

SYNTHESIS AND STRUCTURE OF BIS(4-BROMOPHENOXY)TRIPHENYLANTIMONY

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Interaction of triphenylantimony with 4-bromophenol in the presence of *tert*-butylhydroperoxide in ether has led to the synthesis of *bis*(4-bromophenoxy)triphenylantimony, whose structure has been established by X-ray diffraction analysis. The antimony atom has distorted trigonal-bipyramidal coordination with aryloxy groups in axial positions. The bond lengths equal: 2.094(4), 2.108(5), 2.109(5) Å for Sb–C; 2.062(4) and 2.066(3) Å for Sb–O. The axial angle OSbO equals 172.41(1)°.

Keywords: *bis*(4-bromophenoxy)triphenylantimony, synthesis, molecular structure, X-ray analysis.

Introduction

It is known that reactions of triarylantimony with phenols in the presence of hydrogen peroxide lead to formation of triarylantimony diaroxyde [1, 2]. Oxidative addition reactions with the participation of phenols and some other oxidizing agent were not studied previously. In the present paper *bis*(4-bromophenoxy)triphenylantimony (**1**) has been obtained by way of the oxidative addition reaction with the use of *tert*-butylhydroperoxide as the oxidizing agent; its molecular and crystal structure has been investigated.

Experimental

Synthesis of *bis*(4-bromophenoxy)triphenylantimony (1**).** The mixture of 0.353 g (1.00 mmol) triphenylantimony, 0.346 g (2.00 mmol) 4-bromophenol and 0.128 g 70% aqueous solution of *tert*-butylhydroperoxide (1.00 mmol) in 10 mL ether was kept at room temperature for 24 h. The crystals formed were recrystallized from toluene. The yield was 0.391 g (85%) of compound **1** with m.p. 148 °C. IR spectrum (ν , cm^{-1}): 1577, 1484, 1436, 1278, 1243, 1166, 1098, 1071, 1023, 998, 845, 830, 745, 731, 693, 643, 625, 519, 482, 461. Found, %: C 51.53, H 3.65, Br 22.59. Calculated for $\text{C}_{30}\text{H}_{23}\text{Br}_2\text{O}_2\text{Sb}$, %: C 51.65, H 3.30, Br 22.95.

IR spectrum of compound **1** was recorded by the Bruker Tensor 27 IR spectrometer in paraffin oil between KBr pellets in the range 4000–400 cm^{-1} .

X-ray diffraction analysis of the crystal **1** was performed on the Bruker D8 QUEST automatic four-circle diffractometer (Mo K_{α} -emission, $\lambda = 0.71073$ 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 [3]. All calculations for structure determination and refinement were performed using the SHELXL/PC programs [4]. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The position of hydrogen atoms was refined according to the riding model ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$). The main crystallographic data and refinement results for structure **1** are listed in Table 1, the geometric characteristics of the antimony atom coordination polyhedron are given in Table 2.

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

| Parameter | Value |
|-------------------|--|
| Empirical formula | $\text{C}_{30}\text{H}_{23}\text{O}_2\text{Br}_2\text{Sb}$ |
| Formula weight | 697.05 |
| T , K | 296(2) |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |

| Parameter | Value |
|---|---|
| <i>a</i> , Å | 15.5926(8) |
| <i>b</i> , Å | 9.1094(4) |
| <i>c</i> , Å | 20.5019(10) |
| α , deg | 90.00 |
| β , deg | 111.894(2) |
| γ , deg | 90.00 |
| <i>V</i> , Å ³ | 2702.0(2) |
| <i>Z</i> | 4 |
| ρ (calcd.), g/cm ³ | 1.713 |
| μ , mm ⁻¹ | 4.004 |
| <i>F</i> (000) | 1360.0 |
| Crystal size, mm | 0.29 × 0.28 × 0.05 |
| 2 θ Range of data collection, deg | 6.08 – 52.78° |
| Range of refraction indices | -19 ≤ <i>h</i> ≤ 19, -11 ≤ <i>k</i> ≤ 11, -25 ≤ <i>l</i> ≤ 25 |
| Measured reflections | 36895 |
| Independent reflections | 0.0920 |
| <i>R</i> _{int} | 5523 |
| Refinement variables | 316 |
| <i>GOOF</i> | 1.045 |
| <i>R</i> factors for $F^2 > 2\sigma(F^2)$ | <i>R</i> ₁ = 0.0484, <i>wR</i> ₂ = 0.1019 |
| <i>R</i> factors for all reflections | <i>R</i> ₁ = 0.0839, <i>wR</i> ₂ = 0.1177 |
| Residual electron density (min/max), e/Å ³ | 0.92/-0.66 |

Table 2

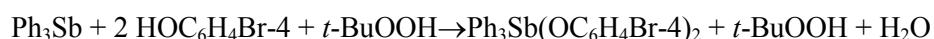
Selected bond lengths and bond angles in the structure of compound 1

| Bond | <i>d</i> , Å | Angle | ω , deg |
|-------------|--------------|-----------------|----------------|
| Sb(1)–O(1) | 2.062(4) | O(1)Sb(1)O(2) | 172.41(15) |
| Sb(1)–O(2) | 2.066(4) | O(1)Sb(1)C(1) | 94.96(19) |
| Sb(1)–C(1) | 2.109(5) | O(1)Sb(1)C(11) | 82.85(17) |
| Sb(1)–C(11) | 2.108(5) | O(2)Sb(1)C(11) | 90.24(17) |
| Sb(1)–C(21) | 2.094(5) | O(2)Sb(1)C(21) | 87.78(18) |
| Br(1)–C(34) | 1.907(6) | C(11)Sb(1)C(1) | 122.9(2) |
| Br(2)–C(44) | 1.903(6) | C(21)Sb(1)C(1) | 112.4(2) |
| O(1)–C(31) | 1.355(6) | C(21)Sb(1)C(11) | 124.7(2) |
| O(2)–C(41) | 1.341(6) | C(31)O(1)Sb(1) | 135.1(3) |

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1043441; deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Results and Discussion

Compound **1** has been obtained from triphenylantimony and 4-bromophenol in the presence of *tert*-butylhydroperoxide (mole ratio 1:2:1, respectively) in ether (20 °C, 18 h).



In order to get monocrystals that are suitable for X-ray structure investigation, compound **1** has been recrystallized from toluene.

According to X-ray diffraction analysis data, the antimony atom in **1** has distorted trigonal-bipyramidal coordination with the oxygen atoms of phenolate ligands in axial positions (Fig. 1).

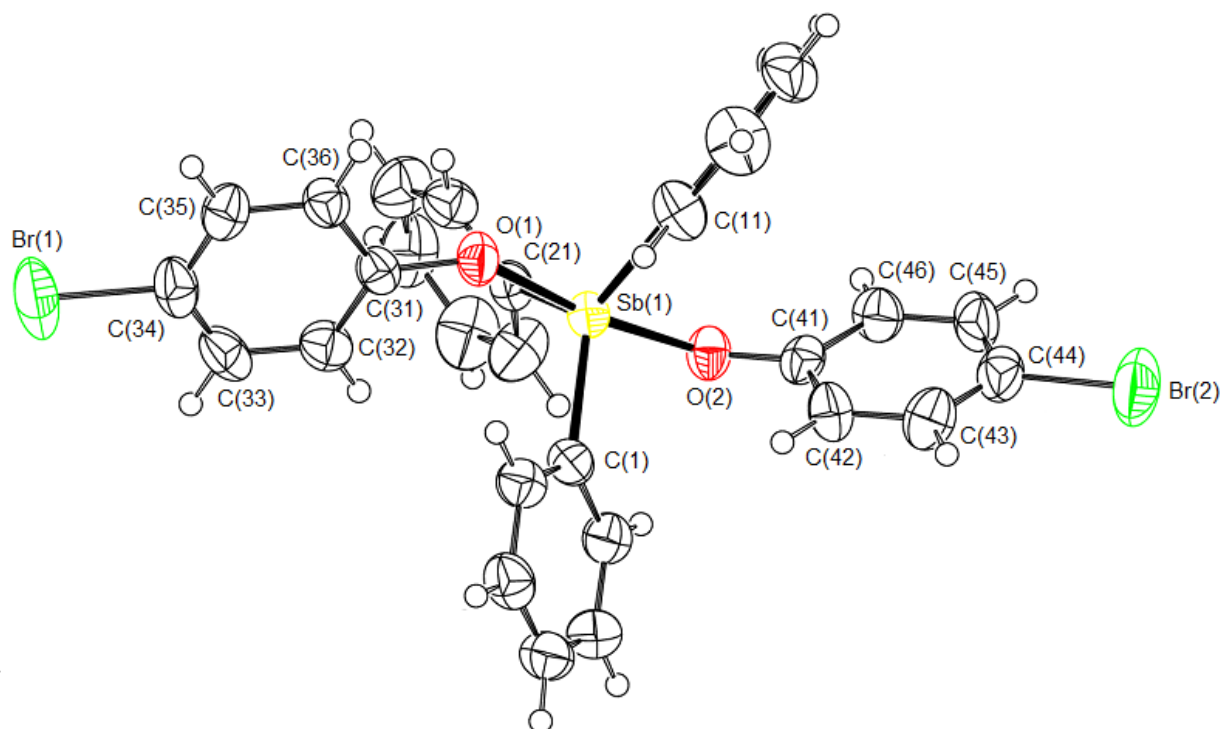


Fig. 1. The structure of compound 1

The axial angle OSbO equals $172.41(15)^\circ$. Three equatorial phenyl groups exist in the least sterically hindered propeller twist conformation. The antimony atom deviates from the equatorial plane [C_3] by 0.007 \AA . The sum of angles CSbC in the equatorial plane equal 360° , at that the values of individual equatorial angles ($112.4(2)^\circ$, $122.9(2)^\circ$, and $124.7(2)^\circ$) differ noticeably. The planes of aryloxy groups [C(31)–C(36)] and [C(41)–C(46)] make angles 81.45° and 53.22° with the equatorial plane [C_3], respectively.

The bond lengths Sb–C(1,11,21) equal $2.109(5)$, $2.108(5)$, $2.094(5) \text{ \AA}$; they approach the observed values of the equatorial bonds in the *bis*(2,4,6-tribromophenoxy)triphenylantimony molecule ($2.095(6)$, $2.105(4)$, $2.106(4) \text{ \AA}$ [1]). The lengths Sb–O(1,2) ($2.062(4)$ and $2.066(4) \text{ \AA}$) are less than the similar bonds in *bis*(2,4,6-tribromophenoxy)triphenylantimony ($2.091(6)$, $2.099(4) \text{ \AA}$ [1]), but more than those in *bis*(phenoxy)triphenylantimony ($2.046(6)$, $2.056(4) \text{ \AA}$ [5]). Note that the sum of the covalent radii of the O and Sb atoms comprises 2.07 \AA [6]. The distances O(1)–C(31) and O(2)–C(41) in **1** equal $1.355(6)$ and $1.341(5) \text{ \AA}$. In the *bis*(phenoxy)triphenylantimony and *bis*(2,4,6-tribromophenoxy)triphenylantimony molecules the similar bonds measure $1.353(2)$, $1.336(2) \text{ \AA}$ and $1.333(5)$, $1.334(5) \text{ \AA}$, respectively.

Conclusions

Hence, the distortion of trigonal-bipyramidal coordination of the central atom in molecule **1** manifests itself in the noticeable deviation of axial and equatorial angles from their theoretical values, which is probably caused not by existence of intramolecular interactions, but by peculiarities of crystal arrangement. In the series of compounds *bis*(phenoxy)triphenylantimony, *bis*(4-bromophenoxy)triphenylantimony, *bis*(2,4,6-tribromophenoxy)triphenylantimony the lengthening of the Sb–O bonds is observed, at that the expected regular shortening of the Sb–O bonds does not occur.

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СИНТЕЗ И СТРОЕНИЕ БИС(4-БРОМФЕНОКСИ)ТРИФЕНИЛСУРЬМЫ

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Взаимодействием трифенилсурьмы с 4-бромфенолом в присутствии трет-бутилгидропероксида в эфире синтезирована бис(4-бромфенокси)трифенилсурьма, строение которой установлено методом РСА. Атом Sb имеет искаженную тригонально-бипирамидальную координацию с ароксигруппами в аксиальных положениях. Длины связей Sb–C 2.094(4), 2.108(5), 2.109(5); Sb–O 2.062(4) и 2.066(3) Å. Аксиальный угол OSbO составляет 172.41(1)°.

Ключевые слова: бис(4-бромфенокси)трифенилсурьма, синтез, строение, рентгеноструктурный анализ.

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