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Synthesis and Structures of Tris(3-Fluorophenyl)antimony Dicarboxylates: $(3\text{-}FC_6H_4)_3Sb[OC(O)R]_2$ ($R = C_6H_3[(NO_2)_2\text{-}3,5)]$, CH_2Br, CH_2Cl, and CH=CHPh)

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Abstract—The reactions of tris(3-fluorophenyl)antimony $(3\text{-}FC_6H_4)_3Sb$ with 3,5-dinitrobenzoic, bromoacetic, chloroacetic, and cinnamic acids in the presence of *tert*-butyl hydroperoxide afford tris(3-fluorophenyl)antimony bis(3,5-dinitrobenzoate (**I**), tris(3-fluorophenyl)antimony bis(bromoacetate (**II**), tris(3-fluorophenyl)antimony bis(chloroacetate) (**III**), and tris(3-fluorophenyl)antimony dicinnamate (**IV**). According to the X-ray diffraction data, the coordination mode of the Sb atoms in all compounds is a trigonal bipyramid (CIF files CCDC nos. 1576022 (**I**), 1576023 (**II**), 1575287 (**III**), and 1576967 (**IV**). The axial angles OSbO are 174.70(6)°, 175.92(15)°, 176.62(6)°, and 175.81(11)°. The Sb–O and Sb–C bond lengths are 2.117(2), 2.137(2), and 2.105(3)–2.119(2) Å in **I**; 2.110(4), 2.129(4), and 2.096(5)–2.112(5) Å in **II**; 2.118(2), 2.136(2), and 2.120(2)–2.128(2) Å in **III**; and 2.142(3) and 2.115(3)–2.119(4) Å in **IV**. The Sb···O intramolecular distances with the carbonyl oxygen atom (2.895(3), 2.968(4) Å (**I**); 2.814(6), 2.930(6) Å (**II**); 2.809(3), 2.933(4) Å (**III**); and 2.601(4) Å (**IV**)) are shorter than the sum of the van der Waals radii of Sb and O by ~1.0 Å.

Keywords: tris(3-fluorophenyl)antimony, dicarboxylates, oxidation synthesis, X-ray diffraction analysis
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INTRODUCTION

It is known that the biological activity of the organic compounds of antimony depends on the types of ligands at the metal atom and the nature of substituents in the ligands [1, 2]. It can be assumed, for instance, that the replacement of the tolyl ligands by fluorophenyls in triarylantimony dicarboxylates results in the enhancement (diminishing) of their biological activity.

Numerous triphenyl- and tritolylantimony dicarboxylates are known to the present time. They were prepared by oxidative addition from triarylantimony and carboxylic acids HX in the presence of peroxide [3–9]. However, the syntheses, structures, and biological activities of tris(4-fluorophenyl)antimony dicarboxylates were discussed only in three works [10–12]. The synthesis and structures of tris(3-fluorophenyl)antimony dicarboxylates were not reported.

Continuing the investigations of the regularities of the synthesis and structure of triarylantimony dicarboxylates, we obtained tris(3-fluorophenyl)antimony bis(3,5-dinitrobenzoate) (**I**), tris(3-fluorophenyl)antimony bis(bromoacetate) (**II**), tris(3-fluorophenyl)antimony bis(chloroacetate) (**III**), and tris(3-fluorophenyl)antimony dicinnamate (**IV**) and studied their molecular and crystal structures.

EXPERIMENTAL

Synthesis of $(3\text{-}FC_6H_4)_3Sb[OC(O)C_6H_3(NO_2)_2\text{-}3,5]_2$ (I). A mixture of tris(3-fluorophenyl)antimony (0.100 g, 0.246 mmol), 3,5-dinitrobenzoic acid (0.104 g, 0.492 mmol), and a 70% solution of *tert*-butyl hydroperoxide (0.032 g, 0.246 mmol) in diethyl ether (30 mL) was kept at 20°C for 24 h. After the slow evaporation of the solvent, colorless crystals (0.200 g, 98%) were obtained. After recrystallization from a benzene–heptane (2 : 1) mixture, the crystals had mp = 195°C.

For $C_{32}H_{18}F_3N_4O_{12}Sb$		
Anal. calcd., %	C, 46.34	H, 2.19
Found, %	C, 46.23	H, 2.28

IR (ν, cm^{-1}): 3099, 1654, 1625, 1587, 1577, 1544, 1473, 1460, 1423, 1413, 1344, 1332, 1317, 1269, 1217,

1180, 1087, 1074, 997, 920, 873, 856, 786, 729, 678, 659, 617, 555, 542, 522, 462, 430.

Compounds **II**–**IV** were synthesized using a similar procedure.

$(3\text{-}FC_6H_4)_3Sb[OC(O)CH_2Br]_2$ (**II**): colorless transparent crystals, 98% yield, mp = 114°C.

For $C_{22}H_{16}F_3O_4Br_2Sb$		
Anal. calcd., %	C, 38.69	H, 2.37
Found, %	C, 38.57	H, 2.44

IR (ν, cm^{-1}): 3099, 3070, 2958, 2927, 1672, 1654, 1585, 1575, 1519, 1471, 1425, 1402, 1323, 1301, 1265, 1215, 1192, 1166, 1149, 1089, 1053, 999, 894, 875, 854, 781, 725, 677, 569, 547, 522, 472, 439.

$(3\text{-}FC_6H_4)_3Sb[OC(O)CH_2Cl]_2$ (**III**): colorless transparent crystals, 97% yield, mp = 140°C.

For $C_{22}H_{16}F_3O_4Cl_2Sb$		
Anal. calcd., %	C, 44.48	H, 2.72
Found, %	C, 44.35	H, 2.83

IR (ν, cm^{-1}): 3101, 3070, 3010, 2954, 2854, 1672, 1656, 1589, 1577, 1521, 1471, 1425, 1411, 1344, 1303, 1267, 1217, 1176, 1166, 1089, 1053, 999, 933, 898, 875, 856, 790, 678, 659, 586, 543, 522, 505, 439, 430.

$(3\text{-}FC_6H_4)_3Sb[OC(O)CH{=}CHPh]_2$ (**IV**): colorless transparent crystals, 98% yield, mp = 163°C.

For $C_{36}H_{26}F_3O_4Sb$		
Anal. calcd., %	C, 61.65	H, 3.74
Found, %	C, 61.47	H, 3.83

IR (ν, cm^{-1}): 3082, 3059, 3024, 1639, 1620, 1577, 1562, 1544, 1519, 1496, 1473, 1450, 1413, 1369, 1303, 1288, 1263, 1217, 1180, 1166, 1089, 999, 975, 871, 850, 794, 773, 748, 717, 680, 657, 590, 543, 522, 484, 445, 432, 416.

The IR spectra of compounds **I**–**IV** were recorded on a Shimadzu IRAffinity-1S IR spectrometer in KBr pellets in a range of 4000–400 cm^{-1}.

X-ray diffraction analyses of crystals of compounds **I**–**IV** were carried out on a D8 QUEST diffractometer (Bruker, MoK_α radiation, λ = 0.71073 Å, graphite monochromator) at 296(2) K. Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [13]. All calculations on structure determination and refinement were performed using the SHELXL/PC [14] and OLEX2 [15] programs. The structures were determined by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The crystallographic data and structure refinement results for compounds **I**–**IV** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The full tables of coordinates of atoms, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1576022 (**I**), 1576023 (**II**), 1575287 (**III**), and 1576967 (**IV**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

It is known that the oxidation of triarylantimony with *tert*-butyl hydroperoxide in the presence of carboxylic acids affords triarylantimony dicarboxylates of the general formula $Ar_3Sb[OC(O)R)]_2$ [4].

We found that the reactions of tris(3-fluorophenyl)antimony with such carboxylic acids as 3,5-dinitrobenzoic, bromoacetic, chloroacetic, and cinnamic acids in the presence of *tert*-butyl hydroperoxide (molar ratio 1 : 2 : 1) occurred in ether to form tris(3-fluorophenyl)antimony dicarboxylates in the yields up to 98%.

$$(3\text{-}FC_6H_4)_3Sb + 2HOC(O)R + t\text{-}BuOOH \rightarrow (3\text{-}FC_6H_4)_3Sb[OC(O)R]_2 + H_2O + t\text{-}BuOH$$

R = $C_6H_3(NO_2)_2$-3,5 (**I**), CH_2Br (**II**), CH_2Cl (**III**), CH=CHPh (**IV**)

According to the X-ray diffraction data, in compounds **I**–**IV**, the Sb atoms lie in the equatorial plane and have a distorted trigonal bipyramidal coordination mode with the oxygen atoms of the carboxylate ligands in the axial positions (Fig. 1). The sum of the angles in the equatorial CSbC plane in the molecules of compounds **I**–**IV** is 360°. The deviation of the antimony atom from the equatorial plane is 0.007, 0.001, 0.004, and 0.000 Å for compounds **I**–**IV**, respectively. The planar aryl rings in the structures of compounds **I**–**IV** are unfolded around the Sb–C bonds in such a way that intra- and intermolecular contacts would be reduced to minimum. The axial OSbO angles in compounds **I**–**IV** are 174.70(6)°, 175.92(15)°, 176.62(6)°, and 175.81(11)°.

The geometric parameters of the molecules of compounds **I**–**IV** somewhat differ in Sb–C and Sb–O bond lengths (2.105(3)–2.119(2) and 2.117(2), 2.137(2) Å in **I**; 2.096(5)–2.112(5) and 2.110(4), 2.129(4) Å in **II**; 2.120(2)–2.128(2) and 2.118(2), 2.136(2) Å in **III**; and 2.115(3)–2.119(4) and 2.142(3) Å in **IV**). As in other triphenylantimony dicarboxylates, compounds **I**–**IV** contain intramolecular contacts Sb···O(=C). The corresponding distances are 2.894(3), 2.968(3) Å in **I**; 2.814(5), 2.930(5) Å in **II**; 2.809(2), 2.933(3) Å in **III**; and 2.601(4) Å in **IV**. It should be mentioned that in a triphenylantimony dicinnamate molecule a similar distance is a little longer (2.664(5) Å [16]) than that in compound **IV**, which differs by the presence of the fluorine atom in the aryl

Table 1. Crystallographic data and experimental and structure refinement parameters for compounds **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
FW	946.41	682.92	594	701.32
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	12.696(7)	12.390(7)	12.359(7)	13.131(11)
b, Å	12.776(7)	11.298(7)	11.222(6)	21.786(13)
c, Å	14.443(6)	17.302(12)	17.345(13)	12.196(8)
α, deg	115.760(17)	90	90	90
β, deg	103.134(17)	105.71(2)	107.06(3)	119.24(3)
γ, deg	96.18(3)	90	90	90
V, Å^3	1996.9(17)	2331(3)	2300(3)	3044(4)
Z	2	4	4	4
ρ_{calcd}, g/cm^3	1.574	1.946	1.716	1.53
μ_{Mo}, mm^{-1}	0.774	4.661	1.483	0.964
F(000)	950	1312	1168	1408
Crystal size, mm	0.76 × 0.38 × 0.33	1.00 × 0.67 × 0.37	0.56 × 0.5 × 0.15	0.69 × 0.46 × 0.26
2θ, deg	5.8–56.5	5.9–56.7	6.0–61.0	6.6–52.7
Ranges of reflection indices	$-16 \le h \le 16$, $-17 \le k \le 17$, $-19 \le l \le 19$	$-16 \le h \le 16$, $-15 \le k \le 15$, $-23 \le l \le 23$	$-17 \le h \le 17$, $-16 \le k \le 16$, $-24 \le l \le 24$	$-16 \le h \le 16$, $-27 \le k \le 27$, $-15 \le l \le 15$
Total number of reflections	170742	36947	63798	34835
Independent reflections	9894	6073	7010	3111
Number of reflections with $F^2 > 2\sigma(F^2)$	8804	4488	5717	2945
Number of refined parameters	570	320	309	255
GOOF	1.084	1.015	1.08	1.126
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0321$ $wR_2 = 0.0793$	$R_1 = 0.0504$ $wR_2 = 0.119$	$R_1 = 0.0283$ $wR_2 = 0.0688$	$R_1 = 0.0299$ $wR_2 = 0.0779$
R factors for all reflections	$R_1 = 0.0399$ $wR_2 = 0.0879$	$R_1 = 0.0773$ $wR_2 = 0.1338$	$R_1 = 0.0404$ $wR_2 = 0.0772$	$R_1 = 0.0327$ $wR_2 = 0.0819$
Residual electron density (min/max), *e*/Å^3	−0.464/0.879	−1.032/2.263	−0.701/0.727	−0.695/0.969

groups. The Sb···O distance observed in molecules of compounds **I–III** in which the organic radicals of the acids contain electronegative groups are comparable with similar distances in other structurally characterized triarylantimony dicarboxylates with similar properties of the acid residues [17–19].

In compounds **I–IV**, the carboxylate groups with the *cis*-orientation relative to the C_3Sb equatorial fragment lie in approximately one plane (dihedral angles between the planes of the carboxy groups are 2.16°, 4.41°, 3.90°, and 2.86°, respectively). For this arrangement of the carboxy groups, the Sb···O(=C) contacts lie from the side of one equatorial CSbC angle, resulting in an increase in the angle (141.08(11)°, 143.0(2)°, 144.51(9)°, and 153.12(15)° in compounds **I**, **II**, **III**, and **IV**, respectively), and two other equatorial angles become smaller than the theoretical value. It should be mentioned that the shortest Sb···O(=C) distance in a

Table 2. Selected interatomic distances and bond angles in the structures of compounds **I–IV***

Bond	*d*, Å	Angle	ω, deg
		I	
Sb(1)–C(21)	2.105(3)	C(21)Sb(1)C(1)	141.08(11)
Sb(1)–C(1)	2.108(3)	C(1)Sb(1)O(1)	90.54(9)
Sb(1)–O(1)	2.1171(19)	C(21)Sb(1)C(11)	110.34(10)
Sb(1)–C(11)	2.119(2)	C(1)Sb(1)C(11)	108.58(11)
Sb(1)–O(7)	2.137(2)	O(1)Sb(1)C(11)	86.91(8)
Sb(1)···O(8)	2.895(3)	O(1)Sb(1)O(7)	174.70(6)
Sb(1)···O(2)	2.968(4)	C(11)Sb(1)O(7)	87.97(8)
		II	
Sb(1)–C(1)	2.096(5)	C(1)Sb(1)C(21)	109.4(2)
Sb(1)–C(21)	2.106(5)	C(1)Sb(1)C(11)	143.0(2)
Sb(1)–O(1)	2.110(4)	C(21)Sb(1)C(11)	107.7(2)
Sb(1)–C(11)	2.112(5)	C(1)Sb(1)O(3)	90.09(19)
Sb(1)–O(3)	2.129(4)	C(21)Sb(1)O(3)	87.4(2)
Sb(1)···O(2)	2.814(6)	O(1)Sb(1)O(3)	175.92(15)
Sb(1)···O(4)	2.930(6)	C(11)Sb(1)O(3)	91.6(2)
		III	
Sb(1)–O(1)	2.1181(18)	O(1)Sb(1)C(21)	88.89(9)
Sb(1)–C(21)	2.120(2)	C(21)Sb(1)C(1)	108.71(9)
Sb(1)–C(1)	2.121(3)	O(1)Sb(1)C(11)	90.84(9)
Sb(1)–C(11)	2.128(2)	C(21)Sb(1)C(11)	106.77(9)
Sb(1)–O(3)	2.136(2)	C(1)Sb(1)C(11)	144.51(9)
Sb(1)···O(3)	2.809(3)	O(1)Sb(1)O(3)	176.62(6)
Sb(1)···O(4)	2.933(4)	C(11)Sb(1)O(3)	91.04(9)
		IV	
Sb(1)–C(1)$^{\#1}$	2.115(3)	C(1)$^{\#1}$Sb(1)C(1)	153.12(15)
Sb(1)–C(11)	2.119(4)	C(1)Sb(1)C(11)	103.44(8)
Sb(1)–O(1)	2.142(3)	C(11)Sb(1)O(1)	87.90(5)
Sb(1)···O(2)	2.601(4)	C(1)$^{\#1}$Sb(1)O(1)$^{\#1}$	91.39(9)
		C(1)Sb(1)O(1)$^{\#1}$	89.59(9)
		O(1)Sb(1)O(1)$^{\#1}$	175.81(11)

* Symmetry transform: $^{\#1}$ $-x + 2, y, -z + 1/2$.

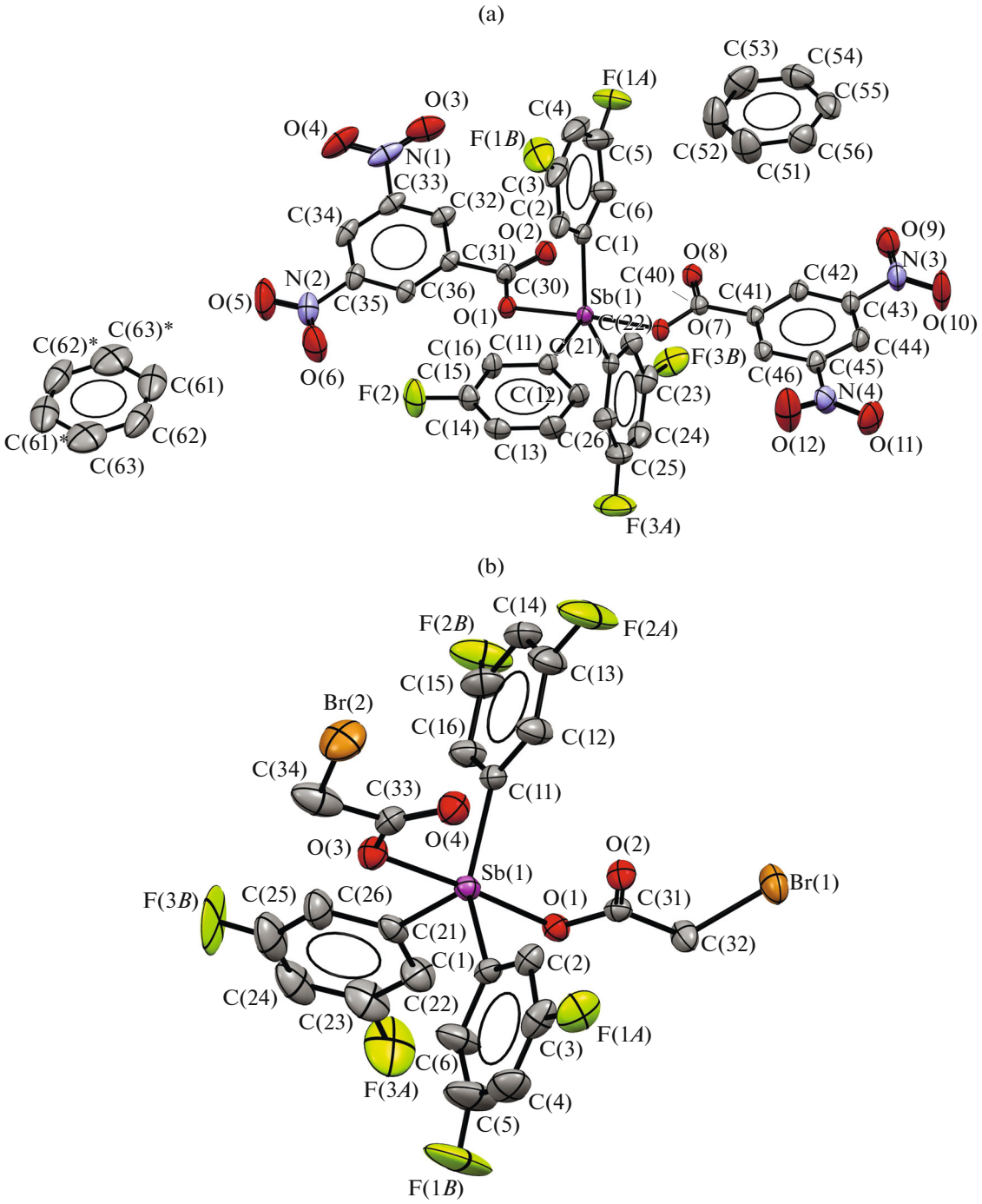
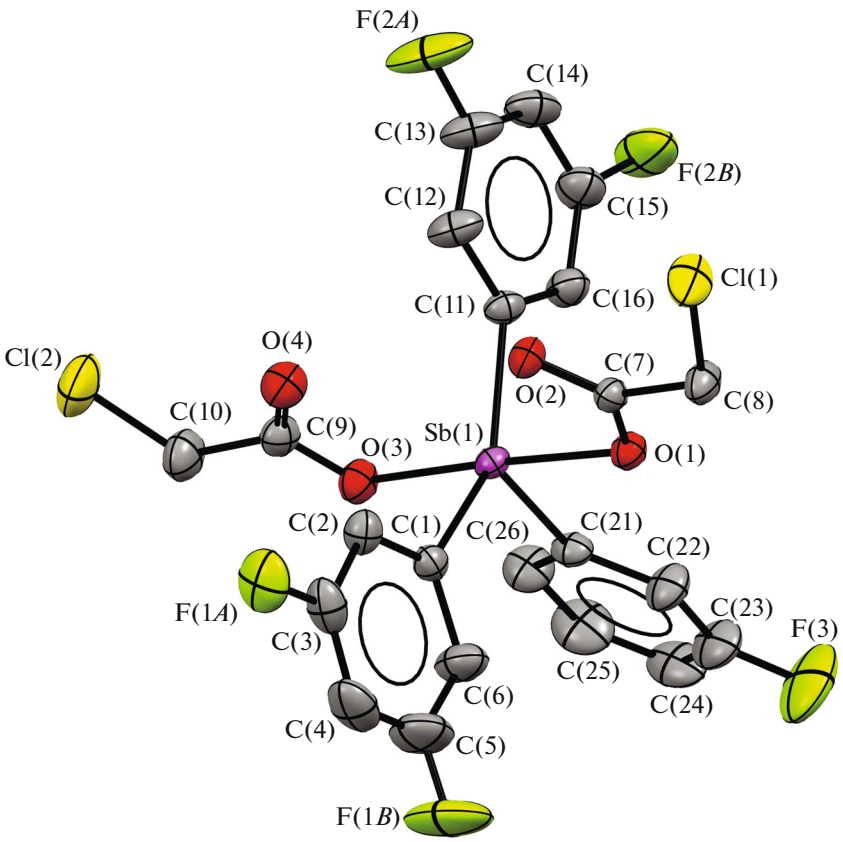


Fig. 1. General view of molecules of compounds (a) **I**, (b) **II**, (c) **III**, and (d) **IV**.

molecule of compound **IV** correlates with the maximum value of the equatorial angles in this molecule. In a molecule of triphenylantimony dicinnamate, the maximum equatorial angle is 151.66(3)° [16].

The planes of the arene rings of the carboxylate ligands in compound **I** are nearly coplanar to the planes of the carboxy groups (the corresponding angles are 5.19° and 14.21°), which assumes a conjugation between them. The p–π conjugation in compound **I** is indicated by the shortening of the C–C(O)O bonds (1.505(3), 1.503(3) Å) compared to these bond lengths in triarylantimony dicarboxylates when no conjugation takes place (1.522(6)–1.547(7) Å [20]).

(c)



(d)

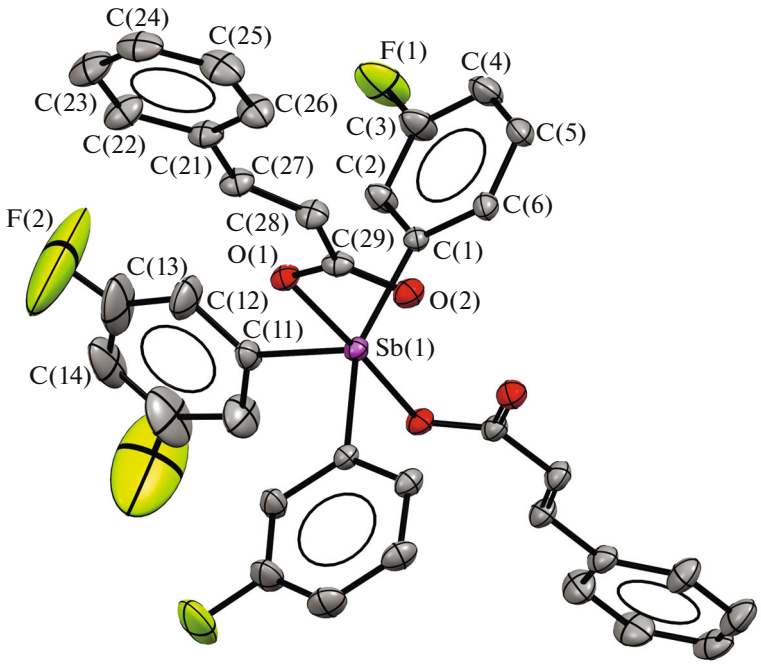


Fig. 1. (Contd.)

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