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2-Methoxy-5-bromophenyl Antimony Compounds. Synthesis and Structure

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Abstract—Reaction of 2-methoxy-5-bromophenyllithium with antimony trichloride in diethyl ether affords tris-(2-methoxy-5-bromophenyl)antimony benzene solvate **I**. Its structure and chemical transformations into the new antimony aryl derivatives were studied.

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Oxidative addition reactions involving triarylantimony, acid (HX) and hydrogen peroxide at a 1:2:1 molar ratio in air are known to yield the antimony derivatives of general formula Ar_3SbX_2 [1–4]. Such reactions of triarylantimony, which aryl ligands contain potential coordination centers, have not been previously studied.

In this paper, tris(2-methoxy-5-bromophenyl)antimony \mathbf{I} was synthesized starting from 2-methoxy-5bromophenyllithium and antimony trichloride in diethyl ether. The oxidative addition with participation of compound \mathbf{I} was investigated.

Aryllithium derivative was obtained via *para*bromoanisole lithiation with phenyllithium at room temperature in air.



The resulting 2-methoxy-5-bromphenyllithium reacts with antimony trichloride. After the aryllithium excess decomposing with water and the solvent removal, the residue was recrystallized from benzene. Yield of the tris(2-methoxy-5-bromophenyl) antimony benzene solvate is 85%.



According to the X-ray diffraction analysis data, the compound I molecule has a trigonal pyramid configuration. Lengths of the Sb–C bonds are 2.1603(15), 2.1631(15), and 2.1569(16) Å. The CSbC bond angles are 92.19(6)°, 94.23(6)°, and 94.52(6)°. The methoxy oxygen atoms are coordinated to the antimony atom (Fig. 1). The intramolecular distances Sb···O are 2.985(1), 3.051(1), and 3.052(1) Å, which corresponds to 81– 82% of the sum (3.7 Å [5]) of the antimony and oxygen van der Waals radii. The presence of the intramolecular contacts causes obviously a decrease in the CSbC bond angles of the molecule I compared to triphenyl- and tri-*para*-tolyl antimony molecules (95.52°–97.36° [6] and 97.31° [7]), where such contacts are absent (Table 1).

In contrast, in a tris[2-(N,N-dimethylamino)methylphenyl]antimony molecule, where the intramolecular Sb…N interactions were observed, the CSbC angles (average value 94.67° [8]) are close to similar parameters of the molecule **I**.

Due to the intermolecular Sb^{\dots}Br contacts [3.742(2) Å, while the van der Waals radii sum of the bromine and antimony atoms is 4.1 Å], the molecules **I** are joined into the polymer chains (Fig. 2).

We found that tris(2-methoxy-5-bromophenyl)antimony I is oxidized with bromine in chloroform solution to give tris(2-methoxy-5-bromophenyl)antimony dibromide II.

$$\mathbf{I} + \mathrm{Br}_2 \rightarrow [(2 - \mathrm{MeO})(5 - \mathrm{Br})\mathrm{C}_6\mathrm{H}_3]_3\mathrm{SbBr}_2.$$

$$\mathbf{II}$$

Under the action of sodium fluoride in a wateracetone medium, tris(2-methoxy-5-bromophenyl)-



Fig. 1. General view of tris(2-methoxy-5-bromophenyl)antimony molecule (benzene molecule is not shown).

antimony dibromide **II** transforms into the tris(2-methoxy-5-bromophenyl)antimony difluoride **III**.

$$\begin{split} \textbf{II} + 2 \, \text{NaF} &\rightarrow [(2\text{-MeO})(5\text{-Br})\text{C}_6\text{H}_3]_3\text{SbF}_2 + 2 \, \text{NaCl}.\\ \textbf{III} \end{split}$$

The oxidation of compound **I** with hydrogen peroxide in the presence of phenols, carboxylic or arylsulfonic acids in diethyl ether at room temperature was shown to result in tris (2-methoxy-5bromophenyl)antimony diaryl oxides, dicarboxylates or diaryl sulfonates, respectively, which are crystalline substances.

$I + 2 HX + H_2O_2$ → [(2-MeO)(5-Br)C₆H₃]₃SbX₂ + 2 H₂O,

The yield of the oxidative addition products is 95%.

In addition, the compound VI was synthesized by the reaction of compound I with benzoyl peroxide in benzene in yield of 98%.

I + PhC(O)OOC(O)Ph → [(2-MeO)(5-Br)C₆H₃]₃Sb[OC(O)Ph]₂.

Thus, the antimony aryl derivatives involving two functional groups (MeO, Br) in the aromatic ring were first obtained. The structure of the first representative of 2-methoxy-5-bromophenyl antimony compounds, the tris(2-methoxy-5-bromophenyl)antimony, was studied.



Fig. 2. Structure of tris(2-methoxy-5-bromophenyl)antimony polymer chain in a crystal.

EXPERIMENTAL

The IR spectra were recorded on an FSM-1201 IR Fourier spectrometer from KBr pellets.

The X-ray analysis of compound I was performed on a Bruker AXS Smart Apex diffractometer (Mo K_{α} irradiation, λ 0.71073 Å, graphite monochromator). The data collection and editing, refining the unit cell parameters and accounting for absorption were made using the SMART and SAINT-Plus software [9]. All calculations to determine and clarify the structure were performed using the SHELXL/PC software [10]. The structure was determined by a direct method and refined by the least squares method in an anisotropic approximation for the nonhydrogen atoms. The main crystallographic data for the structure I are shown in Table 2.

Compound I benzene solvate. To a solution of 9.95 g (51.6 mmol) of 5-bromo-2-methoxyphenyl-lithium, obtained from 9.65 g of (51.6 mmol) of *para*-

Table 1. Bond lengths and valence angles in the structure I

Bond	d, Å	Angle	ω, deg
Sb^1-C^{1A}	2.1603(15)	$C^{1A}Sb^1C^{1B}$	94.23(6)
Sb^1-C^{1B}	2.1631(15)	$C^{1C}Sb^1C^{1A}$	92.19(6)
Sb^1-C^{1C}	2.1569(16)	$C^{1C}Sb^1C^{1B}$	94.52(6)
C^{2A} – O^1	1.3697(19)	$C^{2A}O^1C^{1AM}$	117.44(13)
C^{5A} – Br^1	1.9061(15)	$C^{2B}O^2C^{1BM}$	117.73(14)
C^{1AM} – O^1	1.433(2)	$C^{2C}O^3C^{1CM}$	117.63(14)
C^{2B} – O^2	1.3695(19)	$C^{4A}C^{5A}Br^1$	119.57(12)
C ^{5B} –Br ²	1.9061(16)	$C^{6A}C^{5A}Br^1$	118.83(11)
C ^{5C} -Br ³	1.9068(18)	$C^{4B}C^{5B}Br^2$	119.58(13)
C^{1CM} – O^3	1.430(2)	$C^{6B}C^{5B}Br^2$	119.08(13)

Parameter	Value	
M	718.89	
<i>Т</i> , К	100.0(2)	
Crystal system	Monoclinic	
Space group	$P2_{1}/n$	
<i>a</i> , Å	9.00170(10)	
<i>b</i> , Å	20.9598(3)	
<i>c</i> , Å	13.5361(2)	
β, deg	105.0430(10)	
V, Å ³	2466.39(6)	
Ζ	4	
$d_{\rm calc}$, g cm ⁻³	1.936	
μ , mm ⁻¹	6.002	
<i>F</i> (000)	1380	
Crystal sizes, mm	0.21×0.20×0.20	
Range for data collection	$1.84 < \theta < 31.60$	
Reflection indices ranges	$-13 \le h \le 12$,	
	$-29 \le k \le 30,$	
	$-14 \le l \le 19$	
Reflections measured	6979	
Independent reflections	6022	
Number of variables to refinement	364	
GOOF	1.009	
Reflections with $I > 2\sigma(I)$	5844	
<i>R</i> -Factors on $F^2 > 2\sigma(F^2)$	$R_1 0.0180,$	
	$wR_2 0.0364$	
<i>R</i> -Factors on all reflections	$R_1 0.0259,$	
	$wR_2 \ 0.0384$	
Residual electron density	-0.451/0.530	
(min/max), $e \text{ Å}^{-3}$		

 Table 2. Crystallographic data, experiment and refinement parameters for the structure I

bromoanisole and 60.0 mmol of phenyllithium in diethyl ether, was added 3.69 g (16.2 mmol) of antimony trichloride in 100 ml of diethyl ether. The mixture was stirred and kept overnight. Then it was cautiously decomposed with water (2 ml) at the cooling. After the solvent removal, the residue was recrystallized from benzene. Yield 10.42 g (85%), colorless crystals, mp 198°C. IR spectrum, v, cm⁻¹: 2933, 2834, 1563, 1488, 1425, 1371, 1283, 1261, 1234, 1177, 1136, 1088, 1073, 1042, 1017, 890, 826, 805, 767, 744, 744, 615, 540, 443. Found, %: C 42.12; H 3.07. C₂₇H₂₄O₃Br₃Sb. Calculated, %: C 42.74; H 3.17.

Compound II. To a solution of 0.61 g (0.8 mmol) of tris(2-methoxy-5-bromophenyl)antimony benzene solvate in 30 ml of chloroform was added a solution of 0.13 g (0.8 mmol) of bromine in 20 ml of chloroform under stirring. The solvent was removed. Yield 0.61 g (91%), colorless crystals, mp 254°C. IR spectrum, v, cm⁻¹: 3083, 2930, 2836, 1574, 1469, 1435, 1374, 1284, 1268, 1253, 1179, 1150, 1089, 1045, 1016, 813, 805, 704, 670, 618, 524, 436. Found, %: C 29.56; 2.04. C₂₁H₁₈Br₅O₃Sb. Calculated, %: C 29.89; H 2.49.

Compound III. To a solution of 0.15 g (3.6 mmol) of sodium fluoride in 200 ml of water was added with the stirring a solution of 0.25 g (0.3 mmol) of tris(2-methoxy-5-bromophenyl)antimony dibromide in 25 ml of acetone. The resulting precipitate was filtered off, washed with water, dried and recrystallized from benzene. Yield 0.21 g (90%), mp 234°C. IR spectrum, v, cm⁻¹: 3561, 3115, 2933, 2843, 1575, 1475, 1441, 1375, 1275, 1256, 1181, 1095, 1049, 1013, 817, 810, 802, 622, 538, 524, 442. Found, %: C 34.91; H 2.23. $C_{21}H_{18}Br_3F_2O_3Sb.$ Calculated, %: C 35.10; H 2.51.

Compound IV. To a mixture of 0.61 g (0.8 mmol) of tris(2-methoxy-5-bromophenyl)antimony benzene solvate and 0.53 g (1.6 mmol) of tribromophenol in 50 ml of diethyl ether was added 0.09 ml of 30% aqueous solution of hydrogen peroxide. The mixture was kept for 18 h at 20°C. The resulting crystals were filtered off and dried. Yield 0.98 g (93%), mp 164°C. IR spectrum, v, cm⁻¹: 3073, 3003, 2963, 2836, 2522, 1565, 1457, 1424, 1367, 1278, 1237, 1175, 1136, 1097, 1052, 1007, 904, 858, 807, 729, 690, 613, 561. Found, %: C 29.38; 1.44. C₃₃H₂₂Br₉· O₅Sb. Calculated, %: C 29.50; 1.64.

Compound IX was prepared similarly from a mixture of 0.61 g (0.8 mmol) of tris(2-methoxy-5-bromophenyl)antimony benzene solvate and 0.24 g (1.6 mmol) of cinnamic acid. Yield 0.60 g (78%), mp 239°C. IR spectrum, v, cm⁻¹: 2936, 2832, 1705, 1648, 1558, 1459, 1435, 1374, 1284, 1260, 1232, 1180, 1142, 1085, 1038, 1014, 886, 806, 629, 668, 616, 417. Found, %: C 39.88; H 3.04. $C_{39}H_{32}$ Br₃O₇Sb. Calculated, %: C 40.05; H 3.28.

Compound X was obtained similarly from a mixture of 0.61 g (0.8 mmol) of tris(2-methoxy-5-bromophenyl)antimony benzene solvate and 0.28 g (1.6 mmol) of toluenesulfonic acid. Yield 0.77 g (95%), mp 236°C. IR spectrum, v, cm⁻¹: 3074, 2952, 2842, 1575, 1479, 1369, 1278, 1246, 1175, 1046,

1007, 865, 820, 703, 671, 626, 574, 438, 406. Found, %: C 40.86; H 3.00. $C_{35}H_{32}Br_3O_9S_2Sb.Calculated$, %: C 41.09; H 3.13.

Compounds V (mp 121°C, 74%), VI (mp 201°C, 71%), VII (mp 203°C, 74%), VIII (mp 183°C, 91%), XI (mp 181°C, 93%) were obtained similarly.

Compound VI. A mixture of 0.61 g (0.8 mmol) of tris(2-methoxy-5-bromophenyl)antimony benzene solvate, 0.19 g (0.8 mmol) of benzoyl peroxide and 20 ml of benzene was heated for 3 h at 40°C. The reaction mixture was cooled, the solvent was removed. Yield 0.71 g (98%) of crystals, mp 201°C. IR spectrum, v, cm⁻¹: 3068, 2932, 2835, 1647, 1582, 1479, 1382, 1323, 1291, 1252, 1175, 1123, 1046, 1020, 891, 807, 716, 684, 626, 568, 445. Found, %: C 45.04; H 2.87. $C_{35}H_{28}Br_{3}O_{7}Sb$. Calculated, %: C 45.55; H 3.04.

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