

# INTERACTION OF PENTAPHENYLANTIMONY WITH ACETYLENEDICARBOXYLIC ACID. MOLECULAR STRUCTURE OF BIS(TETRAPHENYLANTIMONY) ACETYLENEDICARBOXILATE

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*Bis(tetraphenylantimony) acetylenedicarboxilate (1) has been synthesized by the interaction of pentaphenylantimony with acetylenedicarboxylic acid (mole ratio 2:1 or 1:1) in toluene. In molecule 1 the acid anion has the bridging role and bonds Ph<sub>4</sub>Sb fragments. The antimony atoms have distorted trigonal bipyramidal coordination with the oxygen atom in the axial position. The Sb–O bond lengths are 2.287(4) and 2.389(4) Å, the Sb–C bond lengths are 2.110(7)–2.179(6) Å and 2.108(6)–2.165(6) Å.*

*Keywords: pentaphenylantimony, acetylenedicarboxylic acid, bis(tetraphenylantimony) acetylenedicarboxilate, molecular structure, X-ray diffraction analysis.*

## Introduction

It is known that the interaction of pentaarylantimony with dicarboxylic acid can give two types of compounds: acidic tetraarylantimony carboxilates and *bis*(tetraarylantimony) carboxilates [1–4]. According to the X-ray diffraction data, the coordination of antimony atoms in these types of molecules is significantly different. In the first case there is a tendency of the Ar<sub>4</sub>Sb fragment to the transformation into the tetrahedric configuration, which is accompanied by increase of the distance between the antimony atom and the oxygen atom of the monodentate carboxylic ligand, which has the bond of coordinating character [1–3].

In binuclear *bis*(tetraarylantimony) carboxilates the antimony atom has a slightly distorted trigonal bipyramidal coordination [SbC<sub>4</sub>O]. As a rule, the bridging carboxylic ligand has anisobidentate type of coordination caused by intramolecular interactions Sb⋯O=C between the antimony atoms and carbonyl oxygen atoms [2, 4–6]. Only oxalate ligand is coordinated to the antimony atom almost symmetrically, thus the antimony atom coordination transforms into the octahedral one [7].

In the continuation of our research of organoantimony dicarboxylic acid derivatives the reactions of pentaphenylantimony with acetylenedicarboxylic acid have been studied. The product structure has been determined by the X-ray diffraction analysis.

## Experimental

**Interaction of pentaphenylantimony with acetylenedicarboxylic acid.** A) A mixture of 0.200 g (0.394 mmol) of pentaphenylantimony and 0.022 g (0.197 mmol) of acetylenedicarboxylic acid in 5 mL of toluene was kept in a sealed glass ampoule at room temperature for 24 h. The solution was concentrated, the crystals were filtered off and dried. The substance was isolated as 0.173 g (90 %) of colorless crystals **1** with  $T_{dec} = 178$  °C. Found, %: C 64.09; H 4.23. For C<sub>52</sub>H<sub>40</sub>O<sub>4</sub>Sb<sub>2</sub>, anal. calcd, %: C 64.20; H 4.11. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3401, 3057, 2989, 1632, 1612, 1577, 1479, 1435, 1389, 1322, 1289, 1184, 1158, 1067, 1021, 996, 774, 731, 691, 670, 460.

B) A mixture of 0.200 g (0.394 mmol) of pentaphenylantimony and 0.044 g (0.394 mmol) of acetylenedicarboxylic acid in 5 mL of toluene was heated in a sealed glass ampoule in a boiling water bath for 15 min. Large crystals of *bis*(tetraphenylantimony) carbonate with  $T_m = 234$  °C were observed on the ampoule walls during cooling. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3050, 1577, 1472, 1429, 1382, 1332, 1304, 1264, 1186, 1157, 1067, 1021, 997, 830, 730, 691, 653, 457.

The supernatant toluene solution was concentrated, the crystals were filtered off and dried. The substance was isolated as 0.149 g (76 %) of colorless crystals of tetraphenylantimony propiolate with

## Organometallic chemistry

$T_m = 174$  °C (with decomposition). Found, (%): C 64.81; H 4.29. For  $C_{27}H_{21}O_2Sb$ , anal. calcd, (%): C 64.96; H 4.21. IR spectrum ( $\nu$ ,  $cm^{-1}$ ): 3277, 3053, 3010, 2990, 2917, 2591, 2361, 2178, 2091, 1967, 1885, 1819, 1621, 1575, 1562, 1477, 1433, 1377, 1333, 1301, 1187, 1158, 1070, 1057, 1020, 997, 883, 782, 737, 693, 658, 643, 601, 586, 462, 447.

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

**The X-ray diffraction analyses** of crystal **1** was performed on the Bruker D8 Quest diffractometer (Mo  $K_\alpha$ -radiation,  $\lambda = 0.71073$  Å, graphite monochromator). The data collection and editing as well as the refinement of unit cell parameters and the absorption accounting were carried out using SMART and SAINT *Plus* program packages [8]. All calculations for the structure determination and refinement were carried out using the SHELXTL/PC [9] and OLEX2 [10] programs packages. The structures were determined by the direct method and refined by least-squares method calculations in anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and structure refinement results for compounds **I** and **II** are given in Table 1, and selected bond lengths and bond angles are listed in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 994821; 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	$C_{52}H_{40}O_4Sb_2$
Formula weight	972.34
$T$ , K	296(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
$a$ , Å	10.0115(4)
$b$ , Å	21.1868(8)
$c$ , Å	22.6148(9)
$\alpha$ , deg	90.00
$\beta$ , deg	91.530(2)
$\gamma$ , deg	90.00
$V$ , Å <sup>3</sup>	4795.2(3)
$Z$	4
$\rho$ (calcd.), g/cm <sup>3</sup>	1.347
$\mu$ , mm <sup>-1</sup>	1.167
$F(000)$	1944.0
Crystal size, mm	0.92×0.18×0.09
2 $\theta$ Range of data collection, deg	6.64 – 46.62°
Range of refraction indices	$-9 \leq h \leq 11$ , $-23 \leq k \leq 22$ , $-25 \leq l \leq 23$
Measured reflections	12802
Independent reflections	6525
$R_{int}$	0.0282
Refinement variables	523
<i>GOOF</i>	1.095
$R$ factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0401$ , $wR_2 = 0.1132$
$R$ factors for all reflections	$R_1 = 0.0576$ , $wR_2 = 0.1226$
Residual electron density (min/max), e/Å <sup>3</sup>	1.02/–0.41

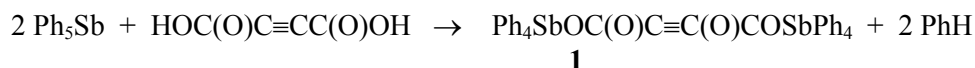
Table 2

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

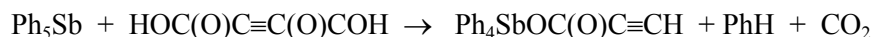
Bond	<i>d</i> , Å	Angle	ω, deg
Sb(1)–O(1)	2.287(4)	C(1)Sb(1)O(1)	84.7(2)
Sb(1)–C(1)	2.110(7)	C(1)Sb(1)C(31)	96.7(2)
Sb(1)–C(31)	2.179(6)	C(1)Sb(1)C(11)	114.6(2)
Sb(1)–C(11)	2.118(6)	C(1)Sb(1)C(21)	124.6(2)
Sb(1)–C(21)	2.133(6)	C(31)Sb(1)O(1)	175.20(18)
Sb(2)–O(3)	2.389(4)	C(11)Sb(1)O(1)	81.91(18)
Sb(2)–C(51)	2.108(6)	C(11)Sb(1)C(31)	93.3(2)
Sb(2)–C(41)	2.119(6)	C(11)Sb(1)C(21)	117.8(2)
Sb(2)–C(61)	2.102(6)	C(21)Sb(1)O(1)	85.49(19)
Sb(2)–C(71)	2.165(6)	C(21)Sb(1)C(31)	97.3(2)
C(7)–O(1)	1.293(7)	C(51)Sb(2)O(3)	89.54(19)
C(7)–O(2)	1.212(7)	C(51)Sb(2)C(41)	119.6(2)
C(10)–O(3)	1.255(7)	C(51)Sb(2)C(71)	94.5(2)
C(10)–O(4)	1.224(7)	C(41)Sb(2)O(3)	82.4(2)
Sb(1)⋯O(2)	3.297(6)	C(41)Sb(2)C(71)	98.5(2)

### Results and Discussion

We have found that the reaction of pentaphenylantimony with dicarboxylic acid (mole ratio 2:1 or 1:1) proceeds in toluene solution at room temperature with the substitution of hydrogen atoms in two carboxyl groups and the formation of *bis*(tetraphenylantimony) acetylenedicarboxylate (**1**). The yield of compound **1** is up to 90%:



Only one carboxyl group reacts with pentaphenylantimony after short-duration heating of equimolar quantities in toluene solution. The second group is decarboxylated in this case.



The yield of tetraphenylantimony propiolate isolated from the reaction mixture is 76%. Its IR spectrum, melting point and parameters of crystal cell correspond to the similar characteristics of the compound synthesized from pentaphenylantimony and propiolic acid [11]. *Bis*(tetraphenylantimony) carbonate ( $\text{Ph}_4\text{Sb})_2\text{CO}_3$  is the second product of this reaction with the yield about 10%. This product has been identified by its melting point and IR spectrum. As shown by X-ray diffraction, the obtained *bis*(tetraphenylantimony) carbonate has triclinic modification described in the paper [12].

According to the X-ray diffraction data, the acid anion in molecule **1** has the bridging role and bonds  $\text{Ph}_4\text{Sb}$  fragments. The Sb(1,2) atoms have distorted trigonal bipyramidal coordination with carboxylate and phenyl ligands in the axial positions (Fig. 1).

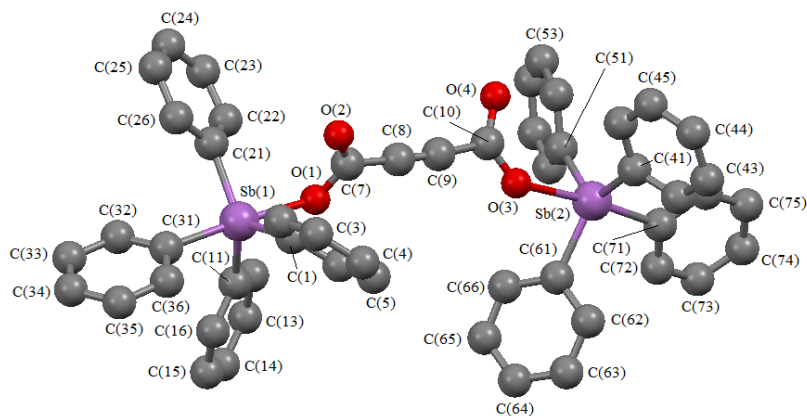


Fig. 1. The structure of compound 1

The axial angles OSb(1,2)C are equal to  $175.2(2)^\circ$  and  $174.7(2)^\circ$ . The sums of the CSbC angles in the equatorial planes are  $357.0(2)^\circ$  and  $356.2(2)^\circ$ , respectively. There is deviation of Sb(1,2) atoms from the equatorial plane towards the carbon atom in the axial position up to  $0.218(2)$  Å and  $0.237(2)$  Å. The angles between the axial and equatorial bonds of OSb(1,2)C are less than  $90^\circ$  ( $81.9(2)$ – $85.5(2)^\circ$ , ( $78.8(2)$ – $89.5(2)^\circ$ ), for CSb(1,2)C they are more than  $90^\circ$  ( $93.3(2)$ – $97.3(2)^\circ$ ,  $94.5(2)$ – $98.5(2)^\circ$ ). The length of Sb(1,2)–C equatorial bonds changes in the ranges  $2.110(7)$ – $2.133(6)$  Å,  $2.108(6)$ – $2.119(6)$  Å. The axial distances Sb(1,2)–C ( $2.179(6)$  Å and  $2.165(6)$  Å) are greater than equatorial ones. The Sb(1)–O(1) ( $2.287(4)$  Å) and Sb(2)–O(3) ( $2.389(4)$  Å) bonds are longer than the sum of covalent radii of antimony and oxygen ( $2.05$  Å [13]). As one would expect, the C(7)–O(1) ( $1.293(7)$  Å), C(10)–O(3) ( $1.255(7)$  Å) distances in the carboxyl group are greater than the C(7)–O(2) ( $1.212(7)$  Å) and C(10)–O(4) ( $1.224(7)$  Å) distances. In structure **1** bidentate properties of the carboxylate ligands almost do not appear. The intramolecular Sb(1)···O(2) and Sb(2)···O(4) distances are  $3.297(6)$  and  $3.794(6)$  Å, while the sum of antimony and oxygen van der Waals radii equals  $3.70$  Å [13]. For comparison: in the *bis*(tetraphenylantimony) maleinate molecule the Sb–O and Sb···O distances equal  $2.206$ ,  $2.218$  Å and  $3.236$ ,  $3.259$  Å [2].

The torsion angle in the dicarboxylic acid anion O(2)C(7)C(10)O(4) is  $-50.3(7)^\circ$ . Acetylene fragment has almost linear structure: the angles C(7)C(8)C(9) and C(10)C(9)C(8) are  $177.8(7)^\circ$  and  $175.2(7)^\circ$ , the distance C(8)–C(9) ( $1.177(9)$  Å) corresponds to the triple bond.

The structural organization of the crystal is formed with the participation of weak hydrogen bonds of (Ph)C–H···O(=C) type.

### Conclusions

Thus, the interaction between pentaphenylantimony with acetylenedicarboxylic acid has the specific feature: under mild conditions both carboxylic groups react. We did not succeed in isolation of acidic tetraphenylantimony carboxylate. Even short-duration heating of reaction mixture is accompanied by the decarboxylation of a carboxyl group in the acid and the formation of tetraphenylantimony propiolate.

In the *bis*(tetraphenylantimony) acetylenedicarboxylate molecule the carboxylate groups are characterized by the monodentate type of the bond.

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## ВЗАИМОДЕЙСТВИЕ ПЕНТАФЕНИЛСУРЬМЫ С АЦЕТИЛЕНДИКАРБОНОВОЙ КИСЛОТОЙ. МОЛЕКУЛЯРНАЯ СТРУКТУРА АЦЕТИЛЕНДИКАРБОКСИЛАТА БИС(ТЕТРАФЕНИЛСУРЬМЫ)

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Взаимодействием пентафенилсурьмы с ацетилендикарбоновой кислотой (2:1 или 1:1 мольн.) в толуоле получен ацетилендикарбоксилат бис(тетрафенилсурьмы) (1). В молекуле 1 остаток кислоты выполняет мостиковую функцию, соединяя фрагменты  $\text{Ph}_4\text{Sb}$ . Атомы сурьмы имеют искаженную тригонально-бипирамидальную координацию с атомом кислорода в аксиальном положении. Длина связей  $\text{Sb}-\text{O}$  2.287(4) и 2.389(4) Å,  $\text{Sb}-\text{C}$  2.110(7)–2.179(6) Å и 2.108(6)–2.165(6) Å.

*Ключевые слова:* пентафенилсурьма, ацетилендикарбоновая кислота, ацетилендикарбоксилат бис(тетрафенилсурьмы), молекулярная структура, рентгеноструктурный анализ.

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### ОБРАЗЕЦ ЦИТИРОВАНИЯ

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