Russian Journal of General Chemistry, Vol. 72, No. 6, 2002, pp. 893–898. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 6, 2002, pp. 956–961.

Synthesis and Structure of Tetra- and Triarylantimony Oximates

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Received August 11, 2000

Abstract—Reactions of pentaphenyl- and penta-*p*-tolylantimony with benzophenone oxime or triarylantimony bis(benzophenone oximate) yield tetraarylantimony benzophenone oximates. Triarylantimony bis(benzophenone oximates) were prepared by oxidative addition from triarylstibine and benzophenone oxime in the presence of hydrogen peroxide. X-ray diffraction analysis was performed to show that benzophenone oxime is a dimer and tetraphenylantimony benzophenone oximate has a trigonal bipyramidal antimony atom and an axial oxime oxygen atom.

It is known that pentaarylantimonies **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) to give unsymmetrical antimony derivatives Ar_4SbX in high yields [1–4]. Such disproportionation reactions involving compound **I** and triarylantimony dioximates were not previously studied.

We found that tetraarylantimony benzophenone oximates can be obtained by this disproportionation reaction from pentaphenyl- and penta-*p*-tolylantimony and triarylantimony bis(benzophenone oximates) in toluene with yields of up to 92%.

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

The IR spectra and melting points of the tetraarylantimony benzophenone oximates prepared by this procedure agree with respective characteristics of the same compounds obtained from pentaarylantimony and benzophenone oxime.

The reactions of pentaphenyl- or penta-*p*-tolylantimony with oximes give tetraarylantimony oximates. The products are colorless crystalline compounds soluble in aromatic hydrocarbons and polar organic solvents.

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

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

Triarylantimony bis(benzophenone oximates) 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 the first compound prepared by this procedure was triphenylantimony diacetate [5]. Later the reaction was used for preparing analogous derivatives of antimony of the general formula Ar_3SbX_2, where X is an electronegative group [1-3, 6], but the preparation of triarylantimony dioximates has not yet been reported.

According to X-ray diffraction data, the antimony atom in compound **Ia** has a usual trigonal bipyramidal coordination typical for five-coordinate antimony compounds (Fig. 1). The O^2 and C^7 atoms are located in the axial position, the bond angle $O^2Sb^1C^7$ is 174.9(2)°, the angles in the equatorial plane vary from 118.8(2)° to 120.2(2)°, and their sum is 348.2(3)°. The angles between the equatorial and axial substituents vary from 81.2(2)° to 95.4(2)°. The acute angles are formed with the participation of the oxygen atom (Table 2). The equatorial Sb–C bonds are equal within the experimental error, and they are slightly smaller than the axial Sb–C^7 bond. The Sb–O distance [2.146(4) Å] is close to Sb–C bond lengths. They are considerably smaller than in the pentavalent antimony compound $Ph_4SbON{=}C(NO)Me$ which is structurally similar to the obtained oximates. The respective

1070-3632/02/7206-0893 $27.00

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

distances in $Ph_4SbON=C(NO)Me$ are 2.266 and 2.235 Å [7].

The geometry of the $Ph_2C=NO$ substituent is usual. The planar trigonal coordination of C^{25} and the N^2–C^{25} distance [1.281(7) Å] correspond to the proposed structure.

The crystal packing of molecules **IIa** is determined by multiple C–H···π contacts and dispersion interactions between parallel benzene rings (Fig. 2).

To reveal peculiar features of the crystal structure of **IIa**, we performed an X-ray diffraction study of benzophenone oxime (**III**). It was shown that two symmetrically independent molecules of compound **III** form a pseudosymmetrical dimer by means of N···HO hydrogen bonds (Fig.3). The $O^1\cdots N^2$ and $O^2\cdots N^1$ distances are 2.841 and 2.747 Å, and the $O^1H^1N^2$ and $O^2H^2N^1$ angles are 140 and 138°, respectively. The planar six-membered ring $O^1H^1N^2O^2H^2N^1$ is formed by hydrogen bonds. Hydrogen bonds produce no considerable distortion of bond angles in molecule **III** (Table 4) but considerably increase O–N distances [1.427(6) and 1.432(7) Å] as compared to organoantimony benzophenone oxime **IIa** [1.387(6) Å].

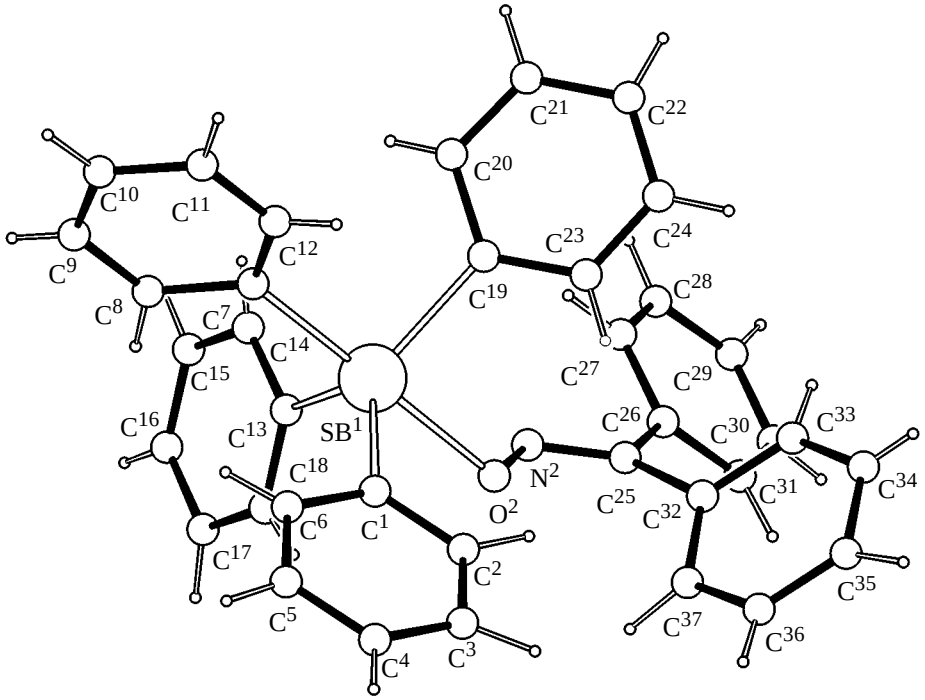

Fig. 1. Spatial arrangement of complex **IIa** in crystal.

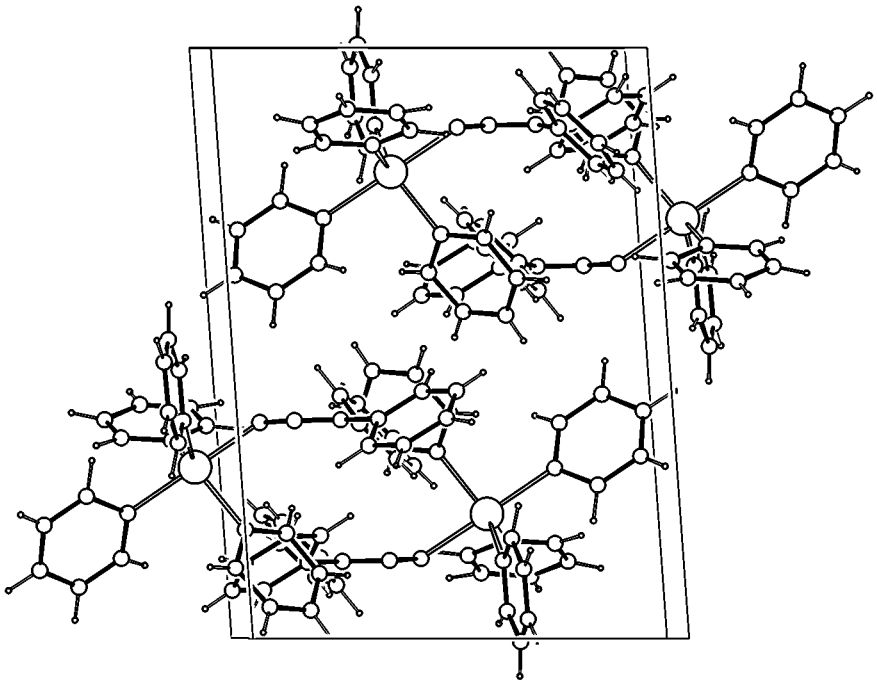

Fig. 2. Crystal packing of molecules **IIa**.

Table 2. Bond lengths (*d*, Å) and bond angles (ω, deg) in structure **IIa**

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)		

EXPERIMENTAL

The IR spectra were recorded on a Hitachi-215 spectrometer for suspensions in Vaseline oil.

Single-crystal X-ray diffraction analysis of tetraphenylantimony benzophenone oximate (IIa). The intensities of 5575 reflections, of which 3138 had $I > 3\sigma$, were measured on an Enraf–Nonius CAD-4 automated four-circle *K*-diffractometer at 20°C (MoK_α radiation, λMoKα 0.71073 Å, graphite monochromator, ω/2θ scanning, $\theta < 29.96°$). Crystals of compound **IIa**, $C_{37}H_{30}NOSb$, are monoclinic; at 20°C, *a* 11.565(1), *b* 16.545(8), *c* 15.713(4) 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 was not considered (μMo 9.52 cm^{-1}). The structure was solved by the direct method by means of the SIR program [8] and refined first isotropically and then anisotropically. Hydrogen atoms were located by difference synthesis and refined isotropically on the final stage. The final divergence factors were *R* 0.038 and R_W 0.043, on 2905 unique reflections with $F^2 > 3\sigma$. All the calculations were performed using the MolEN program package [9] on a DEC Alpha Station computer. Analysis of molecular contacts and molecular drawings were made by means of the WINPL98 program [10].

Single-crystal X-ray diffraction analysis of benzophenone oxime (III). The intensities of 1031 reflections, 938 of which had $I > 3\sigma$, were measured on an Enraf–Nonius CAD-4 automated four-circle *K*-diffractometer at 20°C (MoK_α radiation, λMoK_α 0.71073 Å, graphite monochromator). Crystals of compound **III**, $C_{26}H_{22}N_2$, are monoclinic; at 20°C, *a* 9.466(2), *b* 8.369(2), *c* 26.710(5) Å, β 92.89(3)°, *V* 2113.3(8) Å, *Z* 4, d_{calc} 1.24 g/cm^3, space

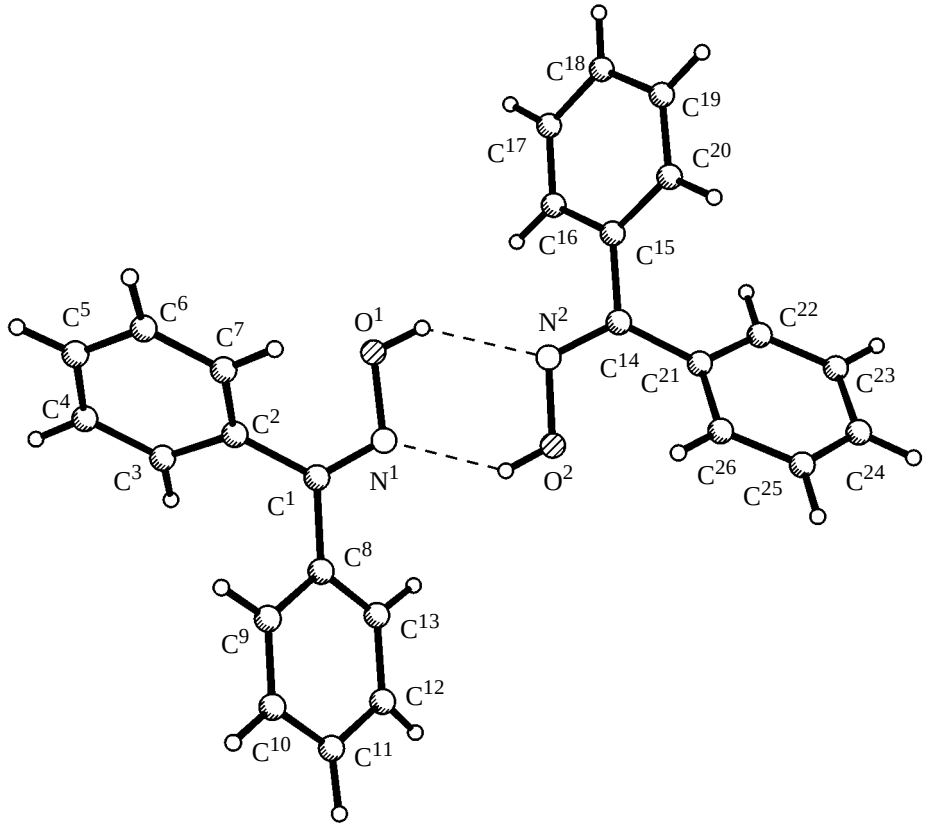

Fig. 3. Spatial arrangement of compound **III** in crystal.

group $P2_1/n$. The structure was solved by the heavy-atom method and refined anisotropically (isotropically for hydrogen atoms) to R 0.0483 and R_W 0.1345. All the calculations were carried out using the SHELXL-97 program package [11].

Tetraarylantimony oximates were synthesized by the following typical procedures.

Table 3. Bond lengths (d, Å) and bond angles (ω, deg) in structure **III**

Bond	d	Bond	d
O^1–N^1	1.432(7)	O^2–N^2	1.427(6)
N^1–C^1	1.251(8)	N^2–C^{14}	1.286(8)
C^1–C^2	1.469(10)	C^{14}–C^{21}	1.471(9)
C^1–C^8	1.479(9)	C^{14}–C^{15}	1.472(9)
Angle	**ω**	**Angle**	**ω**
$C^1N^1O^1$	113.5(6)	$C^{14}N^2O^2$	114.6(6)
$N^1C^1C^2$	124.2(6)	$N^2C^{14}C^{21}$	125.1(6)
$N^1C^1C^8$	116.8(6)	$N^2C^{14}C^{15}$	113.9(7)
$C^2C^1C^8$	119.0(7)	$C^{21}C^{14}C^{15}$	121.0(6)

Tetraphenylantimony benzophenone oximate (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 then removed, and the residue was crystallized from heptane–benzene, 3 : 1. Yield 1.11 g (90%), mp 168°C.

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

Triphenylantimony bis(benzophenone oximate). 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 resulting mixture left to stand for 12 h at 20°C. Colorless crystals formed and were filtered off and dried. Yield 1.52 g (72%), mp 104°C.

Table 4. Atomic coordinates in structure **IIa**, equivalent isotropic thermal 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)

Table 5. Atomic coordinates ($\times 10^4$) and equivalent thermal parameters B ($Å \times 10^3$) in structure **III**

Atom	*x*	*y*	*z*	*B*
O^1	3122(6)	2067(7)	4999(2)	92(2)
N^1	4610(6)	2320(7)	4963(2)	65(2)
C^1	5225(8)	2734(9)	5368(3)	55(2)
C^2	4501(8)	3057(10)	5831(3)	59(2)
C^3	4905(9)	2272(10)	6283(3)	75(2)
C^4	4241(12)	2608(13)	6716(3)	95(3)
C^5	3186(12)	3704(16)	6706(5)	102(4)
C^6	2786(10)	4491(12)	6280(5)	97(3)
C^7	3445(9)	4144(11)	5850(3)	74(2)
C^8	6775(8)	2955(9)	5366(3)	54(2)
C^9	7472(8)	4075(10)	5672(3)	64(2)
C^{10}	8871(10)	4307(10)	5667(3)	75(2)
C^{11}	9666(9)	3401(12)	5354(4)	79(3)
C^{12}	9018(10)	2276(11)	5048(3)	80(3)
C^{13}	7581(9)	2055(10)	5058(3)	71(2)
O^2	4705(5)	1853(7)	3947(2)	90(2)
N^2	3203(5)	1710(7)	3943(2)	61(2)
C^{14}	2590(7)	1622(7)	3503(3)	50(2)
C^{15}	1054(8)	1350(8)	3505(2)	50(2)
C^{16}	480(8)	263(10)	3835(3)	65(2)
C^{17}	–943(10)	44(10)	3833(3)	75(2)
C^{18}	–1849(9)	891(12)	3508(4)	83(3)
C^{19}	–1283(9)	1932(11)	3182(3)	74(2)
C^{20}	137(8)	2188(9)	3171(3)	65(2)
C^{21}	3304(8)	1791(8)	3029(2)	50(2)
C^{22}	2792(8)	928(9)	2615(3)	63(2)
C^{23}	3372(9)	1066(9)	2159(3)	67(2)
C^{24}	4481(9)	2062(11)	2099(3)	70(2)
C^{25}	5013(7)	2941(10)	2498(4)	70(2)
C^{26}	4444(7)	2813(9)	2967(3)	58(2)

The X-ray analysis of tetraphenylantimony benzophenone oximate was carried out at the department of X-ray investigations, Spectral Analytical Center for Collective Use, Russian Fundation for Basic Research (project no. 96-03-40 006).

ACKNOWLEDGMENTS

The authors express their gratitude to V.K. Bel'skii for X-ray diffraction analysis of benzophenone oxime.

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