ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2023, Vol. 49, No. 5, pp. 311–317. © Pleiades Publishing, Ltd., 2023.
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Synthesis and Structure of Tetraphenylstibonium Organosulfonates Ph_4SbOSO_2R, R = $C_{10}H_{15}O$, $C_{10}H_4(OH\text{-}1)(NO_2)_2\text{-}2,4$, $C_{10}H_7\text{-}1$, $C_6H_4(COOH\text{-}2)$

V. S. Senchurin[a], *, V. V. Sharutin[a], O. K. Sharutina[a], and V. V. Krasnoselskaya[a]
[a] *South Ural State University (National Research University), Chelyabinsk, Russia*
**e-mail: senvl@rambler.ru*

Received June 21, 2022; revised August 16, 2022; accepted August 23, 2022

Abstract—The reaction of equimolar amounts of pentaphenylantimony with camphor-10-sulfonic, 2,4-dinitro-1-naphthol-7-sulfonic (flavianic), 1-naphthalenesulfonic, and 2-sulfobenzoic acids in benzene resulted in the synthesis of tetraphenylstibonium organosulfonates $Ph_4SbOSO_2C_{10}H_{15}O{\cdot}H_2O$ (**I**), $Ph_4SbOSO_2C_{10}H_4(OH\text{-}1)(NO_2)_2\text{-}2,4{\cdot}PhH$ (**II**), $Ph_4SbOSO_2(C_{10}H_7\text{-}1){\cdot}H_2O$ (**III**), and $Ph_4SbOSO_2C_6H_4(COOH\text{-}2)$ (**IV**). According to X-ray diffraction data (CCDC no. 2119791 (**I**), 2121381 (**II**), 2116582 (**III**), and 2123516 (**IV**), the crystal of **I** contains trigonal-bipyramidal sulfonate molecules (the axial Sb–C and Sb–O bond lengths are 2.130(3) and 2.565(2) Å, respectively) and hydration water molecules, which form a centrosymmetric eight-membered ring (the S=O···H–O–H···O=S distances are 2.06 and 2.21 Å). In the molecules of **II**, the metal atom geometry is a distorted trigonal bipyramid (the axial Sb–C and Sb–O bonds are 2.133(2) and 2.643(3) Å, respectively). The Sb–O distance (2.842(3) Å) is longer in **III** than in **I** or **II**; the hydration water molecules form centrosymmetric twelve-membered rings with the anions (the S=O···H–O–H···O=S distances are 2.02 and 2.05 Å). Meanwhile, the crystal of compound **IV** consists of tetrahedral tetraphenylstibonium cations and (2-carboxy)benzenesulfonate anions with the intramolecular O–H···O=S hydrogen bond (1.75 Å).

Keywords: tetraphenylstibonium organosulfonate, synthesis, X-ray diffraction studies

DOI: 10.1134/S1070328423700513

INTRODUCTION

The growing interest in organic antimony compounds is largely determined by their identified potential for a wide variety of practical applications: as pharmaceuticals, biocides, fungicides, antioxidants, reagents, and components of catalytic systems for polymerization, fine organic synthesis, etc. [1]. Although antimony compounds are toxic, they are used in therapy as antiparasitic agents, especially in the treatment of leishmaniasis [2]. Some organic antimony compounds are biologically active [3–5] and possess antibacterial [6–8] and antitumor activities [9–14]. Therefore, the synthesis and structural studies of previously unknown organic antimony derivatives are relevant tasks. An efficient method for the preparation of water-soluble tetraarylstibonium arenesulfonates is based on the reaction of pentaarylantimony with sulfonic acids [1, 15].

EXPERIMENTAL

The starting compound, pentaphenylantimony, was prepared by a reported procedure [16]. Commercial high-purity grade (1*S*)-(+)-camphor-10-sulfonic (Alfa Aesar), 1-naphthalenesulfonic (Merck), 2,4-dinitro-1-napthol-7-sulfonic (flavianic), and 2-sulfobenzoic (Alfa Aesar) acids were used. The reactions were carried out in reagent grade benzene.

Synthesis of tetraphenylstibonium camphor-10-sulfonate hydrate (I) was carried out by a known procedure [15] starting from pentaphenylantimony (0.5 g, 0.99 mmol) and (1*S*)-(+)-camphor-10-sulfonic acid (0.23 g, 0.99 mmol) in benzene. **I**. The yield of colorless crystals was 0.56 g (84%), T_{dec} = 201°C. IR (ν, cm^{-1}): 3568, 3491, 3066, 3053, 2963, 2951, 2930, 2886, 1734, 1625, 1578, 1477, 1437, 1408, 1389, 1371, 1308, 1260, 1234, 1211, 1146, 1026, 995, 741, 692, 664, 610, 581, 527, 509, 463, 446.

For $C_{34}H_{37}O_5SSb$

Anal. calcd., %	C, 60.11	H, 5.49
Found, %	C, 60.01	H, 5.58

Other tetraphenylstibonium sulfonates were synthesized in a similar way.

Tetraphenylstibonium 2,4-dinitro-1-naphthol-7-sulfonate benzene solvate (II) was prepared from pentaphenylantimony (0.5 g, 0.99 mmol) and flavianic acid (0.31 g, 0.99 mmol). **III**: yellow crystals, T_{dec} = 146°C. The yield was 0.61 g (75%). IR (ν, cm^{-1}): 3088, 3055, 3032, 1620, 1582, 1518, 1479, 1437, 1402, 1335, 1314, 1260, 1198, 1175, 1159, 1128, 1082, 1070, 1030, 995, 945, 914, 831, 816, 739, 685, 640, 615, 586, 561, 523, 461, 447.

For $C_{40}H_{31}N_2O_8SSb$

Anal. calcd., %	C, 58.49	H, 3.80
Found, %	C, 58.28	H, 3.91

Tetraphenylstibonium 1-naphthalenesulfonate hydrate (III) was obtained from pentaphenylantimony (0.5 g, 0.99 mmol) and 1-naphthalenesulfonic acid (0.21 g, 0.99 mmol). **II**: colorless crystals, T_{dec} = 115°C. The yield was 0.47 g (73%). IR (ν, cm^{-1}): 3559, 3489, 3088, 3053, 2987, 2953, 1627, 1506, 1479, 1435, 1342, 1240, 1200, 1180, 1146, 1070, 1043, 995, 970, 802, 775, 740, 687, 611, 565, 519, 461, 447, 420.

For $C_{34}H_{29}O_4SSb$

Anal. calcd., %	C, 62.31	H, 4.46
Found, %	C, 62.15	H, 4.50

Tetraphenylstibonium (2-carboxy)benzenesulfonate (IV) was obtained from pentaphenylantimony (0.5 g, 0.99 mmol) and 2-sulfobenzoic acid hydrate (0.20 g, 0.99 mmol). **IV**: colorless crystals, T_{dec} = 158°C. The yield was 0.40 g (65%). IR (ν, cm^{-1}): 3049, 1719, 1591, 1570, 1479, 1435, 1296, 1251, 1171, 1067, 995, 800, 739, 689, 619, 571, 527, 447.

For $C_{31}H_{25}O_5SSb$

Anal. calcd., %	C, 58.99	H, 3.99
Found, %	C, 59.92	H, 4.12

IR spectra were measured on a Shimadzu IRAffinity-1S FTIR spectrometer in the 4000–400 cm^{-1} range (KBr pellets).

X-ray diffraction study was carried out on a D8 QUEST Bruker four-circle automated diffractometer (graphite monochromator) at 293 K. The data collection and editing, refinement of unit cell parameters, application of absorption corrections, and structure solution and refinement were carried out using known software programs [17–19]. The structures of **I**–**IV** were solved by the direct method and refined by the least squares method in the anisotropic approximation for non-hydrogen atoms.

The full tables of atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2119791 (**I**), 2121381 (**II**), 2116582 (**III**), and 2123516 (**IV**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Compound **I**: colorless crystals, triclinic, space group $P\overline{1}$, a = 10.473(8), b = 11.531(7), c = 14.721(7) Å, α = 73.15(3)°, β = 82.36(3)°, γ = 66.27(2)°, V = 1557.4(17) Å^3, Z = 2, ρ(calcd.) = 1.449 g/cm^3; μ = 0.992 mm^{-1}, F(000) = 696.0. In total 33 157 reflections were measured, 6924 reflections were unique (R_{int} = 0.0302), the number of refinement parameters was 400: R_1 = 0.0300, wR_2 = 0.0709.

Compound **II**: yellow crystals, triclinic, space group $P\overline{1}$, a = 10.869(7), b = 12.532(5), c = 13.887(5) Å, α = 88.642(16)°, β = 77.50(2)°, γ = 83.79(2)°, V = 1835.9(15) Å^3, Z = 2, ρ(calcd.) = 1.486 g/cm^3; μ = 0.864 mm^{-1}, F(000) = 832.0. In total, 43 168 reflections were measured, 8079 reflections were unique (R_{int} = 0.0292), the number of refinement parameters was 466: R_1 = 0.0263, wR_2 = 0.0635.

Compound **III**: colorless crystals, triclinic, space group $P\overline{1}$, a = 9.469(5), b = 12.561(6), c = 14.007(7) Å, α = 74.103(17)°, β = 79.76(3)°, γ = 68.31(2)°, V = 1483.4(13) Å^3, Z = 2, ρ(calcd.) = 1.467 g/cm^3; μ = 1.037 mm^{-1}, F(000) = 664.0. In total, 38 195 reflections were measured, 6558 reflections were unique (R_{int} = 0.0237), the number of refinement parameters was 369: R_1 = 0.0230, wR_2 = 0.0532.

Compound **IV**: colorless crystals, triclinic, space group $P\overline{1}$, a = 9.529(3), b = 10.584(3), c = 13.745(5) Å, α = 94.619(17)°, β = 97.731(18)°, γ = 90.336(16)°, V = 1369.0(7) Å^3, Z = 2, ρ(calcd.) = 1.531 g/cm^3; μ = 1.123 mm^{-1}, F(000) = 636.0. In total, 34082 reflections were measured, 6043 reflections were unique (R_{int} = 0.0213), the number of refinement parameters was 344: R_1 = 0.0201, wR_2 = 0.0221.

RESULTS AND DISCUSSION

Efficient methods for the synthesis of antimony compounds Ar_4SbX (Ar = Ph, Tol, X = OH acid residue) are based on the reactions of pentaarylantimony with acids or with symmetrical derivatives Ar_3SbX_2 [1].

We continued studying analogous reactions of pentaphenylantimony with (1*S*)-(+)-camphor-10-sulfonic, flavianic, 1-naphthalenesulfonic, and 2-sulfobenzoic acids in benzene. Despite different nature of organic substiuents in sulfonic acids, the reactions resulted in the formation of tetraphenylstibonium organosulfonates in up to 84% yield.

$$Ph_5Sb + HOSO_2R \rightarrow Ph_4SbOSO_2R + PhH, \text{ where}$$

$$\begin{gathered} R = C_{10}H_{15}O{\cdot}H_2O(\mathrm{I}), \\ C_{10}H_4(OH\text{-}1)(NO_2)_2\text{-}2,4{\cdot}PhH(\mathrm{II}), \\ C_{10}H_7\text{-}1{\cdot}H_2O(\mathrm{III}),\ \ C_6H_4(COOH\text{-}2)(\mathrm{IV}). \end{gathered}$$

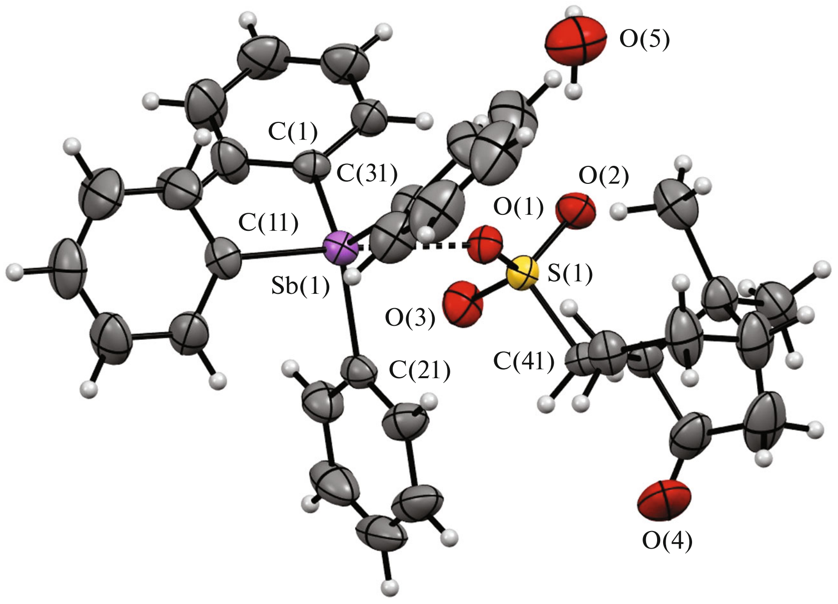

Fig. 1. General view of compound **I**.

Compounds **I** and **III** were isolated from the reaction mixture as hydrates $Ph_4SbOSO_2C_{10}H_{15}O \cdot H_2O$ and $Ph_4SbOSO_2C_{10}H_7$-1$\cdot H_2O$, complex **II** was isolated as the benzene solvate Ph_4SbOSO_2-$C_{10}H_4(OH$-1)$(NO_2)_2$-2,4$\cdot$PhH. Compounds **I**, **III**, and **IV** were colorless crystalline solids, **II** was a yellow crystalline solid. All products were stable to moisture and air oxygen. According to X-ray diffraction data, the antimony atoms in compounds **I**–**III** (Figs. 1–3) have a distorted trigonal bipyramidal geometry with an axial oxygen atom of the sulfonate group. The sums of the CSbC angles in the equatorial plane are 351.63°, 350.1°, and 347.5°, respectively; the antimony atom deviates from the equatorial plane towards the axial carbon atom by 0.355 Å (**I**), 0.386 Å (**II**), and 0.435 Å (**III**). The greatest deviation of the axial CSbO angle from the theoretical value is inherent in the structure of **III** (172.52(8)°), while in **I** and **II**, this angle is less distorted: 176.09(9)° and 175.23(8)°. The equatorial Sb–C bonds in **I**–**III** vary over a narrow range: 2.098(3)–2.109(3), 2.096(2)–2.103(2), and 2.093(2)–2.121(2) Å, which is similar to the sum of the covalent radii of antimony and carbon atoms (2.12 Å) [20]; the axial bond lengths in **I** and **II** coincide (2.130(3) and 2.133(2) Å) and exceed the equatorial bond lengths; in **III**, the axial bond length is 2.117(2) Å, and this value falls into the range of variation of equatorial bonds. The Sb–O distances (2.565(2) (**I**), 2.643(3) (**II**), 2.842(3) Å (**III**)) increase on going from **I** to **III** and exceed the sum of the covalent radii of antimony and oxygen atoms (2.05 Å) [20], which attests to the coordination nature of this bond. It is noteworthy that the Sb(1)–O(1) distance in tetraphenylstibonium 1-naphthalenesulfonate (**III**) is longer by 0.198 Å than this bond in the structurally characterized tetraphenylstibonium 2-naphthalenesulfonate (2.644(2) Å) [15]. The S–O bond lengths for the oxygen atoms coordinated to antimony atoms decrease on going from **I** to **III** (1.471(2) (**I**), 1.4662(17) (**II**), 1.4577(16) Å (**III**)) and exceed the average length of other S–O bonds in sulfonic groups by 0.026(2) (**I**), 0.0246(17) (**II**), and 0.0135(16) Å (**III**). Thus, **III** has the most pronounced distortion of the trigonal-bipyramidal coordination and shows the trend for the Ph_4Sb moiety to pass to a tetrahedral geometry.

A crystal of compound **IV** (Fig. 4) consists of isolated tetrahedral tetraphenylstibonium cations (CSbC angles vary in the 106.77(7)°–112.80(6)° range; the Sb–C bond lengths are in the 2.0811(17)–2.1081(17) Å range) and (2-carboxy)benzenesulfonate anions in which the sulfonate and carboxylate groups form a seven-member heterocycle through intramolecular H(5A)···O(3) hydrogen bond (1.75 Å), which is markedly shorter than sum of the van der Waals radii of hydrogen and oxygen atoms (2.62 Å) [21]. The formation of the strong hydrogen bond leads to elongation of the S(1)–O(3) bond (1.4707(15) Å), which becomes longer than the average S(1)–O(1, 2) bond (1.4430(14) Å) by 0.0277 Å. Note that the hydrogen bond of the same type in known tetraphenylphosphonium (2-carboxy)benzenesulfonate has a similar length of 1.70 Å [22].

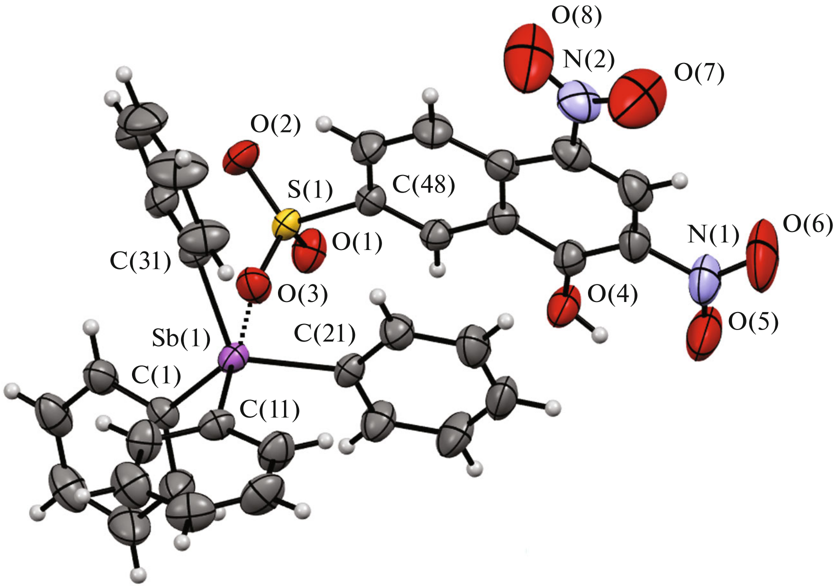

Fig. 2. General view of compound **II** (benzene solvate molecule is omitted).

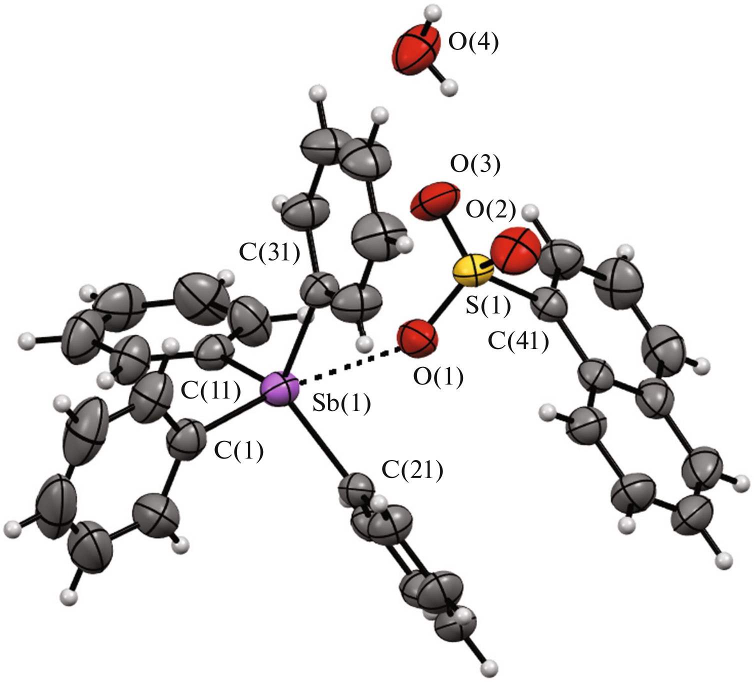

Fig. 3. General view of compound **III**.

Compounds **I** and **III** form centrosymmetric macrocycles with hydration water molecules; the S=O···H–O–H···O=S distances are 2.06, 2.21 Å in **I** and 2.02, 2.05 Å in **III**. However, whereas this ring in **I** involves only the O(2) atoms of the sulfonate ligands of two molecules and is eight-membered (Fig. 5), in the case of **III**, a twelve-membered ring is formed by O(2) and O(3) atoms of both sulfo groups (Fig. 6).

The IR spectra of compounds **I–IV** exhibit intense absorption bands in the 463–446 cm^{-1} range characterizing the Sb–C stretching vibrations. The absorption bands in the 1437–1435 cm^{-1} range are assigned

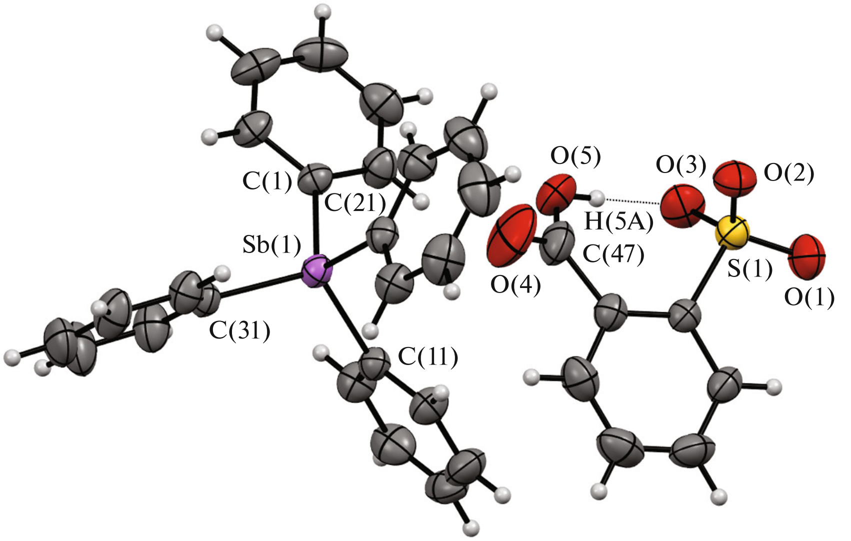

Fig. 4. General view of compound **IV**.

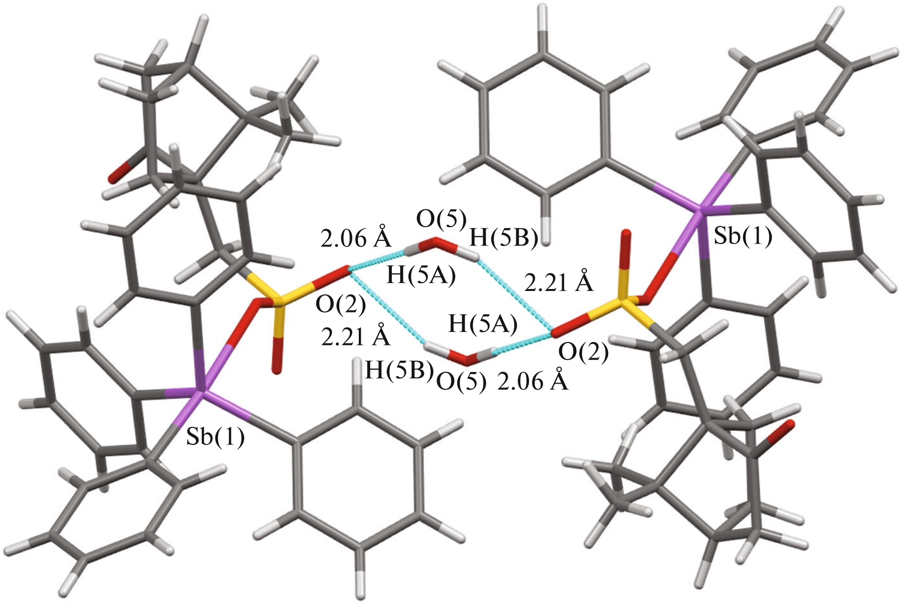

Fig. 5. Eight-membered ring in **I**.

to $\nu_{as}(SO_2)$, while the 1180–1146 cm^{-1} bands correspond to $\nu_s(SO_2)$. The strong absorption bands at 1734 cm^{-1} in **I** and at 1719 cm^{-1} in **IV** are due to the carbonyl stretching modes. The hydration water molecules in **I** and **III** give rise to 3568, 3491 cm^{-1} bands for **I** and 3559, 3489 cm^{-1} bands for **III**. The IR spectrum of compound **II** shows two intense absorption bands: $\nu_{as}(NO_2)$ at 1581 cm^{-1} and $\nu_s(NO_2)$ at 1314 cm^{-1} [23], which means that this compound contains nitro groups.

Thus, the reaction of pentaphenylantimony with sulfonic acids gives new tetraphenylstibonium sulfonates $Ph_4SbOSO_2C_{10}H_{15}O \cdot H_2O$ (**I**), $Ph_4SbOSO_2C_{10}H_4(OH\text{-}1)(NO_2)_2\text{-}2,4 \cdot Ph_4SbOSO_2(C_{10}H_7\text{-}1) \cdot H_2O$ (**III**), and $Ph_4SbOSO_2C_6H_4(COOH\text{-}2)$ (**IV**). In the molecules of **I**–**III**, the antimony atoms are five-coordinate via Sb···O contacts; the crystal of **IV** contains isolated tetraphenylstibonium cations and (2-carboxy)benzenesulfonate anions with an intramolecular hydrogen bonds between the functional groups. Water molecules in **I** and **III** form eight- or twelve-mem-

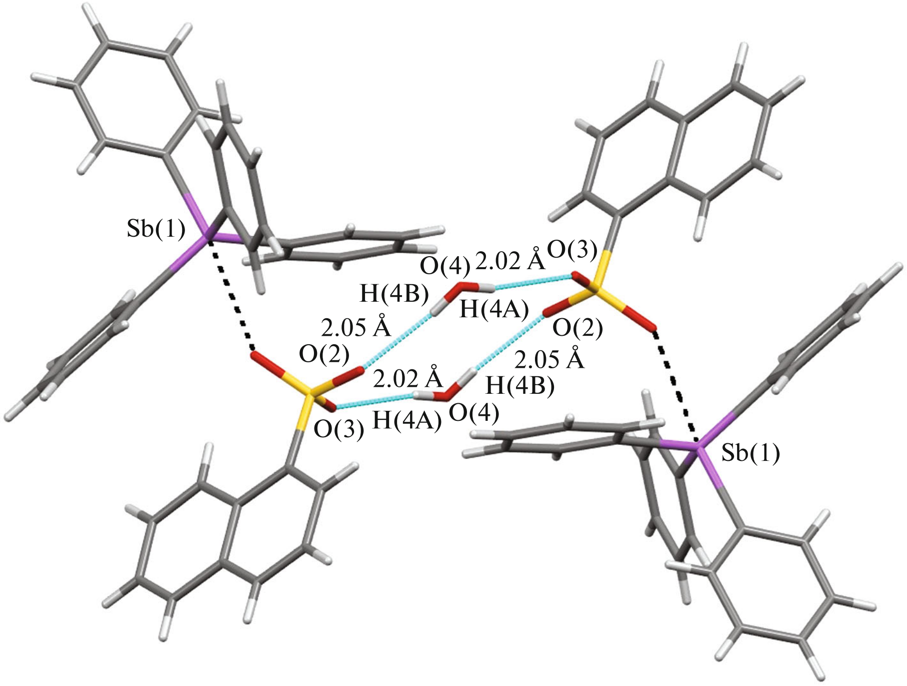

Fig. 6. Twelve-membered ring in **III**.

bered macrocycle involving the oxygen atoms of the sulfonate groups.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by Z. Svitanko