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Tris(fluorophenyl)antimony Bis(arenesulfonates) $(3\text{-}FC_6H_4)_3Sb(OSO_2R)_2$ (R = Ph, $C_6H_3Me_2$-2,4) and $(4\text{-}FC_6H_4)_3Sb(OSO_2Ph)_2$: Synthesis and Structures

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Abstract—The reactions of tris(3-fluorophenyl)antimony and tris(4-fluorophenyl)antimony with benzenesulfonic and 2,4-dimethylbenzenesulfonic acids in the presence of *tert*-butyl hydroperoxide (molar ratio 1 : 2 : 1, respectively) in diethyl ether afford tris(fluorophenyl)antimony bis(arenesulfonates) $(3\text{-}FC_6H_4)_3Sb(OSO_2R)_2$ (R = Ph (**I**) and $C_6H_3Me_2$-2,4 (**II**)) and $(4\text{-}FC_6H_4)_3Sb(OSO_2Ph)_2$ (**III**). The Sb atoms have a distorted trigonal bipyramidal coordination, and the arenesulfonate ligands exist in the axial positions (CIF files CCDC nos. 2055557 (**I**), 2055820 (**II**), and 2060295 (**III**)).

Keywords: tris(3-fluorophenyl)antimony, tris(4-fluorophenyl)antimony, benzenesulfonic and 2,4-dimethylbenzenesulfonic acids, oxidation, *tert*-butyl hydroperoxide, addition, structure, diffraction studies

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INTRODUCTION

It is known that triarylantimony dicarboxylates can exert antitumor, antileishmanial, and antibacterial effects and possess electrochemical, photoluminescence, and photocatalytic properties [1–8]. The synthesis and properties of similar disulfonate derivatives of triarylantimony are studied to a lower extent [8–11]. Bis(arenesulfonato)tris(fluorophenyl)antimony compounds $(3\text{-}FC_6H_4)_3Sb(OSO_2R)_2$ (R = Ph (**I**) and $C_6H_3Me_2$-2,4 (**II**)) and $(4\text{-}FC_6H_4)_3Sb(OSO_2Ph)_2$ (**III**) were synthesized in this work, and specific features of their structures were revealed.

EXPERIMENTAL

Benzenesulfonic and 2,4-dimethylbenzenesulfonic acids (Alfa Aesar) were used. Triarylantimony was synthesized using a described procedure [12]. Prior to use benzene and octane (reagent grade) that served as solvents were dried over calcium chloride. Diethyl ether was dried over sodium.

Bis(benzenesulfonato)tris(3-fluorophenyl)antimony $(3\text{-}FC_6H_4)_3Sb(OSO_2Ph)_2$) (**I**) was synthesized using a described procedure [11]. The yield of colorless crystals was 81%, T_m = 229°C. IR (ν, cm^{-1}): 3073, 1587, 1474, 1422, 1314, 1269, 1250, 1217, 1165, 1157, 1142, 1094, 1067, 1024, 997, 932, 914, 893, 878, 856, 818, 800, 783, 727, 675, 596, 583, 536, 521, 438.

For $C_{30}H_{22}O_6F_3S_2Sb$		
Anal. calcd., %	C, 49.91	H, 3.05
Found, %	C, 49.58	H, 3.13

Compounds **II** and **III** were synthesized using a similar procedure.

Bis(2,4-dimethylbenzenesulfonato)tris(3-fluorophenyl)antimony solvate $(3\text{-}FC_6H_4)_3Sb\text{-}(OSO_2C_6H_3Me\text{-}2,4)_2\cdot 2PhH$ (**II**): colorless transparent crystals, 82% yield, T_m = 175°C. IR (ν, cm^{-1}): 3075, 3030, 1589, 1518, 1474, 1445, 1422, 1315, 1290, 1271, 1223, 1165, 1136, 1094, 1045, 1022, 997, 908, 891, 858, 795, 762, 727, 692, 673, 627, 604, 588, 561, 538, 521, 430.

For $C_{46}H_{42}O_6F_3S_2Sb$		
Anal. calcd., %	C, 59.12	H, 4.50
Found, %	C, 59.02	H, 4.67

Bis(benzenesulfonato)tris(4-fluorophenyl)antimony $(4\text{-}FC_6H_4)_3Sb(OSO_2Ph)_2$ (**III**): colorless transparent crystals, 83% yield, T_{decomp} = 236°C. IR (ν, cm^{-1}): 3055, 1585, 1489, 1472, 1447, 1422, 1396, 1315, 1132, 1101, 1087, 1041, 1020, 997, 937, 907, 823, 752, 729, 691, 624, 608, 582, 557, 509, 419.

For $C_{30}H_{22}O_6F_3S_2Sb$

Anal. calcd., %	C, 49.91	H, 3.05
Found, %	C, 49.85	H, 3.12

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

Elemental analysis to C and H was carried out on a Carlo Erba CHNS-O EA 1108 elemental analyzer. Melting points were measured on a Netzsch 449C Jupiter synchronous thermoanalyzer.

XRD of the crystals of compounds **I**–**III** was carried out on a D8 QUEST automated four-circle diffractometer (Bruker) (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 293 K. The 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 of compounds **I**–**III** were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and structure refinement results for compounds **I**–**III** are listed in Table 1.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2055557 (**I**), 2055820 (**II**), and 2060295 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The method based on oxidative addition is most efficient among the synthetic procedures used for triarylantimony disulfonates. Oxidative addition is used to synthesize the target product from triarylantimony and sulfonic acid in the presence of an oxidant in diethyl ether [8]. Hydrogen peroxide or *tert*-butyl hydroperoxide is used most frequently as the oxidant. Tri-*meta*-tolylantimony bis(benzenesulfonate) [10], tris(5-bromo-2-methoxyphenyl)antimony bis(2,5-dimethylbenzenesulfonate), and tris(4-methylphenyl)antimony bis(3,4-dimethylbenzenesulfonate) [11] were synthesized using this scheme. However, similar reactions were unknown for the tris(fluorophenyl)antimony compounds.

We found that the reaction of tris(3-fluorophenyl)antimony with benzenesulfonic or 2,4-dimethylbenzenesulfonic acid in the presence of *tert*-butyl hydroperoxide at the molar ratio 1 : 2 : 1, respectively, in diethyl ether proceeded via oxidative addition to form tris(3-fluorophenyl)antimony disulfonates $(3\text{-}FC_6H_4)_3Sb(OSO_2R)_2$ (R = Ph (**I**) and $C_6H_3Me_2$-2,4 (**II**)) in the yields up to 89%.

$$(3\text{-}FC_6H_4)_3Sb + 2RSO_2OH + t\text{-}BuOOH \rightarrow (3\text{-}FC_6H_4)_3Sb(OSO_2R)_2 + t\text{-}BuOH + H_2O$$

$$R = Ph(\mathbf{I}),\ \ C_6H_3Me_2\text{-}2,4\ (\mathbf{II}).$$

After recrystallization from a benzene–octane (3 : 1, vol/vol) mixture, compound **II** was isolated as solvate with benzene: $(3\text{-}FC_6H_4)_3Sb(OSO_2C_6H_3Me_2\text{-}2,4)_2 \cdot 2\ PhH$.

Under similar conditions, a similar reaction of tris(4-fluorophenyl)antimony with benzenesulfonic acid afforded bis(benzenesulfonato)tris(4-fluorophenyl)antimony $(4\text{-}FC_6H_4)_3Sb(OSO_2Ph)_2$ (**III**) in a yield of 69%.

$$(4\text{-}FC_6H_4)_3Sb + 2PhSO_2OH + t\text{-}BuOOH \rightarrow \underset{(\mathbf{III})}{(4\text{-}FC_6H_4)_3Sb(OSO_2Ph)_2} + t\text{-}BuOH + H_2O$$

Compounds **I**–**III** are colorless crystalline substances resistant to air moisture and oxygen and highly soluble in aromatic hydrocarbons and polar organic solvents. The DSC curve for the solvate of complex **II** with benzene exhibits two endothermic peaks. One of the peaks (at 80°C) can be attributed to the loss of solvate benzene, and the second peak (at 177°C) is assigned to melting of the formed benzene-free complex **II**. The IR spectra of compounds **I**, **II**, and **III** exhibit intense bands at 438, 430, and 419 cm^{-1} (Sb–C); 1474, 1474, and 1489 cm^{-1} (Ar); and 3072, 3075, and 3067 cm^{-1} ($H\text{–}C_{Ar}$), respectively. In addition, the IR spectrum of complex **II** exhibited a band at 3030 cm^{-1} ($H\text{–}C_{Alk}$). The presence of the intense absorption bands in a range of 1100–1300 cm^{-1} (1093,

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

Parameter	Value		
	I	**II**	**III**
FW	721.34	933.73	721.34
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$
a, Å	17.865(17)	17.015(8)	19.62(3)
b, Å	10.901(13)	22.980(7)	13.832(18)
c, Å	14.619(14)	13.149(9)	12.349(17)
α, deg	90	90	90
β, deg	91.61(4)	123.345(17)	117.45(7)
γ, deg	90	90	90
V, Å^3	2846(5)	4295(4)	2974(7)
Z	4	4	4
ρ_{calc}, g/cm^3	1.684	1.4438	1.611
μ, mm^{-1}	1.180	0.800	1.129
F(000)	1440.0	1903.5	1440.0
Crystal size, mm	0.2 × 0.13 × 0.06	0.55 × 0.25 × 0.19	0.35 × 0.2 × 0.19
Range of data collection over 2θ, deg	7.04–56.998	5.98–57	6.72–59.36
Ranges of reflection indices	$-23 \leq h \leq 23$, $-14 \leq k \leq 14$, $-19 \leq l \leq 19$	$-22 \leq h \leq 25$, $-34 \leq k \leq 34$, $-19 \leq l \leq 19$	$-26 \leq h \leq 26$, $-18 \leq k \leq 18$, $-16 \leq l \leq 16$
Measured reflections	33469	104135	37259
Independent reflections	3592 (R_{int} = 0.0774)	5433 (R_{int} = 0.0394)	4046 (R_{int} = 0.0315)
Reflections with $I > 2\sigma(I)$	2805	4842	3319
Refinement variables	197	275	192
GOOF	1.035	1.080	1.059
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0341$, $wR_2 = 0.0610$	$R_1 = 0.0301$, $wR_2 = 0.0844$	$R_1 = 0.0340$, $wR_2 = 0.0836$
R factors for all reflections	$R_1 = 0.0558$, $wR_2 = 0.0661$	$R_1 = 0.0363$, $wR_2 = 0.0918$	$R_1 = 0.0461$, $wR_2 = 0.0934$
Residual electron density (max/min), e/A^3	0.54/–0.82	0.79/–0.63	0.82/–0.87

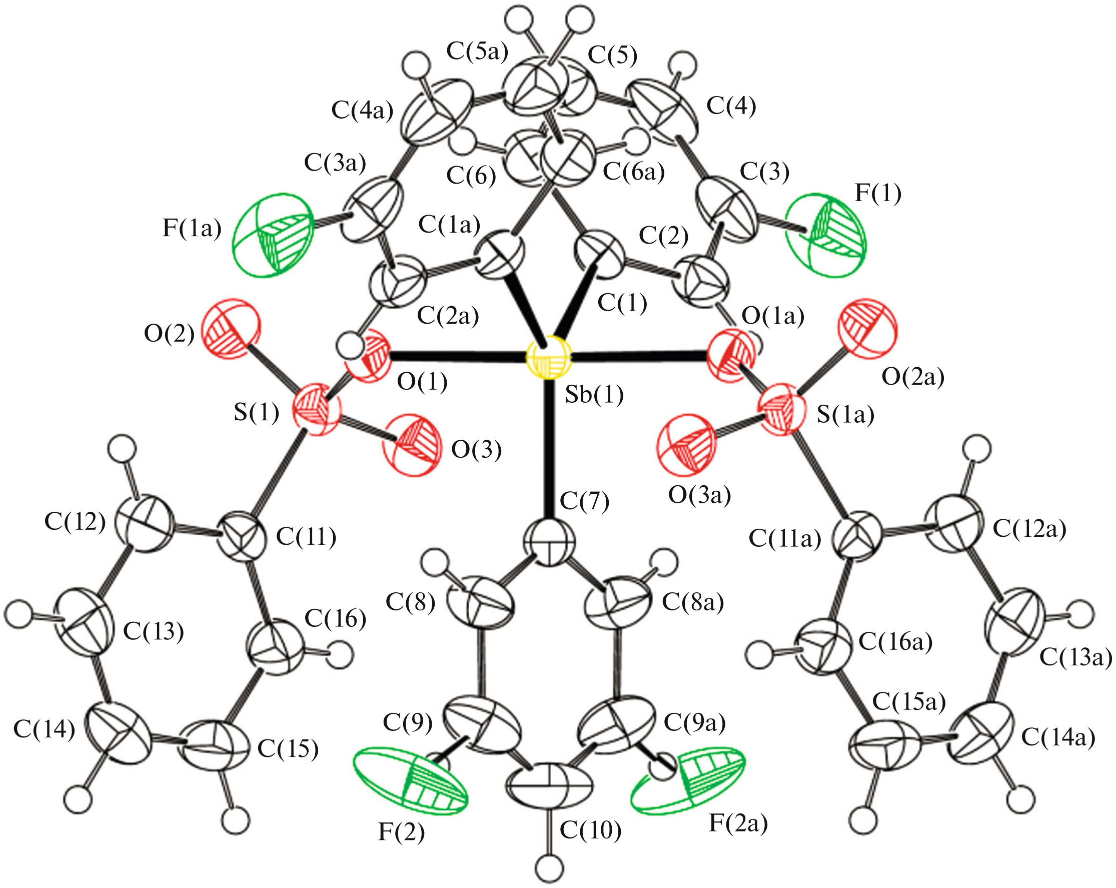

Fig. 1. Structure of compound **I** (in Figs. 1–3 the atoms are shown as thermal vibration ellipsoids with 40% probability).

1165, and 1217 cm^{-1} for **I**; 1094, 1165, and 1223 cm^{-1} for **II**; and 1101, 1171, and 1236 cm^{-1} for **III**) in the IR spectra indicate that complexes **I**–**III** contain sulfo groups [16, 17].

According to the XRD data, in the centrosymmetric molecules of compounds **I**–**III** the Sb atoms have a distorted trigonal bipyramidal coordination with the oxygen atoms of the arenesulfonate ligands in the axial positions, and solvate benzene molecules are observed in the crystal of complex **II** (Figs. 1–3).

The OSbO axial angles in complexes **I**–**III** somewhat differ from the ideal value (180°) and are equal to 178.93(10)°, 176.72(8)°, and 177.04(11)°, respectively. The bond angles between the axial and equatorial bonds (87.36(11)°–93.04(11)°, 85.59(6)°–92.61(6)°, and 87.26(11)°–91.20(11)°) also differ from the theoretical value (90°) (the difference is lower than 5°). In complexes **I**–**III**, the sums of the CSbC angles in the equatorial planes are 360°, and the antimony atoms lie rigidly in the equatorial plane. The individual CSbC angles vary in the ranges usual for Ar_3SbX_2 compounds: 112.74(17)°–123.63(8)°, 113.78(9)°–123.11(4)°, and 117.5(2)°–121.26(10)°, respectively. The highest difference between the maximum and minimum values of the angles is observed in molecules of compound **I**, and the lowest difference takes place in molecules of complex **III**, although their structures differ only in the position of the fluorine atom in the aryl ligands. Note that the insertion of fluorine atoms in the *meta*- or *para*-positions of the aromatic rings affects the Sb–C and Sb–O distances. For example, the Sb–C equatorial bonds in compounds **I**, **II**, and **III** vary in the ranges 2.086(3)–2.096(3), 2.0768(14)–2.086(3), and 2.092(4)–2.094(5) Å, respectively (the maximum values are observed in molecules of complex **III**). The average lengths of the Sb–O axial bonds decrease in the order **I** (2.128(2) Å), **II** (2.1108(18) Å), and **III** (2.098(4) Å) and do not exceed analogous lengths in triorganylantimony dicarboxylates (2.105–2.156 Å) [18] approaching the sum of covalent radii of the indicated atoms (2.14 Å) [19]. Note an insignificant decrease in the intramolecular

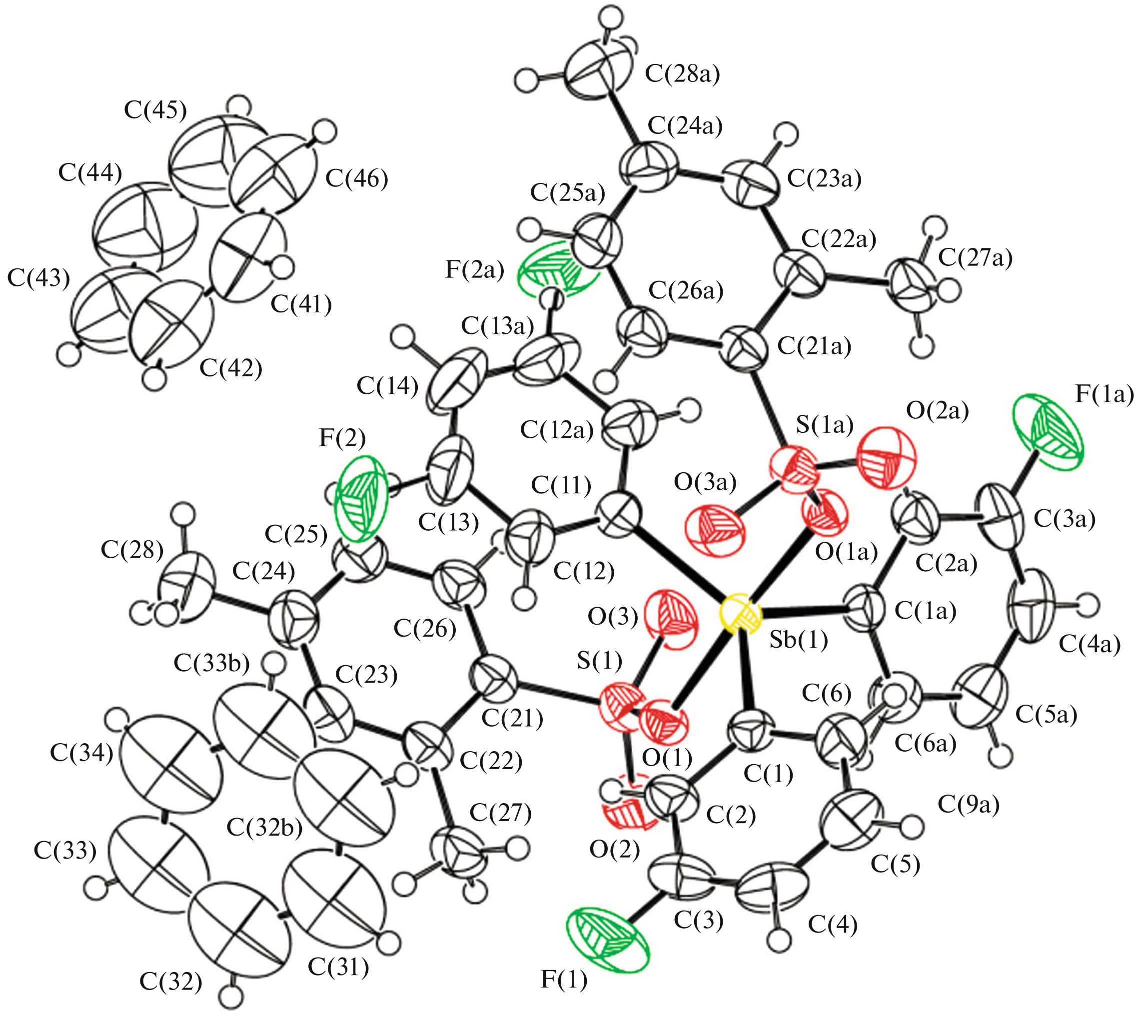

Fig. 2. Structure of solvate **II** with benzene.

distances between the antimony atom and oxygen atoms of the sulfo groups Sb···O=S (3.266(2) Å for **I**, 3.333(2) Å for **II**, and 3.408(4) Å for **III**) compared to the sum of van der Waals radii (3.7 Å [19]). The arenesulfonate ligands in molecules of complexes **I**, **II**, and **III** are arranged relative to the SbC_3 fragment in such a way that the intramolecular Sb···O(=C) contacts are formed inside two equatorial angles, whose values increase to 123.63(8)°, 123.11(4)°, and 121.26(10)°, respectively. A dependence between the strength of the Sb···O contact and maximum CSbC angle can be mentioned. In the arenesulfonate groups of molecules of complexes **I**, **II**, and **III**, the ordinary S–O bond (1.534(2), 1.538(2), 1.518(3) Å) and double S=O bonds (1.430(2), 1.432(2), 1.413(3) Å) differ in length, indicating that the binding of these groups with the antimony atom is covalent. The packing of molecules of triarylantimony disulfonates in the crystal is determined by a complicated system of weak intermolecular hydrogen bonds of the C–H···F (2.4 Å for **I**) and C–H···O (2.6 Å for **II** and 2.4 Å for **III**) types.

Thus, short contacts between the oxygen atoms of the sulfo groups with the central metal atom are observed in compounds **I**–**III** synthesized from tris(fluorophenyl)antimony, arenesulfonic acid, and *tert*-butyl hydroperoxide (molar ratio 1 : 2 : 1) in diethyl ether. The insertion of fluorine atoms in the *meta*- or *para*-positions of the aromatic rings affects the Sb–C and Sb–O distances.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

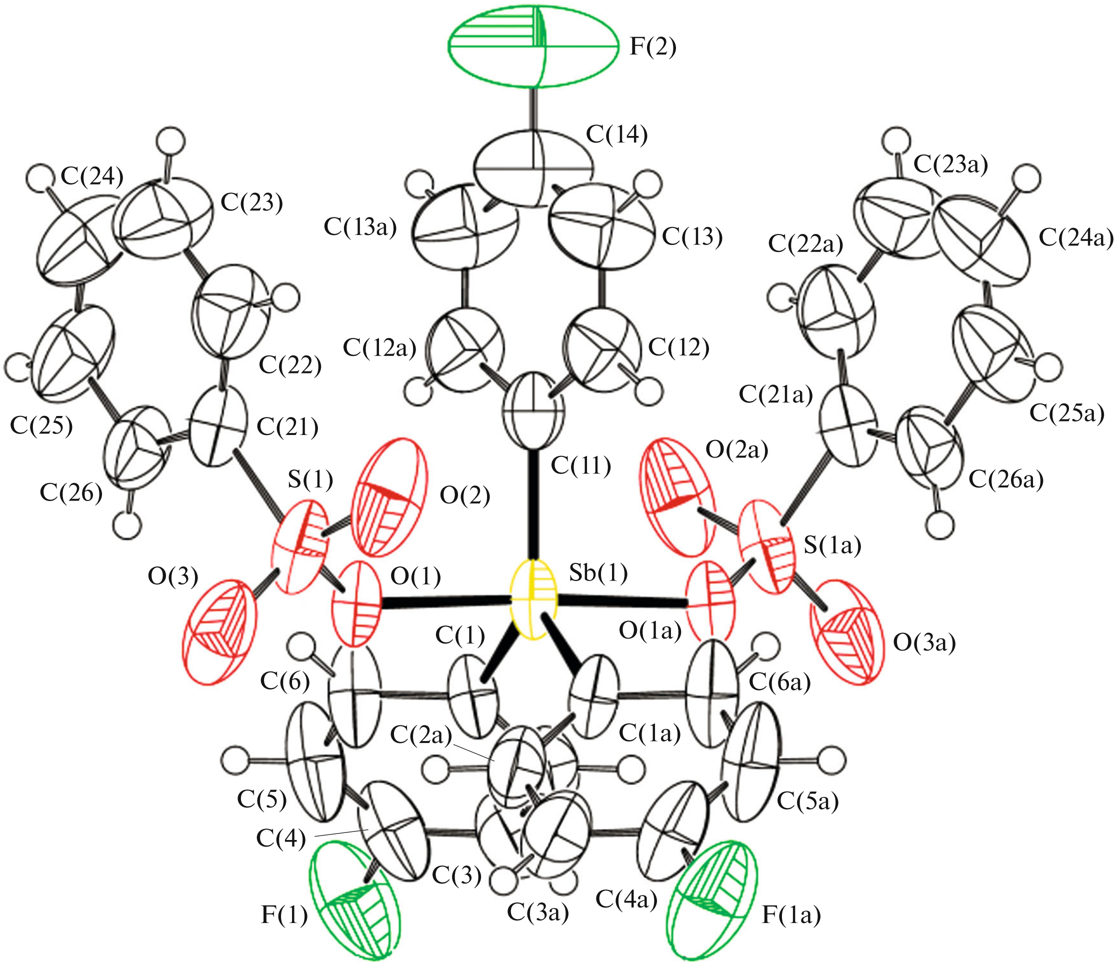

Fig. 3. Structure of compound **III**.

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