaporated, and the residue was recrystallized from water. Tetraphenylantimony 2,4-dimethylbenzenesulfonate was obtained; yield 1.58 g (91%), mp 211°C. IR spectrum, ν, cm^{-1}: 1240 (S=O), 1000 (S–O). Found, %: C 62.23; H 4.95. $C_{32}H_{29}O_3SSb$. Calculated, %: C 62.44; H 4.72.

Reaction of triphenylstibine with triphenylbismuth bis(2,5-dimethylbenzenesulfonate) was performed similarly. Yields of diphenylbismuth 2,5-dimethylbenzenesulfonate and tetraphenylantimony 2,5-dimethylbenzenesulfonate 58 and 89%, respectively.

ACKNOWLEDGMENTS

The single crystal X-ray diffraction study was performed at the department of X-ray diffraction studies of the Spectrum-Analytical Center for Collective Use of the Russian Foundation for Basic Research (project no. 96-03-40 006).

REFERENCES

1. Zinov’eva, T.I., Dodonov, V.A., and Pryakhina, O.I., Abstracts of Papers, *VI Konferentsiya po metalloorganicheskoi khimii* (VI Conf. on Organometallic Chemistry), Nizhni Novgorod, 1995, p. 163.
2. Deacon, G.B., Felder, P.W., Domagala, M., Huber, F., and Rüther, R., *Inorg. Chim. Acta*, 1986, vol. 113, no. 1, pp. 43–48.
3. Straver, L.H. and Schierbeek, A.J., *MolEN. Structure Determination System*, Nonius B.V., 1994, vols. 1, 2.
4. Spek, A.L., *Acta Crystallogr., Sect. A*, 1990, vol. 46, no. 1, pp. 34–36.