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Tetra- and Triarylantimony Pentafluoro- and Pentachlorophenoxides: Synthesis and Structure

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Abstract—2,3,4,5,6-Pentafluorophenoxytetraphenylantimony (**I**), 2,3,4,5,6-pentachlorophenoxytetraphenylantimony (**II**), 2,3,4,5,6-pentafluorophenoxytetra-*p*-tolylantimony (**III**), and 2,3,4,5,6-pentachlorophenoxytetra-*p*-tolylantimony (**IV**) were synthesized by the reaction of pentaarylantimony (Ar = Ph, *p*-Tol) with pentafluoro- and pentachlorophenol in toluene. Compounds **I**–**IV** were also synthesized with yields of up to 95% from pentaarylantimony and triarylantimony diaroxides. Triarylantimony diaroxides $Ph_3Sb(OC_6F_5)_2$ (**V**), $Ph_3Sb(OC_6Cl_5)_2$ (**VI**), *p*-$Tol_3Sb(OC_6F_5)_2$ (**VII**), *p*-$Tol_3Sb(OC_6Cl_5)_2$ (**VIII**) were synthesized from triarylantimony, *tert*-butylhydroperoxide, and phenol in ether. The Sb atoms in compounds **I**–**VIII** had a distorted trigonal bipyramidal coordination with electronegative ligands in axial positions.

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The literature describes the synthesis of tetraphenylantimony aroxides from pentaphenylantimony and phenol [1–6] or triphenylantimony diaroxides and pentaphenylantimony acting in the reaction as a phenylating agent [5, 6]. No similar reactions with pentafluoro- and phentachlorophenols or their antimonyorganic derivatives have been studied earlier.

For continuing the study of synthesis of tetraarylantimony aroxides, four tetraarylantimony aroxides, namely, $Ph_4SbOC_6F_5$ (**I**), $Ph_4SbOC_6Cl_5$ (**II**), *p*-$Tol_4SbOC_6F_5 \cdot 1/2TolH$ (**III**), and *p*-$Tol_4SbOC_6Cl_5 \cdot PhH$ (**IV**) were synthesized in this work by the reactions of pentaphenylantimony and penta-*para*-tolylantimony with pentafluorophenol, pentachlorophenol, or triarylantimony diaroxides. Triarylantimony diaroxides $Ph_3Sb(OC_6F_5)_2$ (**V**), $Ph_3Sb(OC_6Cl_5)_2$ (**VI**), *p*-$Tol_3Sb(OC_6F_5)_2$ (**VII**), and *p*-$Tol_3Sb(OC_6Cl_5)_2$ (**VIII**) were synthesized by the oxidative addition reaction from triarylantimony and phenol in the presence of *tert*-butylhydroperoxide. The structures of compounds **I**, **III**, **IV**, **VI**, **VII**, and **VIII** were determined by X-ray diffraction.

EXPERIMENTAL

Synthesis of 2,3,4,5,6-pentafluorophenoxytetraphenylantimony (I). A mixture of pentaphenylantimony (250 mg, 0.49 mmol), 2,3,4,5,6-pentafluorophenol (92 mg, 0.49 mmol), and toluene (2 mL) was allowed to stand at 24°C for 15 min. The reaction was monitored by thin-layer chromatography. The solvent was then removed. Colorless crystals of compound **I** (0.300 g, 97%, T_m = 191°C) were synthesized.

IR spectrum (ν, cm^{-1}): 3975, 3901, 3838, 3820, 3801, 3689, 3649, 3140, 3103, 3066, 3055, 3030, 3012, 2989, 2962, 2947, 2929, 2904, 2883, 2864, 2831, 2798, 2763, 2736, 2698, 2654, 2621, 2594, 2571, 2544, 2532, 2499, 2455, 2416, 2382, 2349, 2306, 2285, 2258, 2235, 2162, 2144, 2133, 2115, 2086, 2059, 2017, 1990, 1963, 1907, 1884, 1843, 1820, 1772, 1734, 1645, 1618, 1577, 1500, 1475, 1465, 1435, 1377, 1355, 1334, 1303, 1274, 1261, 1242, 1184, 1159, 1097, 1058, 1006, 981, 923, 852, 800, 734, 694, 653, 617, 470, 455, 445. For $C_{30}H_{20}F_5OSb$, anal. calcd. (%): C, 58.71; H, 3.26. Found (%): C, 58.48; H 3.63.

Compounds **II**–**IV** were synthesized in a similar way.

Compound **II** (95%, T_m = 248°C).

IR spectrum (ν, cm^{-1}): 3975, 3961, 3917, 3903, 3853, 3838, 3820, 3802, 3771, 3736, 3726, 3713, 3689, 3676, 3649, 3630, 3614, 3587, 3568, 3527, 3504, 3468, 3446, 3309, 3288, 3275, 3244, 3215, 3201, 3178, 3138, 3091, 3051, 3018, 2985, 2951, 2900, 2889, 2835, 2789, 2725, 2702, 2638, 2592, 2569, 2544, 2517, 2499, 2428, 2405, 2349, 2283, 2254, 2233, 2135, 2081, 2065, 2017, 1988, 1955, 1944, 1882, 1869, 1525, 1508, 1479, 1421, 1363, 1332, 1303, 1253, 1215, 1182, 1159, 1107, 1065, 988, 916, 768, 729, 711, 692, 468, 457, 447. For $C_{30}H_{20}Cl_5OSb$, anal. calcd. (%): C, 51.76; H, 2.88. Found (%): C, 51.63; H, 3.03.

Compound **III** (96%, T_m = 152°C).

IR spectrum (ν, cm^{-1}): 3053, 3018, 2966, 2949, 2920, 2864, 2800, 2767, 2733, 2659, 2627, 2603, 2547, 2461, 2418, 2362, 2310, 2262, 2237, 1647, 1591, 1558, 1500, 1467, 1436, 1394, 1303, 1244, 1188, 1165, 1118, 1064, 1008, 993, 981, 798, 732, 696, 617, 574, 484, 457, 418.

For $C_{75}H_{64}F_{10}O_2Sb_2$, anal. calcd. (%): C, 54.00; H, 3.84. Found (%): C, 53.87; H, 3.98.

Compound **IV** (93%, T_m = 210°C).

IR spectrum (ν, cm^{-1}): 3994, 3975, 3961, 3917, 3901, 3880, 851, 3838, 3820, 3801, 3768, 3724, 3711, 3689, 3668, 3649, 3628, 3618, 3587, 3566, 3547, 3527, 3502, 3462, 3446, 3311, 3275, 3182, 3089, 3070, 3035, 2949, 2920, 2864, 2816, 2733, 2692, 2652, 2601, 2594, 2553, 2532, 2507, 2422, 2395, 2358, 2343, 2322, 2268, 2208, 2175, 2142, 2127, 2077, 2015, 1992, 1951, 1909, 1897, 1869, 1843, 1828, 1807, 1772, 1749, 1734, 1716, 1699, 1635, 1591, 1558, 1523, 1490, 1479, 1411, 1361, 1311, 1282, 1259, 1211, 1186, 1116, 1095, 1064, 1035, 1014, 987, 948, 896, 862, 842, 796, 763, 732, 713, 700, 673, 648, 630, 574, 486, 418. For $C_{40}H_{34}Cl_5OSb$, anal. calcd. (%): C, 57.85; H, 4.10. Found (%): C, 57.75; H, 4.22.

Synthesis of triphenylantimony bis(2,3,4,5,6-pentafluorophenoxide) (V). A mixture of triphenylantimony (100 mg, 0.283 mmol), 2,3,4,5,6-pentafluorophenol (104 mg, 0.566 mmol), and a 70-% *tert*-butylhydroperoxide solution (36 mg, 0.283 mmol) in diethyl ether (30 mL) was allowed to stand at 20°C for 24 h. After the solvent was slowly removed, the solid precipitate was recrystallized from a toluene–octane solvent mixture (2 : 1). Colorless crystals of compound **V** (0.200 g, 98%, T_m = 171°C) were synthesized.

IR spectrum (ν, cm^{-1}): 3838, 3799, 3649, 3153, 3061, 3003, 2972, 2954, 2929, 2887, 2873, 2812, 2767, 2659, 2628, 2600, 2574, 2547, 2532, 2503, 2455, 2430, 2378, 2349, 2310, 2254, 2137, 2073, 1982, 1965, 1888, 1653, 1629, 1577, 1506, 1481, 1465, 1436, 1384, 1361, 1338, 1305, 1269, 1246, 1184, 1157, 1074, 1016, 995, 921, 848, 731, 686, 657, 623, 569, 464, 447, 418. For $C_{30}H_{15}F_{10}O_2Sb$, anal. calcd. (%): C, 50.07; H, 2.09. Found (%): C, 50.09; H, 2.19.

Compounds **VI–VIII** were synthesized in a similar way.

Compound **VI** (95%, T_m = 231°C).

IR spectrum (ν, cm^{-1}): 3147, 3107, 3061, 2989, 2954, 2831, 2723, 2650, 2515, 2445, 2306, 2254, 2225, 2144, 1761, 1683, 1653, 1575,1531,1481, 1436, 1394, 1388, 1354, 1220, 985, 773, 731, 715, 688, 511, 459, 406. For $C_{30}H_{15}Cl_{10}O_2Sb$, anal. calcd. (%): C, 40.74; H, 1.70. Found (%): C, 40.67; H, 1.83.

Compound **VII** (97%, T_m = 138°C).

IR spectrum (ν, cm^{-1}): 3153, 3059, 3026, 2972, 2929, 2870, 2733, 2663, 2625, 2463, 2434, 1917, 1651, 1593, 1510, 1504, 1465, 1398, 1373, 1350, 1305, 1246, 1192, 1161, 1072, 1014, 997, 985, 802, 773, 624, 588, 570, 484, 468, 422. For $C_{33}H_{21}F_{10}O_2Sb$, anal. calcd. (%): C, 52.04; H, 2.76. Found (%): C, 51.87; H, 2.92.

Compound **VIII** (94%, T_m = 205°C).

IR spectrum (ν, cm^{-1}): 3103, 3066, 3022, 2954, 2920, 2854, 2775, 2725, 2650, 2601, 2586, 2551, 2515, 2443, 2403, 2362, 2341, 2312, 2258, 2225, 2167, 2121, 2094, 2071, 2042, 1967, 1924, 1909, 1843, 1809, 1801, 1751, 1683, 1591, 1531, 1490, 1444, 1388, 1354, 1311, 1274, 1265, 1222, 1188, 1128, 1120, 1062, 1035, 1012, 983, 947, 881, 800, 771, 731, 715, 700, 634, 582, 507, 487, 478, 412. For $C_{33}H_{21}F_{10}O_2Sb$, anal. calcd. (%): C, 42.78; H, 2.27. Found (%): C, 42.68; H, 2.34.

Reaction between pentaphenylantimony and bis(pentafluorophenoxy)triphenylantimony. A mixture of pentaphenylantimony (253 mg, 0.500 mmol), bis(pentafluorophenoxy)triphenylantimony (359 mg, 0.500 mmol), and toluene (10 mL) was heated at 100°C for 5 min. The reaction mixture was cooled to –30°C, and then the formed crystals were filtered out and dried. Compound **I** (582 mg, 95%) with T_m = 191°C was synthesized.

Compounds **II** (93%), **III** (90%), and **IV** (94%) were synthesized in a similar way.

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

X-ray diffraction analysis of crystals of compounds **I**, **III**, **IV**, **VI**, **VII**, and **VIII** was performed on a Bruker D8 QUEST diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) at 296 K. The collection and edition of data, the refinement of unit cell parameters, and the application of absorption corrections were performed using the SMART and SAINT-Plus software [7]. All calculations on the solution and refinement of structures were performed using the software SHELXL/PC [8] and OLEX2 [9]. The structures were solved by direct methods and refined by the least-squares technique in the anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and structure refinement results are given in Table 1, and selected bond lengths and bond angles are listed in Table 2.

The complete tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structure Database (no. 1469676 for **I**, no. 1470617 for **III**, no. 1473086 for **IV**, no. 1476218 for **VI**, no. 1474591 for **VII**, and no. 1483785 for **VIII**; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

It is known that tetraarylantimony aroxides can be synthesized from pentaarylantimony and alkylphenols in an aromatic hydrocarbon solution under heating [1–3]. At the same time, the reactions between pentaphenylantimony and phenols containing electron-

Table 1. Crystallographic data, parameters of X-ray diffraction experiment, and refinement details for the structures of compounds **I**, **III**, **IV**, **VI**, **VII**, and **VIII**

Parameter	Value					
	I	**III**	**IV**	**VI**	**VII**	**VIII**
Formula weight	613.21	715.38	829.67	883.67	761.25	925.75
Symmetry system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a, Å	10.3439(5)	11.265(4)	12.6165(7)	15.9913(11)	9.5396(2)	9.7898(5)
b, Å	11.0490(5)	13.131(4)	12.8659(7)	12.3417(8)	11.9366(4)	14.6044(8)
c, Å	13.2699(6)	13.372(4)	12.8779(6)	18.3142(11)	14.0181(5)	15.6781(9)
α, deg	106.937(2)	98.241(13)	106.317(2)	90.00	83.451(2)	107.288(2)
β, deg	95.681(2)	110.895(13)	104.902(2)	113.454(2)	87.6330(10)	98.780(3)
γ, deg	113.006(2)	109.232(13)	94.292(3)	90.00	76.6990(10)	94.547(3)
V, Å^3	1295.84(10)	1666.8(9)	1914.17(18)	3315.9(4)	1543.10(8)	2096.7(2)
Z	2	1	2	4	1	1
ρ_{calc}, g/cm^3	1.572	1.425	1.439	1.770	1.638	1.466
μ, mm^{-1}	1.122	0.883	1.100	1.667	0.984	1.322
$F(000)$	608.0	722.0	836	1728.0	752.0	912.0
Crystal size, mm	0.57 × 0.55 × 0.37	0.82 × 0.46 × 0.15	0.37 × 0.24 × 0.13	0.18 × 0.18 × 0.04	0.38 × 0.21 × 0.05	0.56 × 0.10 × 0.04
2θ range of data collection, deg	6.46–64.24	6.42–65.08	5.48–46.8	6.46–37.74	6.74–55	4.24–48.94
Reflection index ranges	$-15 \le h \le 15$, $-16 \le k \le 16$, $-19 \le l \le 19$	$-17 \le h \le 17$, $-19 \le k \le 17$, $-20 \le l \le 20$	$-14 \le h \le 14$, $-14 \le k \le 14$, $-14 \le l \le 14$	$-14 \le h \le 14$, $-11 \le k \le 11$, $-16 \le l \le 16$	$-11 \le h \le 11$, $-15 \le k \le 15$, $-18 \le l \le 18$	$-11 \le h \le 11$, $-16 \le k \le 17$, $-18 \le l \le 18$
Measured reflections	99593	30548	37229	42820	24536	56267
Independent reflections	18048 $R_{int} = 0.0251$	20068 $R_{int} = 0.0218$	5551 $R_{int} = 0.0449$	2612 $R_{int} = 0.0733$	13041 $R_{int} = 0.0393$	13682 $R_{int} = 0.0687$
Reflections with $I \ge 2\sigma(I)$	16124	15465	4874	2202	9612	10242
Refinement variables	668	811	416	388	835	835
GOOF	1.062	1.114	1.056	1.125	1.015	1.045
R-factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0251$, $wR_2 = 0.0606$	$R_1 = 0.0382$, $wR_2 = 0.0714$	$R_1 = 0.0377$, $wR_2 = 0.0955$	$R_1 = 0.0271$, $wR_2 = 0.0564$	$R_1 = 0.0376$, $wR_2 = 0.0608$	$R_1 = 0.0462$, $wR_2 = 0.1220$
R-factors for all reflections	$R_1 = 0.0307$, $wR_2 = 0.0644$	$R_1 = 0.0611$, $wR_2 = 0.0805$	$R_1 = 0.0454$, $wR_2 = 0.1073$	$R_1 = 0.0385$, $wR_2 = 0.0608$	$R_1 = 0.0680$, $wR_2 = 0.0687$	$R_1 = 0.0757$, $wR_2 = 0.1394$
Residual electron density (max/min), e/Å^3	0.61/–0.44	1.40/–0.48	0.82/–0.46	0.24/–0.26	0.72/–0.38	0.93/–0.46

Table 2. Selected bond lengths (*d*) and bond angles (ω) in the structures of compounds **I**, **III**, **IV**, **VI**, **VII**, and **VIII**

Bond	*d*, Å	Angle	ω, deg
I			
Sb(1)–O(1)	2.285(5)	C(11)Sb(1)C(21)	118.0(3)
Sb(1)–C(11)	2.101(6)	C(11)Sb(1)C(1)	120.5(2)
Sb(1)–C(31)	2.151(7)	C(21)Sb(1)C(1)	118.2(3)
Sb(1)–C(21)	2.115(7)	C(31)Sb(1)O(1)	177.5(3)
Sb(1)–C(1)	2.120(6)	C(11)Sb(1)O(1)	83.3(2)
Sb(2)–C(61)	2.125(6)	C(51)Sb(2)C(61)	116.5(3)
Sb(2)–O(2)	2.272(5)	C(51)Sb(2)C(71)	120.7(2)
Sb(2)–C(51)	2.115(7)	C(71)Sb(2)C(61)	118.6(3)
Sb(2)–C(81)	2.192(7)	C(81)Sb(2)O(2)	176.8(3)
Sb(2)–C(71)	2.118(6)	C(71)Sb(2)O(2)	82.5(2)
III			
Sb(1)–O(1)	2.317(7)	C(21)Sb(1)C(11)	117.2(4)
Sb(1)–C(21)	2.126(11)	C(1)Sb(1)C(21)	119.0(4)
Sb(1)–C(11)	2.148(10)	C(1)Sb(1)C(11)	119.8(4)
Sb(1)–C(1)	2.119(10)	C(31)Sb(1)O(1)	177.3(4)
Sb(1)–C(31)	2.154(8)	C(1)Sb(1)O(1)	83.1(3)
Sb(2)–O(2)	2.271(8)	C(51)Sb(2)C(71)	117.3(4)
Sb(2)–C(81)	2.190(9)	C(51)Sb(2)C(61)	120.3(4)
Sb(2)–C(51)	2.090(9)	C(71)Sb(2)C(61)	118.3(4)
Sb(2)–C(71)	2.118(11)	C(81)Sb(2)O(2)	177.7(3)
Sb(2)–C(61)	2.127(11)	C(71)Sb(2)O(2)	83.8(4)
IV			
Sb(1)–C(15)	2.105(4)	C(15)Sb(1)C(22)	118.08(16)
Sb(1)–C(22)	2.112(4)	C(15)Sb(1)C(8)	121.85(15)
Sb(1)–C(8)	2.115(4)	C(22)Sb(1)C(8)	115.92(15)
Sb(1)–C(1)	2.169(4)	C(1)Sb(1)O(1)	177.03(12)
Sb(1)–O(1)	2.367(3)	C(8)Sb(1)O(1)	82.57(12)
VI			
Sb(1)–C(1)	2.103(6)	C(1)Sb(1)C(21)	114.4(2)
Sb(1)–O(1)	2.100(4)	C(1)Sb(1)C(11)	103.3(2)
Sb(1)–O(2)	2.100(4)	C(11)Sb(1)C(21)	142.3(2)
Sb(1)–C(21)	2.120(6)	O(1)Sb(1)O(2)	174.04(15)
Sb(1)–C(11)	2.109(6)	O(2)Sb(1)C(21)	87.37(19)
VII			
Sb(1)–O(2)	2.103(10)	C(21)Sb(1)C(11)	117.6(6)
Sb(1)–C(1)	2.027(14)	C(1)Sb(1)C(11)	127.6(5)
Sb(1)–C(11)	2.076(15)	C(1)Sb(1)C(21)	114.8(6)
Sb(1)–O(1)	2.094(11)	O(1)Sb(1)O(2)	178.8(5)
Sb(1)–C(21)	2.066(15)	C(11)Sb(1)O(1)	87.3(5)
Sb(2)–O(3)	2.091(10)	C(51)Sb(2)C(61)	127.6(6)
Sb(2)–O(4)	2.057(11)	C(71)Sb(2)C(51)	117.8(6)
Sb(2)–C(51)	2.114(13)	C(71)Sb(2)C(61)	114.5(6)
Sb(2)–C(71)	2.109(13)	O(4)Sb(2)O(3)	179.2(5)
Sb(2)–C(61)	2.137(14)	O(3)Sb(2)C(61)	87.8(5)
VIII			
Sb(1)–O(2)	2.085(12)	C(11)Sb(1)C(1)	101.8(7)
Sb(1)–O(1)	2.122(14)	C(21)Sb(1)C(1)	138.3(6)
Sb(1)–C(1)	2.124(17)	C(21)Sb(1)C(11)	119.9(5)
Sb(1)–C(21)	2.103(17)	O(2)Sb(1)O(1)	174.8(6)
Sb(1)–C(11)	2.101(19)	C(21)Sb(1)O(1)	86.8(6)
Sb(2)–O(3)	2.155(13)	C(51)Sb(2)C(61)	118.7(7)
Sb(2)–O(4)	2.095(11)	C(71)Sb(2)C(61)	138.6(7)
Sb(2)–C(71)	2.100(17)	C(71)Sb(2)C(51)	102.5(6)
Sb(2)–C(61)	2.135(15)	O(4)Sb(2)O(3)	174.8(5)
Sb(2)–C(51)	2.121(13)	C(61)Sb(2)O(3)	85.7(6)

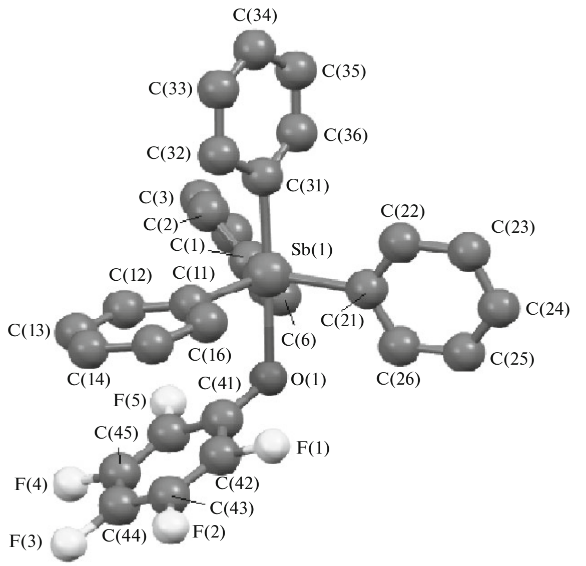

Fig. 1. Molecular structure of pentafluorophenoxytetraphenylantimony (**I*a***).

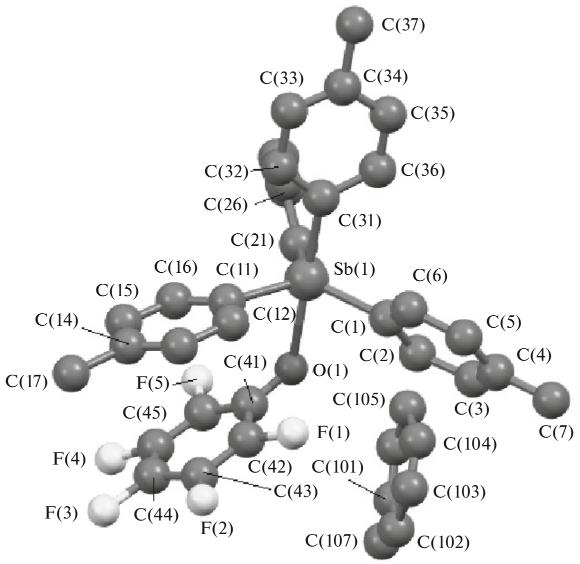

Fig. 2. Molecular structure of pentafluorophenoxytetra-*para*-tolylantimony solvate (**III*a***).

drawing substituents in the aroxy group are completed in 1–2 h and do not require the heating of a reaction mixture [4, 6], in agreement with the pronounced acidic properties of the above-mentioned phenols.

It may be expected that the reaction of pentaarylantimony with pentafluoro- and pentachlorophenol will occur within a much shorter time interval. Actually, we have found that the reactions of pentaphenylantimony and penta-*para*-tolylantimony with pentahalidephenols in an aromatic hydrocarbon are completed in several minutes at room temperature with a yield of up to 97%:

$$\mathrm{Ar_5Sb + HOC_6Hal_5 \rightarrow Ar_4SbOC_6Hal_5 + ArH}$$

$$\mathrm{Ar = Ph, Hal = F\ (\textbf{I}), Cl\ (\textbf{II});}$$
$$\mathrm{Ar = \mathit{p}\text{-}Tol, Hal = F\ (\textbf{III}), Cl\ (\textbf{IV}).}$$

We found that the method based on the ligand redistribution reaction between pentaarylantimony and triarylantimony diaroxides (toluene, 100°C, 5 min) $\mathrm{Ar_5Sb + Ar_3Sb(OAr')_2 \rightarrow 2Ar_4SbOAr}$ with a target product yield of up to 99% is equally efficient for the synthesis of compounds **I**–**IV**.

As follows from the literature data, the oxidative addition reaction underlying the synthesis of many organoantimony compounds with the general formula $\mathrm{Ar_3SbX_2}$ (X is the residue of an H-acid) [10] does not always lead to the formation of triarylantimony diaroxides in the case of phenols when the target product is obtained from triarylantimony and an acid in the presence of a peroxide [11, 12].

However, we synthesized bis(pentahalidearoxy)triarylantimony from triarylantimony and pentahalophenols using *tert*-butylhydroperoxide as an oxidizer (ether, 20°C, 12 h) with a yield of up to 98% as

$$\mathrm{Ar_3Sb + 2HOAr' + \mathit{tert}\text{-}BuOOH}$$
$$\mathrm{\rightarrow Ar_3Sb(OAr')_2 + \mathit{tert}\text{-}BuOH + H_2O}$$

$$\mathrm{Ar = Ph, Hal = F\ (\textbf{V}), Cl\ (\textbf{VI});}$$
$$\mathrm{Ar = \mathit{p}\text{-}Tol, Hal = F\ (\textbf{VII}), Cl\ (\textbf{VIII}).}$$

The structures of compounds **I**–**VIII** were studied by IR spectroscopy and X-ray diffraction.

The IR spectra of compounds **I**–**VIII** contain the absorption bands belonging to the vibrations of Sb–C(Ph) bonds in the $\mathrm{SbC_3}$ moiety [13] at 450–478 $\mathrm{cm^{-1}}$ and the absorption bands characterizing C–O bonds at 1220–1303 $\mathrm{cm^{-1}}$.

According to X-ray diffraction data, the antimony atoms in molecules **I*ab***, **III*ab***, **IV**, **VI**, **VII*ab***, and **VIII*ab*** have a distorted trigonal bipyramidal coordination to axial aroxyl ligands and phenyl groups in the equatorial plane (Figs. 1–6).

The axial OSbC and OSbO angles are 177.5(3)° (**I*a***), 176.8(3)° (**I*b***), 177.3(4)° (**III*a***), 177.7(3)° (**III*b***), 177.03(12)° (**IV**), and 174.04(15)° (**VI**), 178.8(5)° (**VII*a***), 179.2(5)° (**VII*b***), 174.8(6)° (**VIII*a***), 174.8(5)° (**VIII*b***). The sums of $\mathrm{C_{eqv}SbC_{eqv}}$ angles in the equatorial plane are 356.7(3)° (**I*a***), 355.8(3)° (**I*b***), 356.0(4)° (**III*a***), 355.9(4)° (**III*b***), 355.85(15)° (**IV**), 360.0(2)° (**VI**), 360.0(6)° (**VII*a***), 359.9(6)° (**VII*b***), 360.0(6)° (**VIII*a***), and 359.8(7)° (**VIII*b***). The antimony atom in compounds **I*ab***, **III*ab***, and **IV** is out of the equatorial plane towards an axial carbon atom, while the metal atoms in molecules of compounds **VI**, **VII*ab***, and **VIII*ab*** lie in equatorial plane $\mathrm{C_3}$.

The Sb–$\mathrm{C_{eqv}}$ bond lengths in the studied compounds variate within the following ranges: 2.101(6)–2.192(7) Å (**I*ab***), 2.090(10)–2.154(8) Å (**III*ab***),

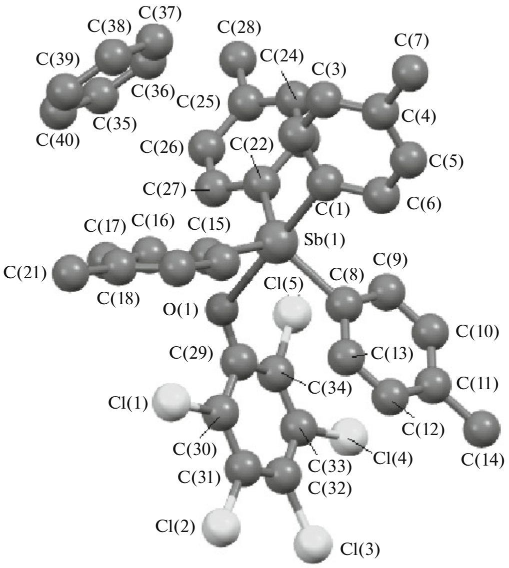

Fig. 3. Molecular structure of pentachlorophenoxytetra-*para*-tolylantimony solvate with benzene (**IV**).

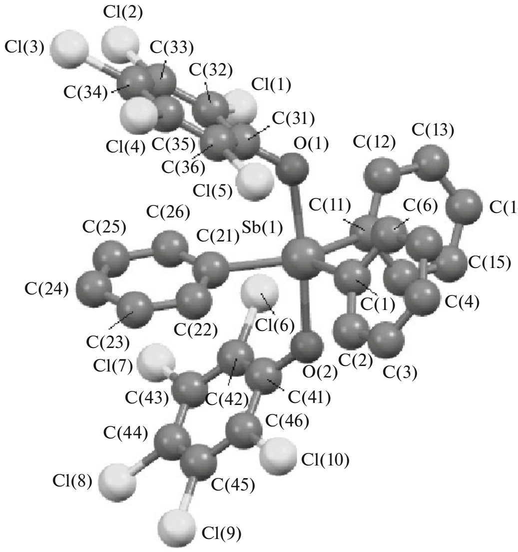

Fig. 4. Molecular structure of bis(pentachlorophenoxy)triphenylantimony (**VI**).

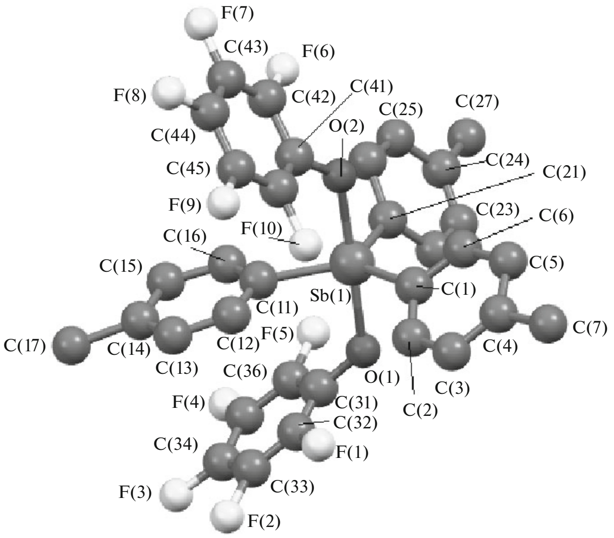

Fig. 5. Molecular structure of bis(pentafluorophenoxy)tri-*para*-tolylantimony (**VII*a***).

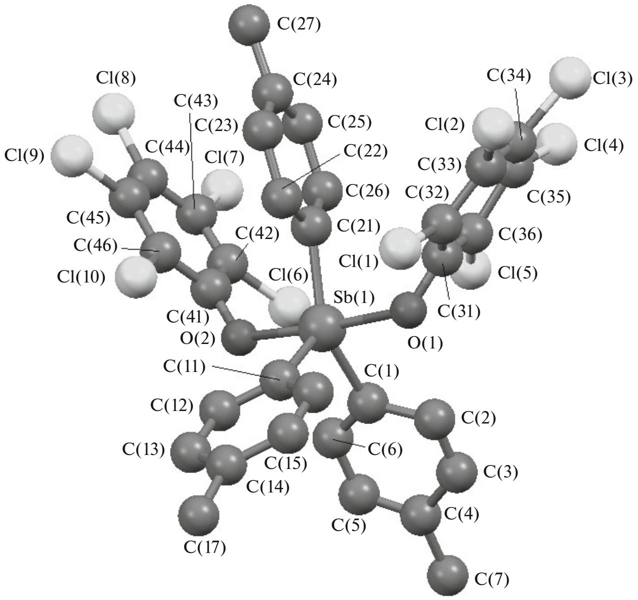

Fig. 6. Molecular structure of bis(pentachlorophenoxy)tri-*para*-tolylantimony (**VIII*a***).

2.105(4)–2.169(5) Å (**IV**), 2.103(6)–2.120(6) Å (**VI**), 2.027(14)–2.137(14) Å (**VII**), 2.101(19)–2.135(15) Å (**VIII**). The Sb–O distances in molecules **I*a*** (2.285(5) Å), **I*b*** (2.272(5) Å), **III*a*** (2.317(7) Å), **III*b*** (2.271(8) Å), and **IV** (2.367(3) Å) are much greater than the antimony and oxygen covalent radii in sum (2.07 Å [14]) due to a higher polarity of the Sb–O bond in tetraarylantimony aroxides. However, the Sb–O distances in the symmetric antimony compounds (2.100(4) Å (**VI**), 2.057(11)–2.103(10) Å (**VII*ab***), 2.085(12)–2.155(13) Å (**VIII*ab***)) indicate a covalent character of bonding between antimony and oxygen atoms.

In a molecule of compound **I*a***, one C(11)–C(17) phenyl ring, whose plane nearly coincides with equatorial plane C_3 (the inclination angle of this ring to the equatorial plane is 32.82°), screens the C(41)–C(47) aroxy group, thus leading to the interaction between their π systems. The ideal geometry for π–π-stacking interaction is distorted: the distance between the centers of the aryl and phenyl π systems is 3.00 Å, and the interplanar angle is 23.43°. This, however, is frequently encountered in such interactions [15, 16]. Similar π–π-stacking interactions are observed in the other molecules of non-symmetric (**I*b***, **III*ab***, **IV**) and symmetric (**VI**, **VII*ab***, **VIII*ab***) structures. Thus, the same interplanar angle in compound **VI** is 35.47°, and the distance between the centers of the aryl and phenyl π-systems is 3.80 Å.

The structural organization in crystals is caused by weak intermolecular hydrogen bonds H···Cl (2.51–2.65 Å in **I**, 2.55–2.67 Å in **III**, 2.84 Å in **VI**, 2.45–2.56 Å in **VII**, 2.87–2.95 Å in **VIII**), and H···O (2.41 Å in **IV**).

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