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Synthesis and Structures of Tetraphenylantimony Aroxides Ph_4SbOAr (Ar = $C_6H_3F_2$-2,4, $C_6H_3F_2$-2,5, C_6H_3Cl-2-F-4)

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Abstract—The reactions of pentaphenylantimony with 2,4-difluoro-, 2,5-difluoro-, and 2-chloro-4-fluorophenol in a benzene–octane mixture of solvents afford tetraphenylantimony aroxides $Ph_4SbOC_6H_3F_2$-2,4 (**I**), $Ph_4SbOC_6H_3F_2$-2,5 (**II**), and $Ph_4SbOC_6H_3$(Cl-2)(F-4) (**III**). According to the X-ray diffraction analysis data (CIF files CCDC nos. 1973286 (**I**), 1975709 (**II**), and 1973305 (**III**)), the antimony atoms in the compounds have the coordination of a distorted trigonal bipyramid with the aroxide oxygen atom in the axial position. The OSbC axial angles in compounds **I**–**III** are 177.86(6)°, 177.29(7)°, and 174.34(6)°, respectively. The geometric parameters of the molecules in compounds **I**–**III** are similar in the Sb–C_{eq} and Sb–O bond lengths (2.118(2)–2.127(2) and 2.1780(16) Å in **I**; 2.122(2)–2.130(2) and 2.179(2) Å in **II**; and 2.116(2)–2.119(2) and 2.1803(16) Å in **III**). The structural organization in crystals of the compounds is due to weak hydrogen bonds involving F atoms and C–H···π interactions. These interactions result in the organization of the molecules in the crystal of compound **I** into a three-dimensional network, paired chains are formed in compound **II**, and the molecules of compound **III** are organized into layers.

Keywords: pentaphenylantimony, phenols, substitution reaction, tetraphenylantimony aroxides, X-ray diffraction analysis

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INTRODUCTION

The organoantimony derivatives of the general formula Ar_4SbX, where X is the ligand linked with the antimony atom through the heteroatom, are rather well studied by X-ray diffraction analysis (XRD) [1–15]. A broad series of structurally characterized tetraphenylantimony aroxides is among these compounds [1, 16–21], the most part of which contain electronegative groups in the phenol residue. These derivatives are synthesized via the substitution reactions from Ph_5Sb and HOAr [16–18] or ligand redistribution between Ph_5Sb and symmetric derivative Ph_3SbX_2 [19–21].

In continuation of the studies of specific features of the structures and synthesis of tetraphenylantimony aroxides with fluorine-containing ligands, we synthesized complexes $Ph_4SbOC_6H_3F_2$-2,4 (**I**), $Ph_4SbOC_6H_3F_2$-2,5 (**II**), and $Ph_4SbOC_6H_3$Cl-2-F-4 (**III**) and studied their molecular structures.

EXPERIMENTAL

The starting reagent (pentaphenylantimony) was synthesized using a described procedure [22]. 2,4-Difluorophenol, 2,5-difluorophenol, and 2-chloro-4-fluorophenol (Alfa Aesar) were used. Benzene and octane (reagent grade) were used as solvents and dried over calcium chloride prior to synthesis.

Synthesis of tetraphenylantimony 2,4-difluorophenoxide (I). A solution of pentaphenylantimony (100 mg, 0.197 mmol) and 2,4-difluorophenol (26 mg, 0.197 mmol) in a benzene–octane (5 : 1 vol/vol) mixture was kept at 20°C to the complete removal of solvents. Colorless crystals of compound **I** with T_m = 154°C were obtained in a yield of 98 mg (89%).

IR (ν, cm^{-1}): 3053, 3014, 3001, 1598, 1577, 1492, 1479, 1435, 1332, 1305, 1247, 1201, 1184, 1159, 1126, 1089, 1064, 1020, 997, 954, 918, 848, 804, 732, 719, 702, 692, 651, 599, 588, 507, 468, 455, 447, 408.

For $C_{30}H_{23}OF_2Sb$		
Anal. calcd., %	C, 4.43	H, 4.15
Found, %	C, 4.37	H, 4.25

Compounds **II** and **III** were synthesized similarly.

Synthesis of tetraphenylantimony 2,5-difluorophenoxide (II). The yield was 86%, T_m = 146°C. IR (ν, cm^{-1}): 3059, 3049, 1637, 1614, 1575, 1566, 1492, 1479, 1458, 1433, 1425, 1413, 1332, 1317, 1282, 1230, 1193, 1163, 1143, 1093, 1064, 1022, 997, 974, 900, 846, 837, 783, 771, 731, 692, 669, 651, 621, 605, 522, 470, 459, 453, 443.

For $C_{30}H_{23}OF_2Sb$

Anal. calcd., %	C, 4.43	H, 4.15
Found, %	C, 64.23	H, 4.24

Synthesis of tetraphenylantimony 2-chloro-4-fluorophenoxide (III). The yield was 72%, $T_m = 168$°C. IR (ν, cm^{-1}): 3105, 3064, 3049, 1591, 1577, 1564, 1473, 1433, 1427, 1396, 1334, 1292, 1242, 1182, 1161, 1116, 1062, 1039, 1020, 997, 900, 848, 808, 794, 732, 692, 650, 615, 569, 543, 487, 472, 460, 453, 441, 428.

For $C_{30}H_{23}OFClSb$

Anal. calcd., %	C, 62.59	H, 4.04
Found, %	C, 62.50	H, 4.12

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

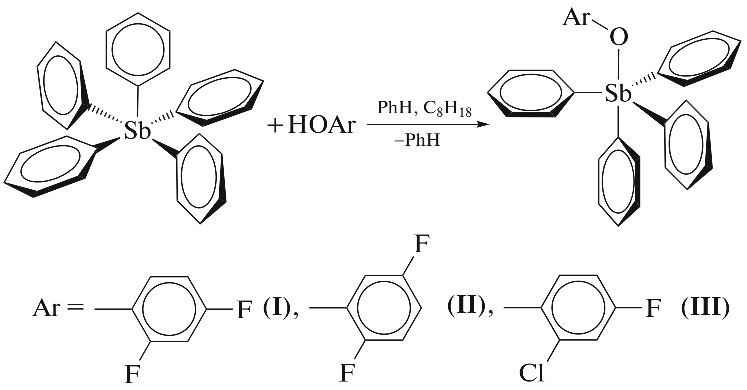
XRD of crystals of compounds **I**–**III** was carried out on a D8 QUEST diffractometer (Bruker, MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 296(2) K. Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [23]. All calculations on structure refinement and determination were performed using the SHELXL/PC [24] and OLEX2 [25] programs. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The crystallographic data and structure refinement results are presented in Table 1.

The full tables of coordinates of atoms, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1973286 (**I**), 1975709 (**II**), and 1973305 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/structures).

RESULTS AND DISCUSSION

The methods based on the reactions of pentaarylantimony with the symmetric derivatives $Ar_3Sb(OAr')_2$ [19–21] or phenols [16–18] are highly efficient for the synthesis of the antimony compounds of the general formula Ar_4SbOAr'. These methods include one synthesis step and are characterized by high yields, purity of the target compound, and mild reaction conditions.

Compounds **I**–**III** were synthesized by the reactions of Ph_5Sb with halophenols.



Compounds **I**–**III** are crystalline colorless substances with a distinct melting point.

The IR spectra of compounds **I**–**III** exhibit an intense absorption band due to the ν(Sb–C) vibrations at 455, 453, and 453 cm^{-1}, respectively. The absorption band at 1247 (**I**), 1230 (**II**), and 1242 (**III**) cm^{-1} characterizes the ν(C–O) vibrations, and the bands at 1577, 1492, and 1435 cm^{-1} (**I**); 1575, 1492, and 1433 cm^{-1} (**II**); 1577, 1473, and 1433 cm^{-1} (**III**) correspond to the stretching vibrations of the carbon skeleton of the aryl groups. The medium-intensity absorption band at 3053 (**I**), 3059 (**II**), and 3064 (**III**) cm^{-1} corresponds to the $\nu(C_{Ar}–H)$ vibrations, and the $\delta(C_{Ar}–H)$ vibrations are associated with the high-intensity bands at 732 and 692 (**I**), 731 and 692 (**II**), and 732 and 692 (**III**) cm^{-1} [26, 27].

According to the XRD data, the Sb atoms in compounds **I**–**III** are characterized by the distorted coordination of a trigonal bipyramid with the axially arranged oxygen atom of the aroxide ligand (Fig. 1).

The OSbC axial angles in compounds **I**–**III** are 177.86(6)°, 177.29(7)°, and 174.34(6)°, respectively, and the last value is the least one of analogous angles in halogen-containing tetraphenylantimony aroxides [1]. The largest angle close to an ideal value of 180° is observed in the structure of tetraphenylantimony 2,4,6-tribromophenoxide [18]. The sums of the CSbC angles in the equatorial plane are 358.09(8)° (**I**),

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

Parameter	Value		
	I	**II**	**III**
FW	559.23	559.23	575.68
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	10.161(4)	10.190(6)	15.201(10)
b, Å	10.472(4)	10.509(5)	10.343(8)
c, Å	13.316(5)	13.395(6)	17.602(11)
α, deg	73.573(18)	76.488(16)	90
β, deg	69.819(14)	67.96(3)	112.500(19)
γ, deg	89.92(2)	89.10(2)	90
V, Å^3	1268.4(8)	1288.6(11)	2557(3)
Z	2	2	4
ρ_{calc}, g/cm^3	1.464	1.441	1.495
μ, mm^{-1}	1.122	1.104	1.211
F(000)	560.0	560.0	1152.0
Crystal size, mm	0.22 × 0.16 × 0.11	0.32 × 0.15 × 0.13	0.65 × 0.41 × 0.05
2θ, deg	6.232–57.506	5.84–57	5.802–56.998
Ranges of reflection indices	$-13 \le h \le 13$, $-14 \le k \le 14$, $-17 \le l \le 17$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-17 \le l \le 17$	$-20 \le h \le 20$, $-13 \le k \le 13$, $-23 \le l \le 23$
Total number of reflections	43002	56904	56784
Independent reflections (R_{int})	6527 (0.0362)	6518 (0.0733)	6480 (0.0360)
Reflections with $I > 2\sigma(I)$	5748	5908	5619
Number of refined parameters	307	307	307
GOOF	1.077	1.077	1.035
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.0251$, $wR_2 = 0.0585$	$R_1 = 0.0305$, $wR_2 = 0.0769$	$R_1 = 0.0218$, $wR_2 = 0.0520$
R factors for all reflections	$R_1 = 0.0321$, $wR_2 = 0.0612$	$R_1 = 0.0355$, $wR_2 = 0.0800$	$R_1 = 0.0281$, $wR_2 = 0.0553$
Residual electron density (max/min), e/Å^3	0.61/–0.55	0.41/–1.24	0.47/–0.46

357.51(9)° (**II**), and 357.43(8)° (**III**). The $O_{ax}SbC_{eq}$ angles are smaller than 90°, and the $C_{ax}SbC_{eq}$ angle is larger than this value. The shifts of the antimony atoms from the equatorial plane [C_3] toward C_{ax} are 0.170 (**I**), 0.195 (**II**), and 0.198 Å (**III**). The presented geometric characteristics are comparable with those of other earlier structurally characterized compounds with the general formula Ph_4SbOAr [1, 16–21].

The equatorial phenyl rings in compounds **I–III** are turned around the $Sb-C_{eq}$ bonds in such a way that intra- and intermolecular interactions would be minimized. The dihedral angles between the ring planes and equatorial plane C(1)C(11)C(21) are as follows: 11.27° C(11)–C(16), 49.39° C(21)–C(26), and 54.63° C(1)–C(6) (**I**); 14.77° C(1)–C(6), 54.97° C(21)–C(26), and 55.50° C(11)–C(16) (**II**); and 23.27° C(11)–C(16), 53.76° C(1)–C(6), and 58.99° C(21)–C(26) (**III**). Interestingly, the partial interaction of the π systems of the phenyl ligand (C(11)–C(16) in **I** and C(1)–C(6) in **II**) arranged nearly in the equatorial plane and of the aromatic ring of the aroxy group is observed in compounds **I** and **II**. The planes of these groups are opposite to each other to form an interplanar angle of 48.17° (**I**) and 40.75° (**II**). The shortest distances between the planes of these π systems are 3.144(3) Å (C(11)···C(41)) in compound **I** and 3.101(4) Å (C(1)···C(41)) and 3.322(5) Å (C(2)···C(46)) in compound **II**, which is less than the sum of the van der Waals radii of two carbon atoms (3.5 Å). Similar interactions are observed in other tetraarylantimony aroxides [1, 21, 28].

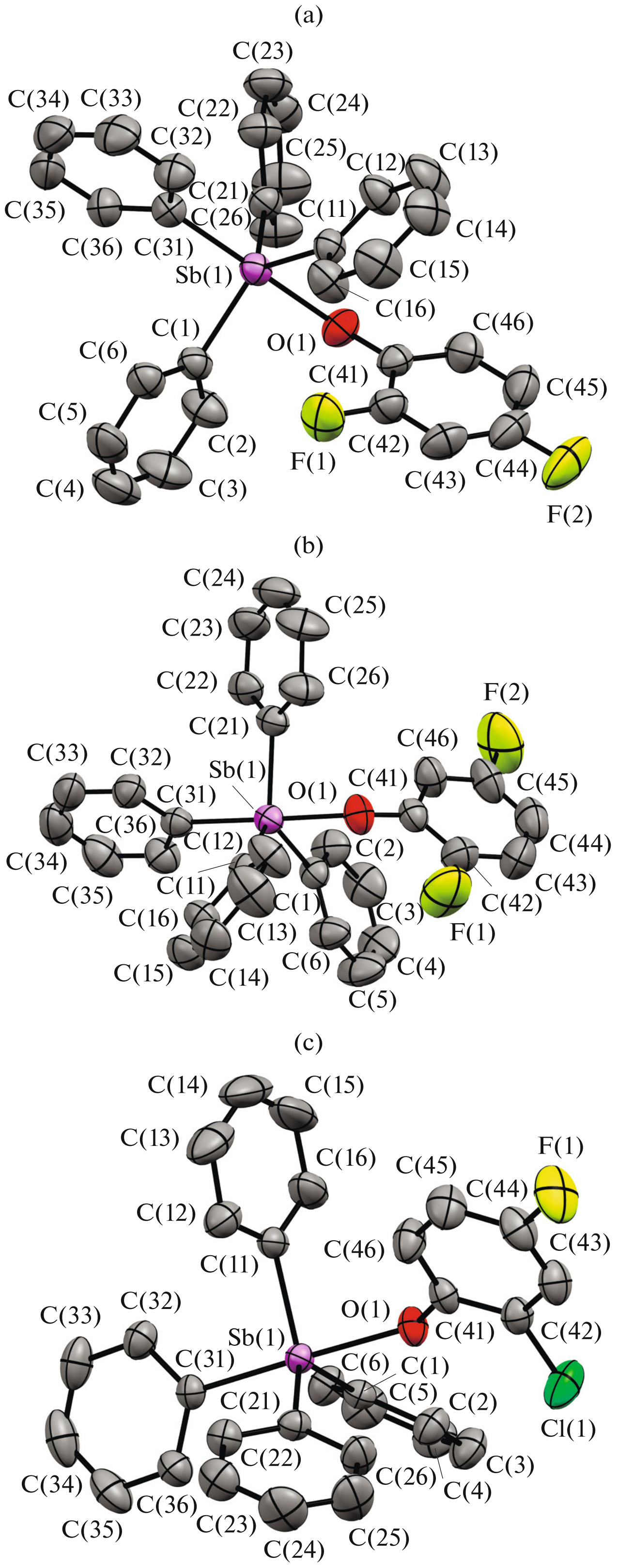


Fig. 1. Structures of compounds (a) **I** (hydrogen atoms are omitted), (b) **II**, and (c) **III**.

The geometric parameters of the molecules in compounds **I**–**III** are similar in the Sb–C_{eq} and Sb–O bond lengths (2.118(2)–2.127(2) and 2.1780(16) Å in **I**; 2.122(2)–2.130(2) and 2.179(2) Å in **II**; 2.116(2)–2.119(2) and 2.1803(16) Å in **III**). The Sb–C_{ax} distances in compounds **I** and **II** exceed the Sb–O bond length (2.188(2) and 2.185(3) Å, respectively), which is met rarely and is typical of tetraphenylantimony 4-iodophenoxide as well [1]. An opposite situation is observed in the most part of structures of tetraphenylantimony haloaroxides, including compound **III** (2.175(2) Å).

It seems interesting to monitor a change in the Sb–O bond length in the series of structurally characterized tetraphenylantimony haloaroxides Ph_4SbOAr (Ar = C_6H_4I-4, $C_6H_3F_2$-2,4 (**I**), $C_6H_3F_2$-2,5 (**II**), C_6H_3Cl-2-F-4 (**III**), $C_6H_3Cl_2$-2,6, $C_6H_2Cl_3$-2,4,6, $C_6H_2Br_3$-2,4,6, C_6F_5). An elongation of the Sb–O distance (from 2.162 to 2.285 Å) is observed in the presented series, indicating a decrease in the strength of the bond. The basicity of the ligands depends directly on the strength of the electronic effects of halogens (–*I* and +*M*), their position in the benzene ring, and amount. This arrangement is not quite reasonable for the bromine- and chlorine-containing phenoxide residues, since the –*I* effects of halogens change in the series I < Br < Cl < F and decay in the series *para* < *meta* < *ortho*. The position of 2,4,6-tribromophenoxide in this series is possibly related to a large volume of bromine atoms, and their total inductive effect affects the basicity of the ligand to a higher extent than more electronegative fluorine atoms, which are present in lower amounts in compounds **I**–**III**. In compounds **I**–**III**, the Sb–O bonds are nearly equal and, hence, the replacement of the fluorine atom by chlorine in the *ortho* position of compound **III** and the change of the *para* position of the F atom by the *meta* position in compound **II** compared to compound **I** exert no effect on the length of this bond.

The organization of the structures of compounds **I** and **III** is due to weak hydrogen bonds involving the F atoms (2.59, 2.57, and 2.63 Å in **I** and 2.52 Å in **III**) and C–H···π interactions. The structure organization of compound **II** is caused by C–H···π interactions only. These interactions organize the molecules in the crystal of compound **I** into the three-dimensional network (Fig. 2a), the molecules of compound **II** are organized in the paired chains arranged along the crystallographic axis *c* (Fig. 2b), and the layers with the thickness of two molecules perpendicular to the *a* axis are formed in compound **III** (Fig. 2c).

Thus, the reactions of pentaphenylantimony with halophenols afford tetraphenylantimony aroxides in the molecules of which the antimony atoms have the configuration of a trigonal bipyramid with the oxygen atom of the aroxide ligand in the axial position. The Sb–C_{ax} distance in compounds **I** and **II** exceeds the

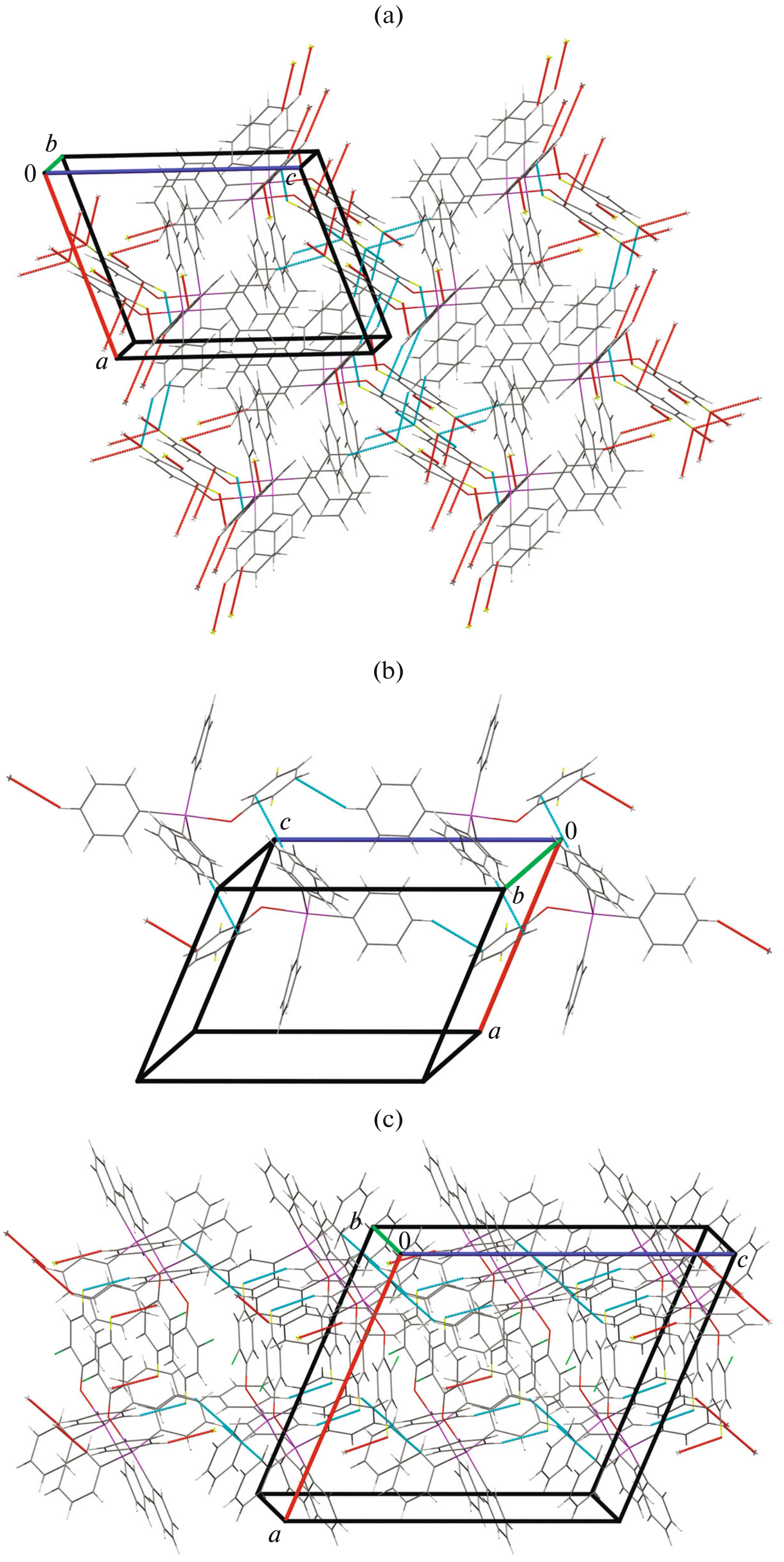


Fig. 2. Structural organization in the crystals of compounds (a) **I**, (b) **II**, and (c) **III**.

Sb—O bond length, which is not characteristic of similar compounds. The partial interaction of the π systems of the phenyl ligand arranged in the equatorial plane and aromatic ring of the aroxy group is observed in these structures. The molecules in the crystals of the compounds are organized into the three-dimensional network (in **I**), paired chains (in **II**), and layers (in **III**) via the F···H hydrogen bonds and C—H···π interactions.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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