Triphenylantimony and Pentaphenylantimony as the Starting Compounds for the Synthesis of Antimony(V) Phenyl Derivatives. Structure of Triphenylantimony, Bis(3,4-difluorobenzoato)triphenylantimony and Tetraphenylantimony Carbonate

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Abstract—The structure of triphenylantimony (**I**) was determined more accurately. Bis(3,4-difluorobenzoato)triphenylantimony $Ph_3Sb[OC(O)C_6H_3F_2-3,4]_2$ (**III**) was obtained by the reaction of equimolar amounts of pentaphenylantimony solvate $(Ph_5Sb \cdot 0.5PhH)$ (**II**) with 3,4-difluorobenzoic acid in benzene and characterized. The structure of the triclinic tetraphenylantimony carbonate (**IV**) was also determined more accurately. According to X-ray diffraction data (CCDC nos. 2117872 (**I**), 121388 (**III**), 2121833 (**IV**)), the crystals were characterized as follows. $C_{36}H_{30}Sb_2$ (**I**): $a = 10.941(11)$, $b = 11.825(16)$, $c = 13.747(13)$ Å; $\alpha = 102.57(5)°$, $\beta = 104.22(5)°$, $\gamma = 108.35(6)°$; $V = 1550(3)$ Å^3; $Z = 2$. $C_{32}H_{21}O_4F_4Sb$ (**III**): $a = 12.652(5)$, $b = 22.466(10)$, $c = 11.561(5)$ Å; $\beta = 120.027(15)°$; $V = 2845(2)$ Å^3; $Z = 4$. $C_{49}H_{40}O_3Sb_2$ (**IV**): $a = 10.093(4)$, $b = 13.994(5)$, $c = 15.665(6)$ Å; $\alpha = 73.917(15)°$, $\beta = 79.76(2)°$, $\gamma = 74.312(15)°$; $V = 2034.0(13)$ Å^3; $Z = 2$. The antimony atoms in **III** have a distorted trigonal-bipyramidal coordination, with the oxygen atoms being located in axial positions (OSbO, 174.13(12)°; Sb−C, 2.101(3)−2.118(4) Å; Sb−O, 2.118(3) Å). The structural organization in the crystals of **III** and **IV** is formed by weak O···H−C intermolecular contacts (2.49 and 2.56 Å, respectively).

Keywords: solvate, pentaphenylantimony, benzene, bis(3,4-difluorobenzoato)triphenylantimony, synthesis, structure, triphenylantimony, tetraphenylantimony carbonate, X-ray diffraction

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INTRODUCTION

An efficient method for the synthesis of pentavalent antimony compounds is the oxidative addition reactions in which aryl derivatives of pentavalent antimony Ar_3SbX_2 are formed from antimony triaryl compounds, acid HX, and a peroxide. This reaction was performed for the first time to prepare triphenylantimony diacetate from triphenylantimony, acetic acid, and H_2O_2 [1]. This approach was also utilized to obtain triphenylantimony dicarboxylates [2], triphenylantimony dioximates [3], and other pentavalent antimony derivatives Ph_3SbX_2 [4].

The structure of the basic reagent for the preparation of phenyl derivatives of pentavalent antimony has been studied previously [5]; however, only in this study, we were able to more accurately determine structural features of triphenylantimony (**I**). According to X-ray diffraction data, the antimony atoms in two crystallographically independent triphenylantimony molecules have a tetragonal coordination, with the phenyl carbon atoms and the lone pair of electrons being located at the tetrahedron vertices (Fig. 1, Table 1). The Sb−C bond lengths and CSbC angles are 2.148(3)−2.166(3) Å and 95.12(13)°−97.87(11)°, respectively.

An equally important phenyl derivative of antimony is pentaphenylantimony (**II**), the first synthesis of which was reported in 1952 [6], while its structural features were studied somewhat later [7−10]. It is known that pentaphenylantimony is a precursor for the preparation of numerous phenyl derivatives of Sb(V) [4]. As a rule, monocarboxylic acids easily detach one phenyl group from **II** [11−15] to give tetraphenylantimony carboxylates, which, in turn, form adducts $Ph_4SbOC(O)R \cdot HOC(O)R$ with the acids [16]. Depending on the reactant ratio, the reactions of dicarboxylic acids may be accompanied by replace-
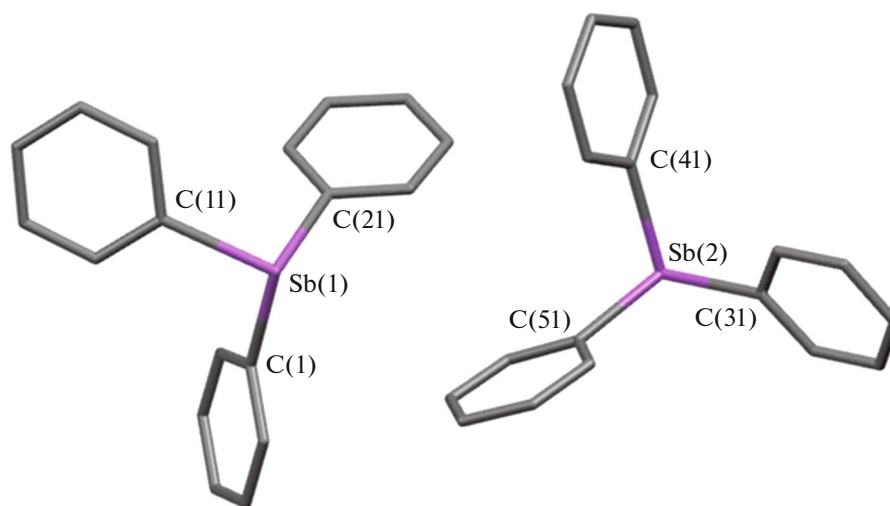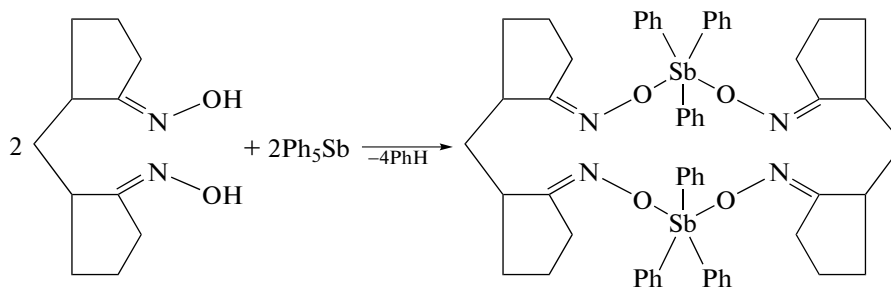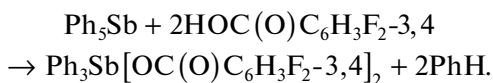
Fig. 1. Structure of compound **I**.

ment of one or two active hydrogen atoms in carboxyl groups [17−19].

It was shown that methylene-2,2'-dicyclopenta-none dioxime reacts with pentaphenylantimony under drastic conditions (90°C, 5 h) at a reactant molar ratio of 1 : 2, respectively, to give a macrocyclic organoanti-mony compound, bis-μ-[(methylene-2,2'-dicyclo-pentanonedioximato)triphenylantimony], in which symmetrical dioxime radicals alternate with triphe-nylantimony structural blocks [20].

Here we describe a similar case of elimination of two phenyl substituents from pentaphenylantimony on treatment with 3,4-difluorobenzoic acid, giving bis(3,4-difluorobenzoato)triphenylantimony **(III)**, despite the equimolar ratio of the starting reactants.

$$Ph_5Sb + 2HOC(O)C_6H_3F_2\text{-}3,4$$
$$\rightarrow Ph_3Sb[OC(O)C_6H_3F_2\text{-}3,4]_2 + 2PhH.$$

The IR spectrum of compound **III** exhibits a medium-intensity absorption band at 428 cm^{-1} corre-sponding to the Sb−C stretching modes. The presence of the carbonyl group is manifested as a strong C=O stretching band at 1634 cm^{-1}. The bands correspond-ing to the ν(C−O) vibrations in carboxylate ligands occur at 1333 cm^{-1}. The IR spectrum of **III** also shows characteristic stretching bands for the carbon skeleton of aromatic moieties at 1508, 1481, and 1425 cm^{-1}. The C$_{Ar}$−H stretching mode is manifested as a medium-

intensity band at 3022 cm^{-1}; the out-of-plane C$_{Ar}$−H bending mode gives rise to bands at 823, 794, and 758 cm^{-1}; the in-plane bending mode of the same bond is responsible for the bands at 1113, 1065, and 1022 cm^{-1} [21−23].

According to X-ray diffraction data, the antimony atoms in the centrosymmetric molecules of **III** have a distorted trigonal-bipyramidal coordination in which the carboxylate oxygen atoms occupy axial positions (Fig. 2).

The sum of the CSbC angles in the equatorial plane of the molecule is 359.96(11)°, while the axial OSbO angle is 174.13(12)°; the antimony atom does not devi-ate from the equatorial plane. The aryl ligands have a propeller-like conformation relative to the [C$_3$] equa-torial plane. The dihedral angles between the benzene ring planes and the equatorial plane are 20.20° [C(1)−C(6)] and 78.01° [C(7)−C(10)]. The Sb−C bonds have similar lengths, 2.101(3) Å and 2.118(4) Å, while

Table 1. Crystallographic data and X-ray experiment and structure refinement details for the structures of **I**, **III**, **IV**

Parameter	Value		
	I	**III**	**IV**
Formula	$C_{36}H_{30}Sb_2$	$C_{32}H_{21}O_4F_4Sb$	$C_{49}H_{40}O_3Sb_2$
M	706.10	667.24	920.31
T, K	293	293	293
System	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a, Å	10.941(11)	12.652(5)	10.093(4)
b, Å	11.825(16)	22.466(10)	13.994(5)
c, Å	13.747(13)	11.561(5)	15.665(6)
α, deg	102.57(5)	90.00	73.917(15)
β, deg	104.22(5)	120.027(15)	79.76(2)
γ, deg	108.35(6)	90.00	74.312(15)
V, Å^3	1550(3)	2845(2)	2034.0(13)
Z	2	4	2
ρ(calcd.), g/cm^3	1.513	1.558	1.503
μ, mm^{-1}	1.764	1.032	1.369
$F(000)$	696.0	1328.0	920.0
Crystal size, mm	$0.5 \times 0.44 \times 0.11$	$0.5 \times 0.45 \times 0.12$	$0.26 \times 0.22 \times 0.05$
Data collection range of 2θ, deg	5.74–54.42	6.6–54.32	5.802–54.44
Ranges of reflection indices	$-13 \le h \le 14$, $-15 \le k \le 15$, $-17 \le l \le 17$	$-16 \le h \le 16$, $-28 \le k \le 28$, $-14 \le l \le 14$	$-12 \le h \le 12$, $-17 \le k \le 17$, $-20 \le l \le 20$
Number of measured reflections	37455	27275	50553
Number of unique reflections	6837	3163	9006
R_{int}	0.0252	0.0291	0.0333
Number of refinement variables	343	187	477
GOOF	1.121	1.107	1.066
R-factors on $F^2 > 2\sigma(F^2)$	$R_1 = 0.0257$, $wR_2 = 0.0605$	$R_1 = 0.0372$, $wR_2 = 0.1058$	$R_1 = 0.0239$, $wR_2 = 0.0522$
R-factors for all reflections	$R_1 = 0.0330$, $wR_2 = 0.0652$	$R_1 = 0.0425$, $wR_2 = 0.1124$	$R_1 = 0.0349$, $wR_2 = 0.0572$
Residual electron density (min/max), e/A^3	$-0.84/0.23$	$-0.53/1.61$	$-0.43/0.77$

the Sb−O distances (2.118(3) Å) are comparable with the Sb−O covalent bond lengths (2.05 Å [24]). The carboxyl group planes are virtually coplanar (the angle between them is 5.24°), while the carboxylate ligands in **III** are arranged in such a way that the intramolecular Sb···O(=C) contacts are formed within the greatest equatorial CSbC angle (137.6(2)°); this is typical of most structurally characterized triarylantimony dicarboxylates [5]. The bidentate carboxylate ligands are symmetrically coordinated to the metal, with the intramolecular Sb···O(=C) distances being 3.014(5) Å, which is smaller than the sum of the Sb and O van der Waals radii (3.58 Å [25]).

Pentaphenylantimony reacts with oxygen [26] and carbon dioxide [27]. Bis(tetraphenylantimony) carbonate isolated in the latter study can react with tetraphenylstibonium salts by adding one more cation via the change in the structural function of the carbonate group from μ_2-chelating bridging to μ_3-bridging one, thus giving ionic complexes with tris(tetraphenylstiboxy)methylium cation [28]. Indeed, crystallization of the products formed in the reaction between pentaphenylantimony and 2,4-dinitrobenzenesulfonic acid from a benzene−octane mixture in air gives not only the target tetraphenylantimony 2,4-dinitrobenzenesulfonate (formed in 32% yield), but also the sol-
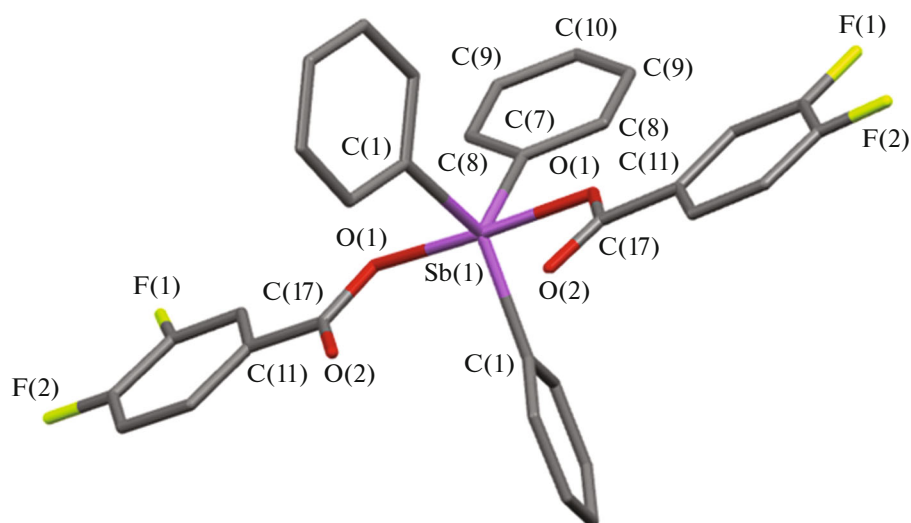
Fig. 2. Structure of compound **III** (the hydrogen atoms are omitted).

vate of the ionic antimony complex containing a three-coordinate carbon atom in the cation, $[(Ph_4SbO)_3C]^+[OSO_2C_6H_3(NO_2)_2-2,4]^-\cdot3PhH$. The cation has a nearly planar CO_3Sb_3 central moiety. The OCO and COSb angles are close to 120°, the C–O bonds vary in the 1.277(4)–1.290(3) Å range, and the Sb–O distances (2.266(2)–2.299(2) Å) are longer than the sum of the Sb and O covalent radii. A minor product is bis(tetraphenylantimony) carbonate (**IV**); in the authors' opinion, particularly this compound is converted to the ionic complex; therefore, it was of interest to study the structure of tetraphenylantimony carbonate in more detail.

Here we determined more accuately the structure of triclinic tetraphenylantimony carbonate **IV**, which was solved previously to the accuracy R = 4.9% [29]. The results of our study of **IV** were more accurate (R = 3.7%) than in [28]. The coordination polyhedra of the two antimony atoms in **IV** are different: one antimony atom has a trigonal bipyramidal environment (OSb-C_{ax}, 176.38(8)°), while the other atom has a distorted octahedral environment (*trans*-angles: CSbO, 154.59(8)°; 157.47(8)° (Fig. 3)).

The variation range of the Sb–C bond lengths in **IV** is 2.0992(15)–2.634(2) Å, and the Sb–O distances vary in the 2.1844(17)–2.3104(17) Å range; this is greater than the sum of the covalent radii of these elements [27]. The C–O bond lengths in the carbonate groups are 1.281(3) Å, 1.277(3) Å, and 1.296(3) Å, with a shorter Sb–O bond corresponding to longer C–O bond.

EXPERIMENTAL

Synthesis of the benzene solvate $Ph_5Sb\cdot0.5PhH$ (II) was performed by recrystallization of pentaphenylan-

timony from benzene. The product was formed as colorless crystals with T_{dec} = 135.5 °C.

For $C_{32}H_{21}O_4F_4Sb$

Anal. calcd., %	C, 72.49	H, 5.13
Found, %	C, 72.41	H, 5.19

Synthesis of bis(3,4-difluorobenzoato)triphenylantimony $Ph_3Sb[OC(O)C_6H_3F_2-3,4]_2$ (III). A mixture of pentaphenylantimony benzene solvate (0.150 g, 0.27 mmol) and 3,4-difluorobenzoic acid (0.043 g, 0.27 mmol) in benzene (10 mL) was heated for 5 min at 80°C and cooled down to room temperature; then octane (2 mL) was added. After 24 h, colorless crystals of **III** were isolated in 0.06 g (41%). T_{dec} = 134°C.

IR (ν, cm^{-1}): 3022, 2953, 1634, 1599, 1508, 1481, 1425, 1333, 1273, 1227, 1200, 1113, 1065, 1023, 997, 937, 901, 839, 802, 779, 770, 733, 692, 638, 546, 489, 451, 428.

For $C_{32}H_{21}O_4F_4Sb$

Anal. calcd., %	C, 57.55	H, 3.15
Found, %	C, 57.37	H, 3.21

Elemental analysis for C and H was carried out on a Carlo Erba CHNS-O EA 1108 analyzer. The IR spectrum of compound **III** was recorded on a Shimadzu IRAffinity-1S FT IR spectrometer in KBr pellets in the 4000–400 cm^{-1} range. The melting points were measured on a Netzsch 449C Jupiter simultaneous thermal analyzer. The DTG and DSC curves for sample **III** are shown in Fig. 4.

X-ray diffraction analysis of the crystals was carried out on a D8 QUEST Bruker four-circle automated diffractometer (MoK_α radiation, λ = 0.71073 Å,
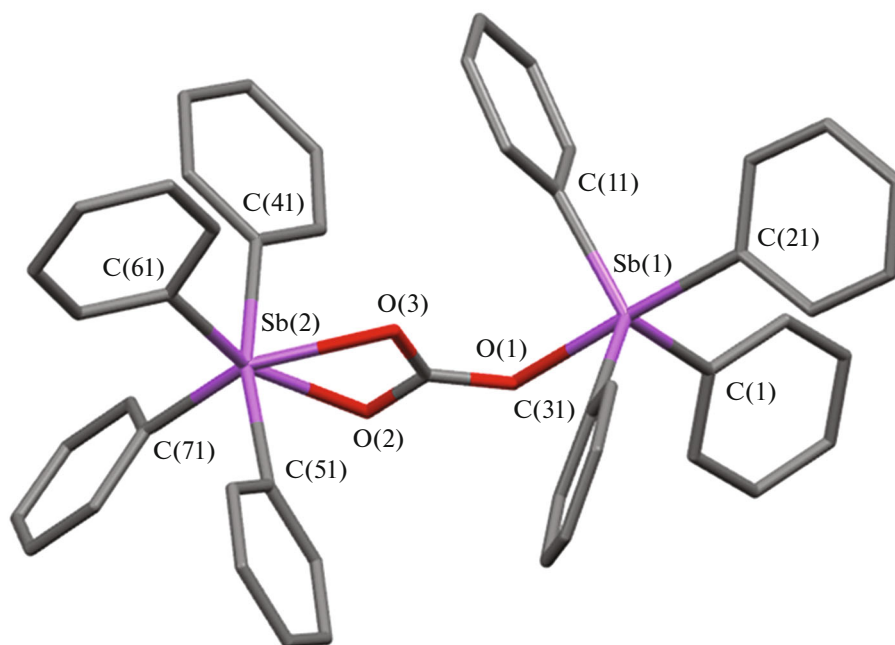
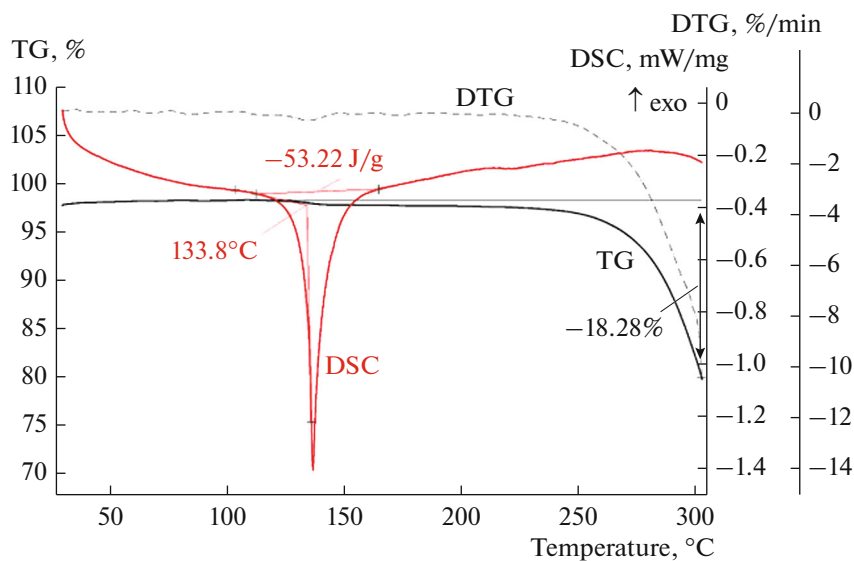**Fig. 3.** Structure of compound **IV** (the hydrogen atoms are omitted).

Fig. 4. DTG and DSC curves for sample **III**.

graphite monochromator). The data collection and editing and refinement of unit cell parameters were performed and the absorption corrections were applied using the SMART and SAINT-Plus software [30]. All calculations for structure determination and refinement were carried out using the SHELXL/PC [31] and OLEX2 [32] programs. The structures were solved by the direct methods and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The hydrogen atom positions were refined by the riding model (U_{iso}(H) = $1.2U_{equiv}$(C)). The crystal data and structure refinement details are summarized in Table 1, and geometrical characteristics of the antimony coordination polyhedron are given in Table 2.

Thus, bis(3,4-difluorobenzoato)triphenylantimony (**III**) was obtained by the reaction of equimolar amounts of the solvate (Ph$_5$Sb·0.5PhH) and 3,4-difluorobenzoic acid in benzene and structurally characterized. The structures of triphenylantimony and

Table 2. Bond lengths and bond angles of compounds **I**, **III**, and **IV**

Bond	d, Å	Angle	ω, deg
I			
Sb(1)−C(1)	2.163(3)	C(11)Sb(1)C(1)	95.87(11)
Sb(1)−C(11)	2.155(3)	C(11)Sb(1)C(21)	95.55(11)
Sb(1)−C(21)	2.158(4)	C(21)Sb(1)C(1)	97.46(14)
Sb(2)−C(51)	2.148(3)	C(51)Sb(2)C(31)	97.65(12)
Sb(2)−C(31)	2.165(3)	C(51)Sb(2)C(41)	95.12(13)
Sb(2)−C(41)	2.166(3)	C(31)Sb(2)C(41)	95.43(12)
III			
Sb(1)−O(1)	2.118(3)	O(1)Sb(1)O(1)[1]	174.13(12)
Sb(1)−O(1)[1]	2.118(3)	C(1)[1]Sb(1)C(7)	111.18(11)
Sb(1)−C(7)	2.118(4)	C(1)Sb(1)C(7)	111.18(11)
Sb(1)−C(1)	2.101(3)	C(1)[1]Sb(1)C(1)	137.6(2)
Sb(1)···O(2)	3.014(5)	C(1)Sb(1)O(1)[1]	91.87(13)

Symmetry codes: [1] $2 - x, y, 3/2 - z$.

Bond	d, Å	Angle	ω, deg
IV			
Sb(1)−C(31)	2.117(3)	C(31)Sb(1)C(1)	115.22(11)
Sb(1)−O(1)	2.2505(17)	C(11)Sb(1)C(1)	116.55(9)
Sb(1)−C(1)	2.119(2)	C(21)Sb(1)O(1)	176.38(8)
Sb(1)−C(11)	2.0992(15)	C(51)Sb(2)C(41)	167.09(9)
Sb(1)−C(21)	2.168(3)	C(71)Sb(2)O(3)	154.59(8)
Sb(2)−O(3)	2.3104(17)	C(71)Sb(2)C(7)	125.66(8)
Sb(2)−O(2)	2.1844(17)	C(61)Sb(2)O(2)	157.47(8)
Sb(2)−C(51)	2.169(2)	C(61)Sb(2)C(51)	92.76(10)
Sb(2)−C(71)	2.162(2)	C(61)Sb(2)C(71)	106.18(10)
Sb(2)−C(7)	2.634(2)	C(61)Sb(2)C(7)	128.14(9)
Sb(2)−C(61)	2.162(3)	C(61)Sb(2)C(41)	91.79(10)
Sb(2)−C(41)	2.173(2)	C(41)Sb(2)C(7)	84.92(8)

triclinic tetraphenylantimony carbonate were determined more accurately.

CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interest.

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