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Synthesis and Structure of Tetra- and Triarylantimony Oximates

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Abstract — Pentaphenyl- and penta-*p*-tolylantimony were reacted with benzophenone oxime or triarylantimony bis(benzophenonoximate) in toluene to obtain tetraarylantimony benzophenonoximate. Triarylantimony bis(benzophenonoximates) were prepared by oxidative addition from tryarylstibine and oxime in ether in the presence of hydrogen peroxide. X-ray diffraction analysis of tetraphenylantimony benzophenonoximate was performed to show that coordination of the antimony atom is trigonal-bipyramidal and the oxime oxygen atom is axial.

It is known that pentaarylstibines **I** react with antimony derivatives of the general formula Ar_3SbX_2 (Ar = Ph, *p*-Tol; X = Cl, Br, OC(O)R, OSO_2Ar', NO_3, SCN), giving unsymmetrical antimony derivatives Ar_4SbX in high yields [1–4]. Analogous disproportionation reactions involving compound **I** and triarylantimony dioximates has not yet been studied.

We found that tetraarylantimony benzophenonoximates can be prepared by the above-mentioned reaction in 92% yield from pentaphenyl- and penta-*p*-tolylantimony and triarylantimony bis(benzophenonoximates) in toluene.

$$Ar_5Sb + Ar_3Sb(ON{=}CPh_2)_2 \longrightarrow 2Ar_4SbON{=}CPh_2,$$
$$Ar = Ph,\ 4\text{-}MeC_6H_4.$$

The IR spectra and the melting points of the tetraarylantimony benzophenonoximates prepared by this method were consistent with respective characteristics of the compounds obtained from pentaarylantimony and benzophenone oxime.

The reactions of pentaphenyl- or penta-*p*-tolylantimony with oximes give tetraarylantimony oximates.

$$\underset{\mathbf{I}}{Ar_5Sb} + HON{=}CRR' \longrightarrow \underset{\mathbf{IIa–IIj}}{Ar_4SbON{=}CRR'} + ArH,$$

Ar = Ph; R = R' = Ph (**a**), R = H, R' = C_6H_3(OH)-2-(Br)-5 (**b**), R = H, R' = $C_6H_4(NO_2)$-3 (**c**), R, R' = cyclohexyl (**d**). Ar = C_6H_4(Me)-4; R = Ph, R' = Me (**e**), R = H, R' = C_4H_3O (**f**), R = R' = Ph (**g**), R = H, R' = C_6H_3(OH)-2-(Br)-5 (**h**), R = H, R' = $C_6H_4(NO_2)$-3 (**i**), R, R' = cyclohexyl (**j**).

The products are colorless crystalline substances soluble in aromatic hydrocarbons and polar organic solvents.

The yields of tetraarylantimony oximates in this case reach 98% (see Table 1).

Triarylantimony bis(benzophenonoximates) were obtained by oxidative addition of benzophenone oxime to triarylantimony in the presence of hydrogen peroxide.

$$Ar_3Sb + 2HON{=}CPh_2 + H_2O_2 \longrightarrow Ar_3Sb(ON{=}CPh_2)_2 + 2H_2O.$$

Note that this method was first used for preparing triphenylantimony diacetate and then analogous antimony derivatives of the general formula Ar_3SbX_2, where X is an electronegative group [1, 3–6], but the synthesis of triarylantimony dioximates by this method has not been reported.

According to X-ray diffraction data, the antimony atom in compound **IIa** has a usual trigonal-bipyramidal coordination typical of five-coordinate antimony compounds (Fig. 1). The O^2 and C^7 atoms are axial, the $O^2Sb^1C^7$ bond angle is 174.9(2)°, equatorial angles vary from 118.8(2) to 120.2(2)°, and their sum is 348.2(3)°. The angles between axial and equatorial substituents are in the range 81.2(2)°–95.4(2)°, and acute angles involve oxygen atoms (Table 2). Equatorial Sb–C bonds are equal to each other within the experimental errors and are slightly shorter than the axial Sb–C^7 bond. The Sb–O bond [2.146(4) Å] is close to Sb–C. This is much shorter than in the penta-

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Table 1. Yields, melting points, and elemental analyses of tetraarylantimony oximates

Comp. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
IIa	90	168	70.02	4.89	2.37	$C_{37}H_{30}NOSb$	70.93	4.79	2.24
IIb	96	150	56.97	3.95	2.02	$C_{31}H_{25}BrNO_2Sb$	57.67	3.88	2.17
IIc	92	139	62.31	4.58	4.95	$C_{31}H_{25}N_2O_3Sb$	62.52	4.20	4.71
IId	70	122	66.20	5.76	2.79	$C_{30}H_{30}NOSb$	66.42	5.53	2.58
IIe	98	Oil	70.44	6.57	2.61	$C_{36}H_{36}NOSb$	69.68	5.81	2.26
IIf	97	〃	67.03	5.88	2.62	$C_{33}H_{32}NO_2Sb$	66.44	5.37	2.35
IIg	98	148	71.65	5.90	2.38	$C_{41}H_{38}NOSb$	72.14	5.57	2.05
IIh	87	166	60.53	4.89	1.86	$C_{35}H_{33}BrNO_2Sb$	59.91	4.71	2.00
IIi	97	125	64.02	4.73	4.00	$C_{35}H_{33}N_2O_3Sb$	64.52	5.07	4.30
IIj	84	158	67.69	6.81	2.11	$C_{34}H_{38}NOSb$	68.23	6.35	2.34

valent antimony derivative $Ph_4SbON{=}C(NO)Me$ (2.266 and 2.235 Å, respectively [7]) which is structurally similar to the obtained oximates. The geometry of the $Ph_2C{=}NO$ substituent is usual. The trigonal-planar coordination of the C^{25} atom and the N^2–C^{25} bond length of 1.281(7) Å agree with the proposed structure. The crystal packing of molecules **IIa** is determined by multiple CH···π contacts and dispersion interactions between parallel benzene rings (Fig. 2).

EXPERIMENTAL

The IR spectra were registered on a Hitachi-215 spectrometer (suspension in Vaseline oil).

Single-crystal X-ray diffraction analysis of tetraphenylantimony benzophenonoximate IIa. The intensities of 5575 reflections, 3138 of which had $I > 3\sigma$, were measured at 20°C on an Enraf–Nonius CAD-4 automatic four-circle *K*-diffractometer (MoK_α radiation, λMoK_α 0.71073 Å, graphite monochromator, ω/2θ scanning, θ < 29.96°). Crystals of **IIa**, $C_{37}H_{30}NOSb$, are monoclinic; at 20°C, *a* 11.565(1), *b* 16.545(8), *c* 15.713(3) Å, β 94.09(2)°, *V* 2999(2) Å^3, *Z* 4, d_{calc} 1.39 g/cm^3, space group $P2_1/n$. Absorption corrections were not applied (μMo 9.52 cm^{-1}). The structure was solved by the direct method using the SIR program [8] and refined first

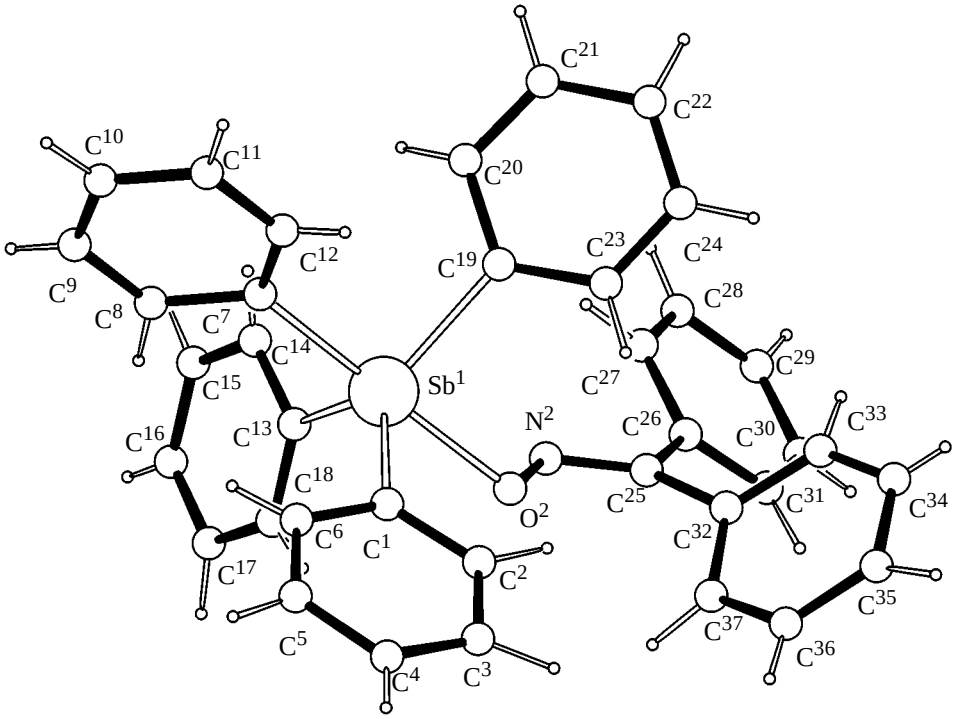

Fig. 1. Geometry of complex **IIa** in crystal.

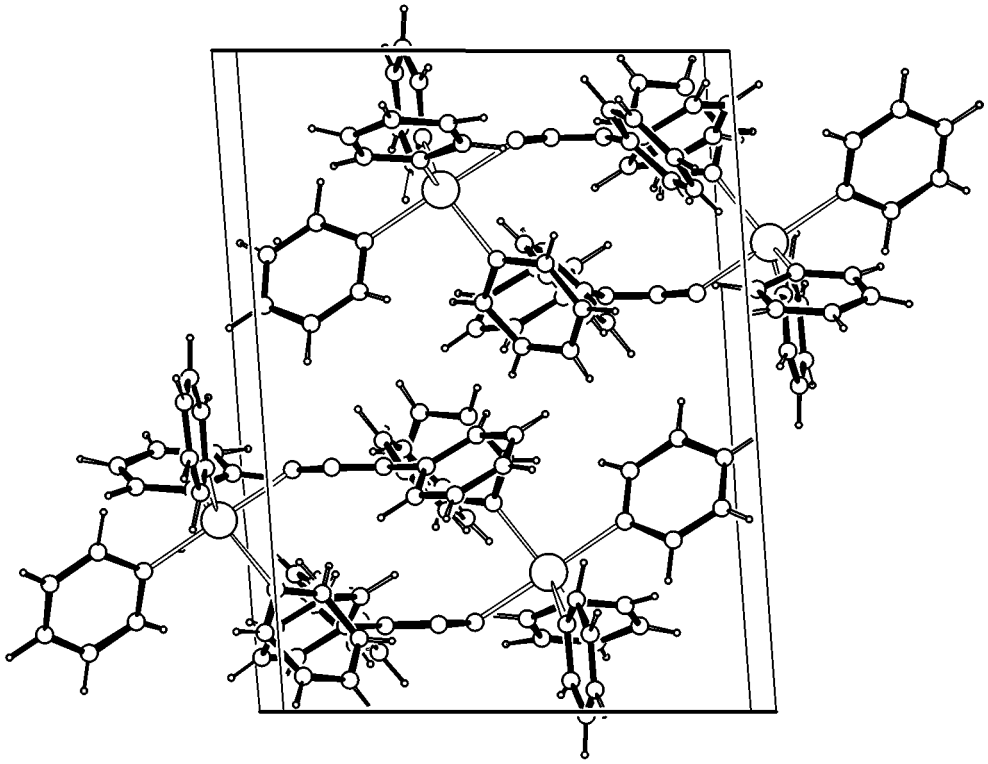

Fig. 2. Crystal packing of molecules **IIa**.

isotropically and then anisotropically. Hydrogen atoms were revealed from differential electron density series and refined isotropically in the final stage. Final divergence factors: R 0.038 and R_W 0.043, on 2905 unique reflections with $F^2 > 3\sigma$. All calculations were peformed using the MolEN program complex [9] on a DEC AlphaStation 200 compter. Analysis of intermolecular contacts and the molecular drawings were performed by the WINPL98 program [10].

Tetraarylantimony oximates were obtained according to the following typical procedures.

Tetraphenylantimony benzophenonoximate (IIa). *a*. A mixture of 1.00 g of pentaphenylantimony, 0.39 g of benzophenone oxime, and 10 ml of toluene was kept for 1 h at 90°C. The solvent was removed, and the residue was crystallized from a 3:1 heptane–benzene mixture. Yield 1.11 g (90%), mp 168°C.

b. A mixture of 0.40 g of pentaphenylantimony and 0.59 g of triphenylantimony bis(benzophenonoximate) in 10 ml of toluene was kept for 1 h at 90°C. The solvent was removed, and the residue was crystallized from a 3:1 heptane–benzene mixture. Yield 0.96 g (97%), mp 168°C.

Triphenylantimony bis(benzophenonoximate). To a solution of 1.00 g of triphenylstibine and 0.76 g of benzophenone oxime in 20 ml of ether, 0.32 ml of 31% aqueous hydrogen peroxide was added. The

Table 2. Pricipal geometric parameters of structure **Ia**: bond lengths (d, Å) and bond angles (ω, deg)

Bond	d	Bond	d
$Sb^1–O^2$	2.146(4)	$O^2–N^2$	1.387(6)
$Sb^1–C^1$	2.135(6)	$N^2–C^{25}$	1.281(7)
$Sb^1–C^7$	2.180(5)	$C^{25}–C^{26}$	1.501(8)
$Sb^1–C^{13}$	2.120(6)	$C^{25}–C^{32}$	1.499(8)
$Sb^1–C^{19}$	2.132(6)		
Angle	**ω**	**Angle**	**ω**
$O^2Sb^1C^1$	81.2(2)	$C^7Sb^1C^{19}$	93.8(2)
$O^2Sb^1C^7$	174.9(2)	$C^{13}Sb^1C^{19}$	119.2(2)
$O^2Sb^1C^{13}$	88.8(2)	$Sb^1O^2N^2$	112.2(3)
$O^2Sb^1C^{19}$	86.6(2)	$O^2N^2C^{25}$	114.3(5)
$C^1Sb^1C^7$	94.2(2)	$N^2C^{25}C^{26}$	114.9(5)
$C^1Sb^1C^{13}$	118.8(2)	$N^2C^{25}C^{32}$	126.3(5)
$C^1Sb^1C^{19}$	120.2(2)	$C^{26}C^{25}C^{32}$	118.6(5)
$C^7Sb^1C^{13}$	95.4(2)		

Table 3. Atomic coordinates in structure **IIa**, equivalent isotropic termal parameters of non-hydrogen atoms $B = 4/3 \sum_{i=1}^{3} \sum_{j=1}^{3} (a_i a_j) B(i, j)$ (Å^2), and isotropic thermal parameters of hydrogen atoms

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
Sb[1]	0.90643(4)	0.22897(2)	0.28967(3)	2.959(7)	C[33]	1.3745(6)	0.3089(4)	0.3034(4)	4.7(2)
O[2]	1.0640(3)	0.2548(2)	0.3652(3)	3.46(9)	C[34]	1.4153(6)	0.3859(4)	0.2919(5)	5.7(2)
N[2]	1.1400(4)	0.1898(3)	0.3687(3)	3.3(1)	C[35]	1.3762(7)	0.4502(4)	0.3386(6)	5.7(2)
C[1]	0.8628(5)	0.3460(3)	0.3348(4)	3.3(1)	C[36]	1.2990(6)	0.4348(4)	0.3972(5)	5.3(2)
C[2]	0.9479(6)	0.4021(4)	0.3600(5)	5.1(2)	C[37]	1.2573(6)	0.3584(4)	0.4104(4)	4.1(2)
C[3]	0.9173(7)	0.4773(4)	0.3899(6)	6.1(2)	H[2]	0.531(4)	0.110(3)	0.853(3)	4(1)
C[4]	0.8037(7)	0.4970(4)	0.3956(5)	5.2(2)	H[3]	0.989(6)	0.512(5)	0.398(5)	10(2)
C[5]	0.7175(6)	0.4419(4)	0.3701(4)	4.6(2)	H[4]	0.785(7)	0.544(5)	0.418(5)	13(3)
C[6]	0.7484(6)	0.3665(4)	0.3394(4)	4.1(2)	H[5]	0.143(4)	0.045(3)	0.882(3)	4(1)
C[7]	0.7443(5)	0.2143(3)	0.2116(4)	3.0(1)	H[6]	0.189(5)	0.170(3)	0.826(3)	5(1)
C[8]	0.6506(5)	0.1704(4)	0.2405(4)	3.9(2)	H[8]	0.667(5)	0.148(3)	0.301(3)	5(1)
C[9]	0.5477(5)	0.1656(4)	0.1915(5)	4.6(2)	H[9]	0.495(4)	0.137(3)	0.209(3)	4(1)
C[10]	0.5324(6)	0.2055(4)	0.1152(5)	4.8(2)	H[10]	0.458(5)	0.207(3)	0.081(3)	5(1)
C[11]	0.6222(6)	0.2510(4)	0.0865(5)	4.7(2)	H[11]	0.108(4)	0.222(3)	0.531(3)	4(1)
C[12]	0.7241(6)	0.2550(4)	0.1353(4)	4.0(2)	H[12]	0.278(3)	0.215(2)	0.623(2)	0.8(8)
C[13]	0.8819(5)	0.1272(3)	0.3684(4)	3.1(1)	H[14]	0.843(6)	0.041(4)	0.276(4)	10(2)
C[14]	0.8632(7)	0.0515(4)	0.3309(5)	4.9(2)	H[15]	0.827(5)	–0.059(3)	0.351(4)	5(1)
C[15]	0.8432(7)	–0.0141(4)	0.3827(5)	6.5(2)	H[16]	0.826(6)	–0.052(4)	0.504(4)	8(2)
C[16]	0.8412(6)	–0.0062(4)	0.4677(5)	6.0(2)	H[17]	0.866(4)	0.074(3)	0.565(3)	5(1)
C[17]	0.8582(6)	0.0681(5)	0.5057(5)	5.2(2)	H[18]	0.900(4)	0.177(3)	0.475(3)	4(1)
C[18]	0.8809(6)	0.1339(4)	0.4541(4)	4.6(2)	H[20]	0.921(5)	0.136(4)	0.121(4)	8(2)
C[19]	1.0113(5)	0.2172(3)	0.1842(4)	3.0(1)	H[21]	1.031(5)	0.119(3)	0.010(4)	7(2)
C[20]	0.9797(6)	0.1624(4)	0.1191(4)	4.5(2)	H[22]	1.185(8)	0.182(6)	0.004(6)	14(3)
C[21]	1.0521(6)	0.1548(4)	0.0532(5)	5.6(2)	H[23]	0.626(4)	0.199(3)	0.720(3)	2(1)
C[22]	1.1475(7)	0.2030(5)	0.0474(5)	6.3(2)	H[24]	1.241(4)	0.291(3)	0.107(3)	3(1)
C[23]	1.1073(6)	0.2647(4)	0.1780(4)	4.4(2)	H[27]	1.228(5)	0.066(3)	0.293(3)	5(2)
C[24]	1.1760(6)	0.2572(5)	0.1098(5)	6.1(2)	H[28]	1.354(5)	–0.033(3)	0.293(3)	6(2)
C[25]	1.2472(5)	0.2097(3)	0.3702(4)	3.1(1)	H[29]	1.535(5)	–0.030(3)	0.366(4)	6(2)
C[26]	1.3303(5)	0.1399(4)	0.3715(4)	3.9(2)	H[30]	1.576(5)	0.085(3)	0.450(3)	5(1)
C[27]	1.3005(6)	0.0704(4)	0.3265(5)	4.9(2)	H[31]	1.462(4)	0.189(3)	0.451(3)	5(1)
C[28]	1.3769(7)	0.0061(5)	0.3276(6)	7.0(2)	H[33]	1.409(4)	0.270(3)	0.275(3)	4(1)
C[29]	1.4808(7)	0.0112(5)	0.3729(6)	7.5(2)	H[34]	0.959(4)	0.106(3)	0.758(3)	3(1)
C[30]	1.5105(7)	0.0786(5)	0.4187(5)	6.6(2)	H[35]	0.087(4)	0.000(3)	0.178(3)	5(1)
C[31]	1.4360(6)	0.1443(4)	0.4185(5)	5.2(2)	H[36]	1.270(5)	0.473(4)	0.426(4)	7(2)
C[32]	1.2942(5)	0.2938(3)	0.3638(4)	3.2(1)	H[37]	0.710(4)	0.152(3)	0.958(3)	4(1)

resulting mixture was kept for 12 h at 20°C. Colorless crystals formed and were filtered off and dried to obtain 1.52 g (72%) of triphenylantimony bis(benzophenonoximate), mp 104°C.

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