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Synthesis and Structure of Tetraphenylantimony 1-Adamantanecarboxylate and Triphenylantimony bis(1-adamantanecarboxylate)

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Abstract—Reaction of pentaphenylantimony with triphenylantimony bis(1-adamantylcarboxylate) yielded the solvate of tetraphenylantimony 1-adamantylcarboxylate with benzene. Triphenylantimony bis(1-adamantylcarboxylate) was prepared from triphenylantimony and 1-adamantylcarboxylic acid in the presence of hydrogen peroxide in ether. X-ray studies showed that in the first and in the second product antimony atom has the distorted trigonal bipyramide coordination (OSbO and CSbO *trans*-angles are 179.42° and 174.58°, respectively). Sb–O interatomic distances are 2.154 and 2.202 Å, respectively. The carbonyl group oxygen atom is coordinated with the central atom, Sb···O interatomic distances are 2.570 and 3.396 Å, respectively.

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As known, an effective procedure for preparing the antimony derivatives of the general formula $R_4SbOC(O)R$ is based on the reaction of pentaorganylantimony with triorganylantimony dicarboxylates [1–3]. The latter compounds are prepared conveniently by means of oxidative method from triorganylantimony and carboxylic acid in presence of peroxide [3–6]. Both these reactions were studied on the sufficient number of examples, but it was noted that the increase in size of the organic radical in carboxylic acid often decreases their efficiency.

In this study syntheses of triphenylantimony bis(1-adamantylcarboxylate) **I** and tetraphenylantimony 1-adamantylcarboxylate **II** were carried out, and the crystalline and molecular structures of these substances were established.

Reaction of oxidative addition with the participation of triphenylantimony, hydrogen peroxide, and 1-adamantylcarboxylic acid (1:1:2 molar ratio) proceeds in ether at room temperature to form the compound **I**.

$$Ph_3Sb + 2HOC(O)C_{10}H_{15} + H_2O_2 \xrightarrow{Et_2O} \underset{\mathbf{I}}{Ph_3Sb[OC(O)C_{10}H_{15}]_2} + 2HO_2.$$

Large colorless crystals of compound **I** well soluble in the organic solvents were isolated from the reaction mixture. Yield of the target product reached 92%.

Compounds **I**, **II** studied by XRD analysis. Parameters of the experiment are presented in Table 1, atomic coordinates and their isotropic equivalent temperature parameters, in Table 2, and bond angles, in Table 3. General view of structures of compounds **I, II** are presented in Figs. 1, 2.

According to X-ray studies antimony atom in the molecules of compound **I** has the distorted trigonal bipyramide coordination with the oxygen atoms of carboxylate ligands in the axial positions. OSbO axial angle (179.42°) has practically the ideal value. Angles between the axial and equatorial bonds deflect from their theoretical values on ≈1°. SbC_3 group of atoms has the flat structure (sum of angles in the equatorial plane is 360°). Deviation from the trigonal bipyramide coordination is revealed most of all in the values of CSbC equatorial angles which strongly differ from one another: 161.48°, 99.26°, and 99.28°. Sb–C interatomic distances are 2.123, 2.127, and 2.127 Å, Their average value is close to the upper limit of the range of variation of the mean values of equatorial bonds in the structurally characterized trialkylantimony dicarbo-

Table 1. Crystallographic data, parameters of the experiment and refining of structures of complexes **I** and **II**

Parameter	Value	
	I	**II**
M	711.51	687.49
T, K	90	100
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*1
a, Å	19.8775(6)	10.1644(2)
b, Å	13.0253(4)	11.4880(2)
c, Å	12.7896(3)	14.6546(3)
α, deg		93.2200(10)
β, deg	98.8460(10)	98.2280(10)
γ, deg		107.5380(10)
V, Å^3	3271.97(16)	1605.90(5)
Z	4	2
ρ(calc), g cm^{-3}	1.444	1.422
μ, mm^{-1}	0.885	0.894
F(000)	1472	708
Form of the crystal (size, mm)	Plate (0.02×0.11×0.18)	Plate (0.045×0.145×0.158)
Range of data collection by θ, deg	1.88–32.47	1.87–31.39
Intervals of reflection indexes	$-26 \le h \le 27, -18 \le k \le 18, -18 \le l \le 12$	$-10 \le h \le 14, -15 \le k \le 16, -19 \le l \le 18$
Reflections measured	18474	20128
Independent reflections	4763	8648
Refining parameters	205	397
GOOF	0.999	1.078
R factors by $F^2 > 2\sigma(F^2)$	R_1 0.0251, wR_2 0.0520	R_1 0.0394, wR_2 0.0658
R factors by all reflections	R_1 0.0359, wR_2 0.0558	R_1 0.0472, wR_2 0.0684
Residual electronic density (min/max), *e* Å^{-3}	–0.375/0.546	–1.291/0.525

xylates (2.100–2.125 Å). Sb–O distances in compound **I** are equal to one another (2.154 Å). Note that the largest Sb–O distances were found in triphenylantimony dicynnamate (2.156 Å) [7].

In compound **I** carboxylate ligands are prone to behave as bidental. Nonvalent interaction of the central atom with the oxygen atoms of carbonyl groups results in the significant decrease in Sb···O=C distances which are equal to 2.570 Å (sum of van der Waals radii of the antimony and oxygen atoms is 3.70 Å [8]). Symmetry of coordination of carboxylate ligands on the antimony atom in product **I** is the highest in the series of triorganylantimony dicarboxylates. Hence, the ratio of the Sb···O=C distance to the length of Sb–O bond accepted as a measure of dissymmetry of bidentate ligand for triorganylantimony dicarboxylates as a rule is 1.31–1.52 while for compound **I** it is 1.19. In triphenylantimony dicynnamate Sb···O=C distances are equal to 2.664 Å, and the given ratio is 1.24. Hence, it may be stated that in the formation of Sb···O=C intramolecular contacts one of the decisiue factors is the *n*-donating ability of the carbonyl oxygen. In the molecule of compound **I** the increase in the donating properties of the carbonyl oxygen atoms is caused by the positive inductive effect of the hydrocarbon adamantyl substituents.

Sufficiently strong Sb···O=C interactions lead to the insignificant redistribution of electron density in the carboxy groups. C–O bond length (1.300 Å) belongs to the interval of variation of these characteristics in the carboxylic acids. (1.293–1.308 Å) while the C=O bonds (1240 Å) are insignificantly larger than the reported data (1.214–1.229 Å [9]). But the existence of the Sb···O=C contact causes the distortion of Sb^{1}O^{1}C^{1}angles (101.56°) as compared to the theoretical value 120°.

Table 2. Atomic coordinates ($\times 10^4$) and their isotropic equivalent temperature parameters ($\times 10^3$) in the structures **I**, **II**

Atom	x	y	z	U_{eq}, Å^2
I				
Sb^1	0	2124.27(12)	2500	7.54(4)
O^1	–1080.7(6)	2132.6(9)	1957.5(9)	11.7(2)
O^2	–764.1(6)	524.6(9)	2241.9(9)	13.1(2)
C^1	–1227.8(8)	1157.5(12)	1998.8(12)	11.0(3)
C^2	–1971.4(8)	856.2(12)	1748.3(12)	9.7(3)
C^{111}	0	3754.2(17)	2500	10.5(4)
C^{112}	–199.4(8)	4294.6(13)	1559.8(13)	12.1(3)
C^{113}	–196.0(9)	5363.9(13)	1562.3(14)	13.9(3)
C^{114}	0	5895.3(18)	2500	14.1(5)
C^{121}	198.9(8)	1861.5(12)	935.1(13)	10.8(3)
C^{122}	–217.3(9)	1290.6(13)	175.6(13)	14.7(3)
C^{123}	–54.3(10)	1201.9(13)	–839.1(14)	17.4(4)
C^{124}	519.1(9)	1682.9(13)	–1099.4(13)	16.1(3)
C^{125}	930.1(9)	2262.4(13)	–347.1(14)	16.4(3)
C^{126}	769.8(9)	2360.3(13)	669.1(13)	13.7(3)
C^{131}	–2276.3(9)	1289.1(14)	658.0(13)	15.7(3)
C^{132}	–2356.3(9)	1319.3(15)	2595.2(14)	18.8(4)
C^{133}	–2055.6(9)	–312.5(13)	1731.9(14)	15.1(3)
C^{134}	–3034.3(9)	1011.6(14)	407.4(14)	18.1(4)
C^{135}	–3112.1(9)	–155.3(14)	402.0(14)	17.7(4)
C^{136}	–2812.8(9)	–589.2(13)	1481.8(14)	17.0(4)
C^{137}	–3191.9(10)	–134.9(16)	2325.9(15)	21.7(4)
C^{138}	–3115.5(9)	1032.6(16)	2340.2(15)	22.0(4)
C^{139}	–3410.2(9)	1471.7(15)	1255.8(17)	23.1(4)
II				
Sb^1	3989.24(16)	1594.13(14)	2680.16(11)	8.43(4)
O^1	3144.5(16)	–418.1(14)	2620.2(11)	13.0(3)
O^2	862.3(17)	–634.2(15)	2525.7(12)	17.0(4)
C^1	1850(2)	–1048(2)	2647.8(16)	11.2(5)
C^2	1652(2)	–2367(2)	2877.5(16)	10.8(5)
C^{111}	2727(2)	1497(2)	1383.6(16)	11.2(5)
C^{112}	2391(2)	476(2)	736.2(17)	13.9(5)
C^{113}	1650(2)	470(2)	–137.4(17)	17.1(5)
C^{114}	1219(2)	1465(2)	–368.4(18)	19.8(5)
C^{115}	1518(3)	2466(2)	285.7(19)	21.0(6)
C^{116}	2284(2)	2497(2)	1154.0(18)	15.7(5)
C^{121}	3128(2)	1530(2)	3916.0(16)	11.8(5)
C^{122}	3574(3)	946(3)	4637.2(19)	25.0(6)
C^{123}	2901(3)	783(3)	5401.0(19)	29.2(7)
C^{124}	1771(3)	1204(2)	5439.0(18)	20.4(6)
C^{125}	1345(3)	1815(3)	4733.8(18)	22.6(6)
C^{126}	2022(2)	1985(2)	3968.2(18)	18.8(5)
C^{131}	5880(2)	1157(2)	2669.6(16)	11.9(5)
C^{132}	7147(2)	2059(2)	3025.5(17)	15.0(5)
C^{133}	8399(2)	1824(2)	2995.4(18)	16.7(5)
C^{134}	8412(2)	700(2)	2603.2(17)	15.8(5)
C^{135}	7157(2)	–192(2)	2241.7(17)	14.6(5)
C^{136}	5893(2)	25(2)	2274.6(16)	13.2(5)
C^{141}	4999(2)	3567(2)	2821.0(17)	11.8(5)
C^{142}	5255(2)	4287(2)	3662.4(17)	14.3(5)
C^{143}	6009(2)	5528(2)	3751.6(18)	17.8(5)
C^{144}	6517(2)	6064(2)	3001.2(19)	18.1(5)
C^{145}	6293(2)	5358(2)	2156.6(18)	15.6(5)
C^{146}	5542(2)	4121(2)	2066.4(17)	13.1(5)
C^{151}	192(2)	–3217(2)	2422.8(18)	14.3(5)
C^{152}	1774(3)	–2353(2)	3937.6(17)	15.3(5)
C^{153}	2767(2)	–2882(2)	2566.6(17)	13.4(5)
C^{154}	–32(2)	–4523(2)	2701.3(18)	16.6(5)
C^{155}	98(3)	–4491(2)	3758.3(19)	20.8(6)
C^{156}	1551(3)	–3665(2)	4218.7(18)	19.3(5)
C^{157}	2665(3)	–4160(2)	3892.2(18)	19.9(5)
C^{158}	2544(2)	–4190(2)	2838.0(18)	15.0(5)
C^{159}	1086(2)	–5018(2)	2377.2(18)	16.3(5)
C^3	6561(3)	4131(2)	–292.0(19)	23.8(6)
C^4	5443(3)	3057(3)	–457.1(18)	23.1(6)
C^5	5565(3)	2007(2)	–89.2(18)	20.3(6)
C^6	6804(3)	2021(2)	448.5(18)	20.4(6)
C^7	7932(3)	3090(2)	611.8(19)	22.3(6)
C^8	7809(3)	4143(2)	238.9(19)	24.5(6)

Carboxylate ligands have a *cis*-orientation were respect to the SbC_3 ligand (dihedral angle between the planes of carboxy groups is 15.25°) what causes a significant increase in one of the equatorial angles $C^{121}Sb^1C^{121a}$ to 161.48°.

As four oxygen atoms and C^{111} carbon atom of one of the phenyl rings are located approximately in the same plane as the antimony atom, it may be considered as the equatorial plane of pentagonal bipyramid whose axial positions are occupied by C^{121} and C^{121a} atoms of two phenyl groups.

Molecule of compound **I** has its own non-crystallographic C_{2v} symmetry. The second order axis passes through the C^{114} and C^{111} atoms of the phenyl

Table 3. Interatomic distances and bond angles in the structures **I, II**

Bond *d*, Å		Bond angle ω, deg		Bond *d*, Å		Bond angle ω, deg	
I				**II**			
$Sb^1–O^1$	2.1536(11)	$O^{1\#1}Sb^1O^{1}$ [a]	179.43(6)	$Sb^1–O^1$	2.202(2)	$C^{111}Sb^1O^1$	88.68(8)
$Sb^1–C^{111}$	2.123(2)	$C^{111}Sb^1O^1$	89.71(3)	$Sb^1–C^{111}$	2.112(2)	$C^{111}Sb^1C^{121}$	120.50(9)
$Sb^1–C^{121}$	2.127(2)	$C^{111}Sb^1C^{121}$	99.26(4)	$Sb^1–C^{121}$	2.117(2)	$C^{111}Sb^1C^{131}$	117.03(9)
$Sb^1–O^2$	2.570(1)	$C^{121}Sb1O^{1\#1}$	89.05(5)	$Sb^1–C^{131}$	2.129(2)	$C^{111}Sb^1C^{141}$	96.15(9)
$O^1–C^1$	1.306(2)	$C^{121}Sb^1O^1$	91.04(5)	$Sb^1–C^{141}$	2.172(2)	$C^{121}Sb^1O^1$	82.84(7)
$O^2–C^1$	1.240(2)	$C^{121}Sb^1C^{121\#1}$	161.47(8)	$Sb^1–O^2$	3.396(2)	$C^{121}Sb^1C^{131}$	119.39(9)
$C^1–C^2$	1.515(2)	$C^1O^1Sb^1$	101.56(10)	$O^1–C^1$	1.305(3)	$C^{121}Sb^1C^{141}$	96.77(9)
$C^2–C^{131}$	1.539(2)	$O^1C^1C^2$	117.41(14)	$O^2–C^1$	1.229(3)	$C^{131}Sb^1O^1$	80.95(7)
$C^2–C^{132}$	1.542(2)	$O^2C^1O^1$	119.62(15)	$C^1–C^2$	1.530(3)	$C^{131}Sb^1C^{141}$	94.60(8)
$C^2–C^{133}$	1.531(2)	$O^2C^1C^2$	122.96(14)	$C^2–C^{151}$	1.540(3)	$C^{141}Sb^1O^1$	174.57(7)
$C^{111}–C^{112\#1}$	1.397(2)	$C^{112}C^{111}Sb^1$	120.25(11)	$C^2–C^{152}$	1.540(3)	$C^1O^1Sb^1$	125.93(14)
				$C^2–C^{153}$	1.538(3)	$O^1C^1C^2$	113.98(19)
				$C^{111}–C^{112}$	1.390(3)	$O^2C^1O^1$	124.3(2)
				$C^{111}–C^{116}$	1.396(3)	$O^2C^1C^2$	121.7(2)

[a] Symmetric transformations: $^{\#1}$ $-x, y, -z + 1/2$

ligand, through the $Sb^1–C^{111}$ bond and divides in half the bond angle between two equivalent carboxylate substituents. Adamantyl groups of carboxylate ligands have the eclipsed conformation.

It is established that pentaphenylantimony reacts with triphenylantimony bis(1-adamantylcarboxylate) to form the solvate of tetraphenylantimony 1-adamantylcarboxylate with benzene in 88% yield.

$$Ph_5Sb + Ph_3Sb[OC(O)C_{10}H_{15}]_2 \xrightarrow{PhH} 2Ph_4SbOC(O)C_{10}H_{15}{\cdot}PhH.$$

II

Reaction was carried out in the aromatic hydrocarbon solution at room temperature, but the short time heating of reaction mixture on a boiling water bath is needed for its completion.

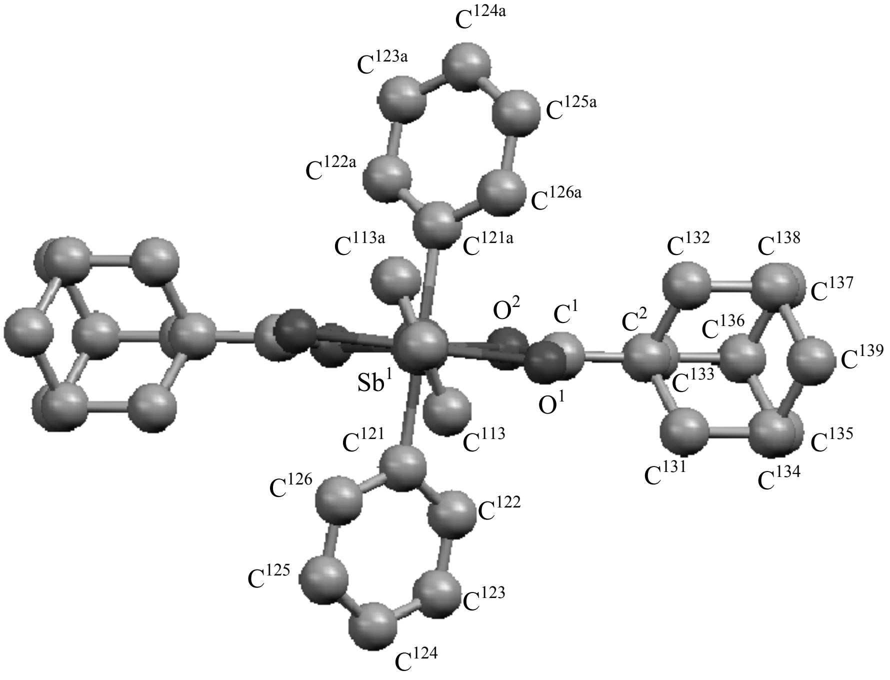

Fig. 1. Spatial arrangement of compound **I**.

According to X-ray data antinomy atom in compound **II** has the distorted trigonal bipyramid coordination which is revealed in the deviation of all bond angles of the antimony atom from the theoretical values. Hence, axial CSbO angle is 174.58°, CSbC angles in the equatorial plane are 117.03, 119.39, and 120.50° (total 356.9°). The angles between the axially located oxygen atom and the equatorial carbon atoms OSbC$_{eq}$ are smaller than 90° (80.94°, 82.85°, 88.68°), while the values of C$_{ax}$SbC$_{eq}$ angles are larger (96.15°, 96.77°, 94.60°). All the presented data agree with the values observed usually for tetraarylantimony carboxylates [10].

Sb–C$_{eq}$ Distances (2.112, 2.117, 2.127 Å) are shorter than the axial Sb–C bond (2.172 Å). In tetraarylantimony carboxylates the interval of variation of the mean values of equatorial bonds is 2.079–2.127 Å while for the axial ones it is 2.117–2.180 Å [10]. Sb–O bond (2.202 Å) is abnormally short, while Sb···O=C intramolecular distance (3.396 Å) is the longest in the series of tetraarylantimony carboxylates (2.223–2.530 Å and 3.112–3.509 Å respectively). The coordination dissymmetry of carboxylate ligand in the product **II** is evaluated at 1.54. Hence, the higher is the strength of the covalent Sb–O bond the weaker is the donor-acceptor interaction with the participation of *d*-orbitals of the metal atom and the unshared electron pair of oxygen.

Interatomic distances (C=O and C–O) in compound **II** (1.229 and 1.304 Å) coincide with the data for carboxylic acids. SbO^{1}C^1 angle is equal to 125.93°.

Hence, it was established that the reaction of oxidative addition and redistribution of ligands leads to the synthesis of triphenylantimony bis(1-adamantylcarboxylate) **I** and tetraphenylantimony 1-adamantylcarboxylate **II** respectively in high yields. The trend to show bidentate properties by adamantly-carboxylate ligands depends on the type of compound.

EXPERIMENTAL

X-ray study of crystals of compounds **I** and **II** was carried out on an automatic four-circle Bruker-Nonius X8Apex diffractometer (two-coordinate CCD detector) using the MoK_α radiation, λ = 0.71073 Å and graphite monocromator. Reflection intensities were measured by means of φ-scanning of the narrow (0.5°) frames up to 2θ 50°. The extination was accounted for empirically (SADABS) [11]. Structure was solved by the direct method and refined by means of the full-matrix root-mean-square method in the anisotropic approximation for the nonhydrogen atoms (SHELX-97) [12].

Main crystallographic data and the results of refining of structures are listed in Table 1, the coordinates and temperature factors of atoms in Table 2,

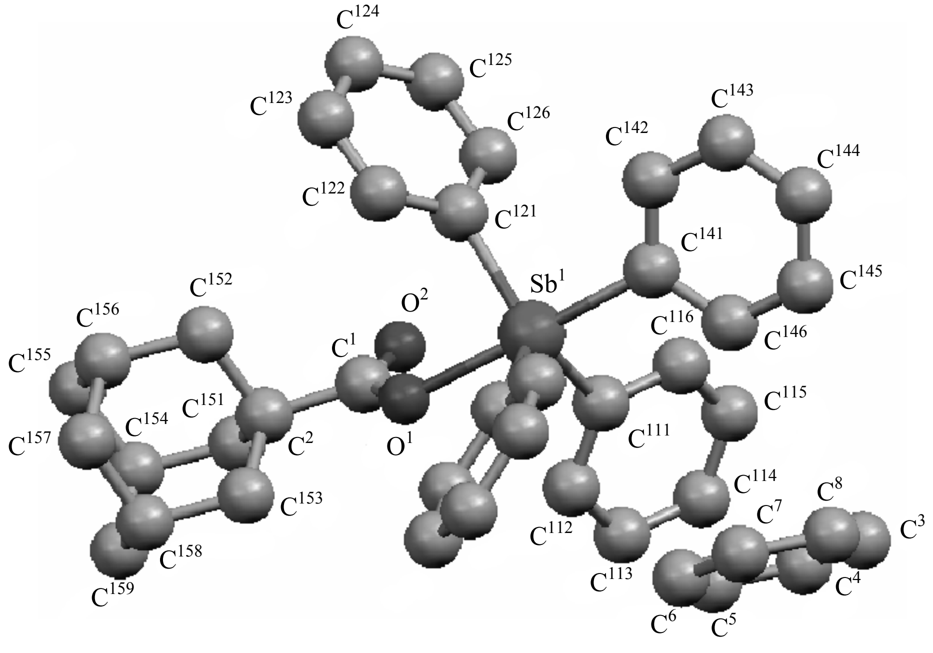

Fig. 2. Spatial arrangement of compound **II**.

and the main interatomic distances and bond angles, in Table 3.

IR spectra were recorded on the IR Fourier spectrometer from KBr pellets.

Triphenylantimony bis(1-adamantylcarboxylate) (I). A mixture of 0.50 g of triphenylantimony, 0.51 g of 1-adamantylcarboxylic acid, and 20 ml of diethyl ether was treated with 0.16 ml of 30% hydrogen peroxide and kept for 18 h at 20°C. Crystals of the compound **I** were formed, yield 0.92 g (92%), mp 228°C. IR spectrum, ν, cm^{-1}: 3048, 2930, 2849, 1597, 1571, 1495. 1452, 1429, 1284, 1251, 1186, 1103, 1084, 1063, 1019, 997, 913, 810, 732, 695, 529, 460. Found, %: C 67.32, H 6.30. $C_{40}H_{45}O_4Sb$. Calculated, %: C 67.51, H 6.33.

Tetraphenylantimony 1-adamantylcarboxylate (II). A mixture of 0.51 g of pentaphenylantimony, 0.71 g of triphenylantimony bis(1-adamantylcarboxylate) and 10 ml of benzene was heated for 15 min on a boiling water bath and concentrated to ~2 ml. The crystals formed were filtered off and dried to give 1.22 g (88%) of compound **II**, mp 165°C. IR spectrum, ν, cm^{-1}: 3048, 2913, 1634, 1575, 1479, 1433, 1317, 1188, 1065, 1000, 910, 813, 736, 690, 464. Found, %: C 70.71, H 6.09. $C_{41}H_{41}O_2Sb$. Calculated, %: C 71.62, H 5.97.

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