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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XXVI *. THE STRUCTURE OF *O*-TRIMETHYLSTANNYL-*N*-PHENYL-*N*-BENZOYLHYDROXYLAMINE

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Summary

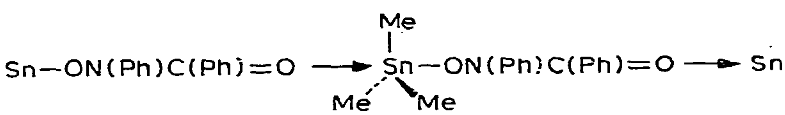
The structure of the title compound has been determined by Patterson and Fourier methods from four-circle diffractometer data to a final "*R*"-value of 0.0353 using 2792 independent non-zero reflections. Crystals are monoclinic, space group $P2_1$ with $a = 10.778(4)$, $b = 17.083(8)$, $c = 10.399(4)$ Å, $\beta = 120.79(7)°$, $Z = 2$. The asymmetric unit of $Me_3Sn[ON(Ph)COPh]$ consists of two crystallographically independent, non-interacting molecules, both of which possess distorted "local" trigonal-bipyramidal *cis*-$[SnC_3O_2]$ geometry. In one molecule, the axial Sn—C bond distance is significantly longer (2.22(2) Å) than the two equatorial Sn—C distances (mean 2.04(2) Å), whilst in the other converse pertains, the equatorial Sn—C distances being marginally longer (mean 2.18(1) Å) than the axial Sn—C distance (2.16(1) Å). In both molecules, the axial coordinate Sn—O bond is longer than the equatorial Sn—O bond (2.263(6) Å vs. 2.152(6) Å; 2.392(6) Å vs. 2.064(6) Å.

Introduction

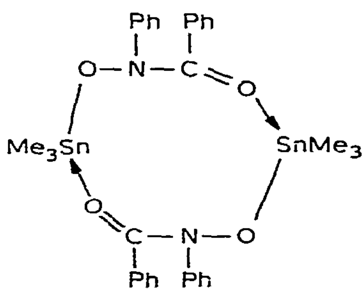
Tin-119 Mössbauer recoil-free fraction temperature coefficient-effective vibrating mass studies [1] appear to support earlier spectroscopic evidence [2] that $Me_3Sn[ON(Ph)COPh]$ is associated in the solid state. Although the triphenyltin homologue also exhibited mass spectral fragments in excess of the monomer parent ion [2], we subsequently demonstrated that crystals consisted of non-interacting monomeric units with a distorted trigonal bipyramidal *cis*-$[Sn_3O_2]$ geometry at tin [3]. The structural ambiguities posed by the spectro-

* For part XXV see ref. 13.

scopic properties of the title compound have led us previously [2] to propose several possible structures containing either five- or six-coordinate tin (I—V). A simple intermolecularly coordinated one-dimensional polymeric structure such as I may be excluded since only one infrared active Sn—C stretching frequency would be expected, contrary to observation [2]. Of the three dimeric species (II, IV and V), dimerisation via stannoxane ring formation as in structure IV, which is very common in organotin chemistry, would appear most likely. In order to resolve these structural difficulties, we have determined the crystal structure using X-ray diffraction, which study is reported here.



(I)



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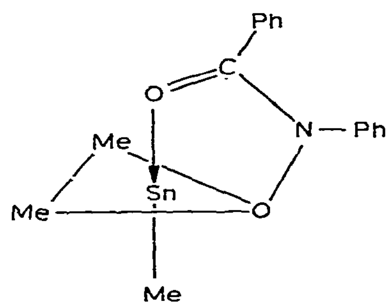
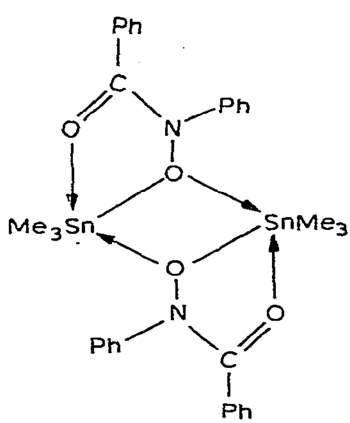
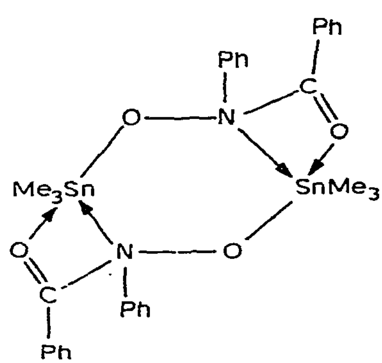


(III)



(IV)



(V)

Experimental

The title compound was prepared and purified by initial recrystallisation from cyclohexane and subsequent slow evaporation of a benzene/n-pentane solution. Analysis: Found: C, 51.65; H, 5.53; N, 3.70. $C_{16}H_{19}NO_2Sn$ calcd.: C, 51.10, H, 5.10, N, 3.72%. M.p. 120—123°C (lit. [2] m.p. 120—122°C).

Crystal data

$C_{16}H_{19}NO_2Sn$, M = 376.04, monoclinic, a = 10.778(4), b = 17.083(8), c = 10.399(4) Å, β = 120.79(7)°, Z = 2, F(000) = 752. Space group $P2_1$ from systematic absences: $0k0$ for k odd. Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 15.64 cm^{-1}.

A crystal of dimensions 0.5 × 0.25 × 0.3 mm was loaded in a Lindemann capillary tube, and used for initial photography and subsequent data collection. The space group was determined from oscillation and zero- and first-layer Weissenberg photographs. The intensities of 3026 independent non-zero reflections were measured by use of a Hilger and Watts four-circle automatic diffractometer. Reflections with $I < 3\sigma(I)$ were considered non-observed, reducing the number of reflections used to 2792. Accurate unit cell dimensions were obtained by least-squares refinement of data for ca. 20 reflections. Lorentz and polarisation corrections were applied, but none were made for absorption effects, due to the low μ value.

Structure determination and refinement

A Patterson synthesis was used to locate the positional parameters of the two tin atoms in the asymmetric unit, which were then used to phase the initial structure-factor calculation. After two cycles of full matrix least-squares isotropic refinement, in which the y-ordinate of the position of one tin was fixed (due to the presence of a screw axis along y in $P2_1$, the y-ordinate of one atom, usually the heavy atom, is fixed to define the origin of the unit cell), a Fourier synthesis yielded the positions of nine light atoms. After two further cycles of refinement, six of these atoms were rejected because of their high thermal parameters, and, following a Fourier synthesis, the positions of nine new light atoms were located. Two subsequent cycles of isotropic refinement and a Fourier synthesis yielded three light atoms. At this point, the tin atoms were allowed to vary anisotropically, and two cycles of mixed least-squares refinement afforded the positions of a further eighteen light atoms. Inspection of the atomic thermal parameters after two more cycles of mixed refinement, resulted in the rejection of two of the light atoms, however, two of outstanding five carbon atoms were found following a subsequent Fourier synthesis. The positions of the three remaining unlocated carbon atoms, all directly bonded to Sn(1), were found after two more cycles of mixed refinement and a Fourier synthesis.

The positional parameters of atoms in the respective non-interacting molecules were further refined in separate blocks. After six cycles of mixed, blocked refinement, the positions of N(1) and C(10) were interchanged, which, after four further cycles of mixed refinement, was found to have improved their thermal parameters. Anisotropy was not conferred on all the atoms, and three cycles of blocked refinement produced a convergence at an "R" value of 0.0379.

At this point, a weighting scheme, based on a Chebychev series in $T(n)(X)$ to five terms was applied to each reflection:

$$w = \frac{1}{A(0)\ T(0)\ (X) + A(1)\ T1)\ (X)\ ...\ A(n-1)\ T(n-1)\ (X)}$$

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATES IN $Me_3Sn[ON(Ph)CO \cdot Ph]$ (estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c
Molecule 1			
Sn(1)	0.33326(6)	−0.0524	0.14252(6)
O(1)	0.2029(9)	−0.0655(3)	−0.0966(7)
O(2)	0.2787(7)	−0.1805(3)	0.0877(6)
N(1)	0.1675(7)	−0.1382(4)	−0.1505(7)
C(1)	0.2920(30	0.0736(9)	0.0860(20)
C(2)	0.2690(40)	−0.0710(20)	0.2950(20)
C(3)	0.5400(10)	−0.0640(2)	0.1930(30)
C(4)	0.1865(8)	−0.2792(5)	−0.0981(9)
C(5)	0.1510(10)	−0.3296(6)	−0.0160(10)
C(6)	0.1350(10)	−0.4097(6)	−0.0470(10)
C(7)	0.1590(10)	−0.4382(6)	−0.1560(10)
C(8)	0.1940(10)	−0.3905(6)	−0.2370(10)
C(9)	0.2113(9)	−0.3087(5)	−0.2050(10)
C(10)	0.2080(8)	−0.1975(5)	−0.0554(9)
C(11)	0.7770(80)	−0.1433(4)	−0.3100(9)
C(12)	−0.0518(8)	−0.1812(5)	−0.3775(9)
C(13)	−0.1349(9)	−0.1834(6)	−0.5333(9)
C(14)	−0.0920(10)	−0.1442(7)	−0.6190(10)
C(15)	0.0360(10)	−0.1037(6)	−0.5500(10)
C(16)	0.1232(9)	−0.1020(5)	−0.3950(10)
Molecule 2			
Sn(2)	0.65257(5)	0.82490(4)	0.84271(6)
O(3)	0.6823(6)	0.7624(4)	0.6906(7)
O(4)	0.4279(6)	0.7681(4)	0.6589(7)
N(2)	0.5700(6)	0.7169(4)	0.5854(7)
C(17)	0.8800(10)	0.8515(8)	0.9560(10)
C(18)	0.5400(10)	0.9362(6)	0.7600(20)
C(19)	0.6110(20)	0.7600(10)	0.9960(20)
C(20)	0.6076(7)	0.6774(4)	0.4875(8)
C(21)	0.7385(7)	0.6395(6)	0.5511(3)
C(22)	0.7790(10)	0.6022(5)	0.4580(10)
C(23)	0.6850(10)	0.6040(5)	0.3020(10)
C(24)	0.5540(9)	0.6444(7)	0.2421(9)
C(25)	0.5142(8)	0.6810(5)	0.3328(8)
C(26)	0.4442(8)	0.7201(5)	0.5778(9)
C(27)	0.3222(8)	0.6662(5)	0.4799(9)
C(28)	0.3450(10)	0.5875(5)	0.4700(10)
C(29)	0.220(10)	0.5378(6)	0.3880(10)
C(30)	0.0860(10)	0.5700(8)	0.3190(10)
C(31)	0.0660(10)	0.6481(8)	0.3300(10)
C(32)	0.1831(9)	0.6979(6)	0.4100(10)

where $A(n)$ = coefficient of the n^{th} term and $X = F_0/F_0(\max)$.

The coefficients $A(0) - A(4)$, calculated by least-squares methods to minimise $\Sigma(F_0 - F_c)$ [4] over all reflections, are 261.7, 448.4, 293.2, 137,7 and 36.9 respectively. A final "R" value of 0.0353 was obtained after a further four cycles of blocked, anisotropic least-squares refinement.

All calculations were made using the CRYSTALS suite of programs [4] and the scattering factors used were those for neutral atoms [5].

Final fractional atomic coordinates and corresponding thermal parameters

TABLE 2

FINAL ANISOTROPIC THERMAL PARAMETERS IN $Me_3Sn[ON(Ph) \cdot CO \cdot Ph]$ (estimated standard deviations in parentheses) [a]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn(1)	6.40(3)	7.13(4)	5.35(3)	−1.87(3)	2.82(2)	−1.73(3)
O(1)	11.0(2)	3.8(3)	5.6(3)	−0.1(3)	0.9(4)	−1.2(3)
O(2)	9.0(4)	4.5(3)	4.5(3)	−0.2(2)	1.9(3)	−0.2(3)
N(1)	6.3(4)	3.9(3)	5.1(4)	−0.8(3)	1.3(3)	−0.2(3)
C(1)	2.9(3)	5.3(7)	1.2(1)	−1.6(8)	5.0(10)	1.0(10)
C(2)	4.8(4)	2.6(3)	1.8(2)	−1.4(2)	2.5(3)	−2.3(3)
C(3)	5.8(7)	2.8(3)	2.5(2)	−1.7(2)	6.0(10)	3.0(10)
C(4)	4.2(4)	3.8(4)	4.1(4)	−0.2(3)	1.2(3)	−0.2(3)
C(5)	6.0(5)	5.7(5)	5.0(4)	1.2(4)	2.4(4)	0.2(4)
C(6)	8.3(7)	4.5(6)	7.7(6)	1.1(5)	3.2(5)	−0.7(5)
C(7)	8.8(8)	3.8(5)	8.7(8)	−0.6(5)	3.2(7)	−0.5(4)
C(8)	8.0(6)	6.0(6)	6.0(5)	−0.4(4)	3.5(5)	1.3(4)
C(9)	5.3(4)	5.1(5)	5.7(4)	−0.5(4)	2.1(4)	0.9(4)
C(10)	4.4(4)	4.9(4)	5.04(4)	0.2(3)	1.6(3)	0.0(3)
C(11)	5.2(4)	3.4(3)	5.2(4)	0.4(3)	1.7(3)	0.5(3)
C(12)	4.9(4)	5.5(3)	5.4(4)	0.2(4)	1.6(3)	−1.0(4)
C(13)	6.1(4)	6.3(5)	5.5(4)	0.3(4)	1.1(4)	−0.6(4)
C(14)	7.7(6)	7.2(7)	5.6(5)	1.7(5)	2.0(5)	0.1(5)
C(15)	7.2(6)	7.1(6)	7.8(6)	1.2(5)	4.0(5)	0.0(5)
C(16)	4.8(4)	4.6(5)	7.0(5)	0.7(4)	2.3(4)	−0.1(3)
Sn(2)	5.27(3)	6.65(3)	6.51(3)	−2.11(3)	3.16(2)	−1.22(3)
O(3)	5.0(3)	7.8(4)	7.0(4)	−3.5(3)	3.2(3)	−2.3(3)
O(4)	5.6(3)	8.0(4)	7.3(4)	3.1(3)	4.1(3)	−2.0(3)
N(2)	4.4(3)	6.0(4)	4.9(3)	−1.3(3)	1.9(3)	−0.7(3)
C(17)	4.9(5)	11.5(9)	8.9(7)	−4.0(7)	3.0(5)	−1.0(5)
C(18)	7.9(7)	5.3(6)	18.0(10)	0.8(7)	4.6(8)	1.3(5)
C(19)	14.0(10)	15.0(10)	8.0(8)	−1.0(8)	6.4(9)	−6.0(10)
C(20)	4.6(4)	4.0(4)	4.7(4)	−0.4(3)	2.8(3)	−0.6(3)
C(21)	4.9(3)	4.9(4)	5.5(4)	0.6(4)	2.6(3)	−0.2(4)
C(22)	6.2(5)	6.0(5)	7.5(5)	0.1(4)	3.7(4)	0.2(4)
C(23)	7.7(6)	6.1(5)	6.5(5)	−0.6(4)	4.5(5)	−0.7(4)
C(24)	7.0(5)	6.4(6)	5.0(4)	−0.1(4)	3.3(4)	−1.7(5)
C(25)	4.9(4)	6.3(5)	3.9(3)	0.7(3)	2.1(3)	0.1(4)
C(26)	5.1(4)	5.2(4)	5.4(4)	−0.4(3)	3.1(4)	−0.7(3)
C(27)	4.0(4)	6.2(5)	4.4(4)	−0.1(3)	2.3(3)	−1.0(3)
C(28)	7.4(5)	4.8(5)	6.9(5)	−0.6(4)	4.2(5)	−1.4(4)
C(29)	8.2(7)	6.2(6)	8.7(7)	−1.6(5)	4.6(6)	−1.7(5)
C(30)	7.6(7)	9.6(8)	6.6(6)	−2.1(6)	3.1(5)	−4.5(6)
C(31)	5.3(5)	10.0(10)	7.6(6)	−1.0(5)	2.5(4)	−2.7(5)
C(32)	5.1(4)	7.3(6)	6.3(5)	−0.6(5)	2.7(4)	−1.1(4)

[a] U_{ij} are of the form $10^2 \exp - 2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2\,hkU_{12}a^*b^* + 2\,klU_{23}b^*c^* + 2\,hlU_{13}a^*c^*)$.

are listed in Tables 1 and 2 respectively, and the intramolecular bond lengths and angles in Table 3. The molecular geometry and atomic labelling are shown in Fig. 1, and the arrangement of molecules in the unit cell, projected onto the *ab* plane, shown in Fig. 2.

Discussion

The asymmetric unit of $Me_3Sn[ON(Ph)COPh]$ consists of two, independent, non-interacting molecules, in which the chelating ligand has forced a *cis*-

(Continued on p. 207)

TABLE 3

FINAL INTERATOMIC BOND LENGTHS (Å) AND ANGLES (°) IN $Me_3Sn[ON(Ph)CO \cdot Ph]$
(standard deviations in parentheses)

Molecule 1

(a) Lengths

Sn(1)—C(1)	2.220(20)	C(4)—C(5)	1.360(10)
Sn(1)—C(2)	2.060(20)	C(5)—C(6)	1.390(10)
Sn(1)—C(3)	2.020(10)	C(6)—C(7)	1.380(10)
Sn(1)—O(1)	2.152(6)	C(7)—C(8)	1.371(20)
Sn(1)—O(2)	2.263(6)	C(8)—C(9)	1.390(10)
		C(9)—C(4)	1.400(10)
O(1)—N(1)	1.336(9)		
N(1)—C(4)	1.320(10)	C(11)—C(12)	1.400(10)
N(1)—C(10)	1.430(10)	C(12)—C(13)	1.400(10)
C(10)—C(11)	1.450(10)	C(13)—C(14)	1.370(20)
C(10)—O(2)	1.310(10)	C(14)—C(15)	1.360(20)
		C(15)—C(16)	1.430(10)
		C(16)—C(11)	1.360(10)

(b) Angles

C(1)—Sn(1)—C(2)	104.0(10)	Sn(1)—O(1)—N(1)	117.4(5)
C(1)—Sn(1)—C(3)	102.0(10)	O(1)—N(1)—C(4)	114.9(7)
C(1)—Sn(1)—C(1)	82.6(5)	O(1)—N(1)—C(10)	118.9(6)
C(1)—Sn(1)—O(2)	151.9(5)	C(4)—N(1)—C(10)	126.1(7)
C(2)—Sn(1)—C(3)	123.0(10)	N(1)—C(10)—O(2)	117.2(7)
C(2)—Sn(1)—O(1)	126.7(8)	N(1)—C(10)—C(11)	124.6(7)
C(2)—Sn(1)—O(2)	84.3(7)	C(11)—C(10)—O(2)	118.1(7)
C(3)—Sn(1)—O(1)	105.7(7)	C(10)—O(2)—Sn(1)	115.2(5)
C(3)—Sn(1)—O(2)	94.4(7)		
O(1)—Sn(1)—O(2)	71.1(2)		
N(1)—C(4)—C(5)	122.2(8)	C(10)—C(11)—C(12)	117.1(8)
N(1)—C(4)—C(9)	116.8(7)	C(10)—C(11)—C(16)	122.6(8)
C(5)—C(4)—C(9)	120.8(8)	C(12)—C(11)—C(16)	120.0(8)
C(4)—C(5)—C(6)	119.4(8)	C(11)—C(12)—C(13)	120.0(10)
C(5)—C(6)—C(7)	120.8(8)	C(12)—C(13)—C(14)	119.0(10)
C(6)—C(7)—C(8)	119.0(9)	C(13)—C(14)—C(15)	121.0(10)
C(7)—C(8)—C(9)	121.6(9)	C(14)—C(15)—C(16)	119.0(10)
C(8)—C(9)—C(4)	118.2(8)	C(15)—C(16)—C(11)	119.0(10)

Molecule 2

(a) Lengths

Sn(2)—C(17)	2.155(9)	C(20)—C(21)	1.380(10)
Sn(2)—C(18)	2.180(10)	C(21)—C(22)	1.410(10)
Sn(2)—C(19)	2.170(10)	C(22)—C(23)	1.400(10)
Sn(2)—O(3)	2.064(6)	C(23)—C(24)	1.400(10)
Sn(2)—O(4)	2.392(6)	C(24)—C(25)	1.370(10)
		C(25)—C(20)	1.400(10)
O(3)—N(2)	1.383(8)		
N(2)—C(20)	1.441(9)	C(27)—C(28)	1.380(10)
N(2)—C(26)	1.320(10)	C(28)—C(29)	1.430(10)
C(26)—O(4)	1.252(9)	C(29)—C(30)	1.370(20)
C(26)—C(27)	1.500(10)	C(30)—C(31)	1.360(20)
		C(31)—C(32)	1.390(10)
		C(32)—C(27)	1.400(10)

(b) Angles

C(17)—Sn(2)—C(18)	106.2(5)	Sn(2)—O(3)—N(2)	118.7(4)
C(27)—Sn(2)—C(19)	108.1(6)	O(3)—N(2)—C(20)	112.0(5)
C(17)—Sn(2)—O(3)	87.1(3)	O(3)—N(2)—C(26)	118.7(6)
C(17)—Sn(2)—O(4)	157.8(3)	C(20)—N(2)—C(26)	129.0(6)
C(18)—Sn(2)—C(19)	117.0(7)	N(2)—C(26)—O(4)	118.8(7)
C(18)—Sn(2)—O(3)	114.9(5)	N(2)—C(26)—C(27)	122.2(7)
C(18)—Sn(2)—O(4)	84.7(4)	C(27)—C(26)—O(4)	118.9(7)
C(19)—Sn(2)—O(3)	117.9(5)	C(26)—O(4)—Sn(1)	111.7(5)

TABLE 3 (continued)

C(19)—Sn(2)—O(4)	82.7(4)		
O(3)—Sn(2)—O(4)	70.7(2)		
N(2)—C(20)—C(21)	118.1(6)	C(26)—C(27)—C(28)	121.6(9)
N(2)—C(20)—C(25)	119.7(6)	C(26)—C(27)—C(32)	116.7(8)
C(21)—C(20)—C(25)	122.1(7)	C(28)—C(27)—C(32)	121.4(8)
C(20)—C(21)—C(22)	119.2(7)	C(27)—C(28)—C(29)	119.0(10)
C(21)—C(22)—C(23)	119.3(8)	C(28)—C(29)—C(30)	119.0(10)
C(22)—C(23)—C(24)	119.5(8)	C(29)—C(30)—C(31)	121.1(9)
C(23)—C(24)—C(25)	121.2(7)	C(30)—C(31)—C(32)	121.0(10)
C(24)—C(25)—C(20)	118.6(7)	C(31)—C(32)—C(27)	118.0(10)

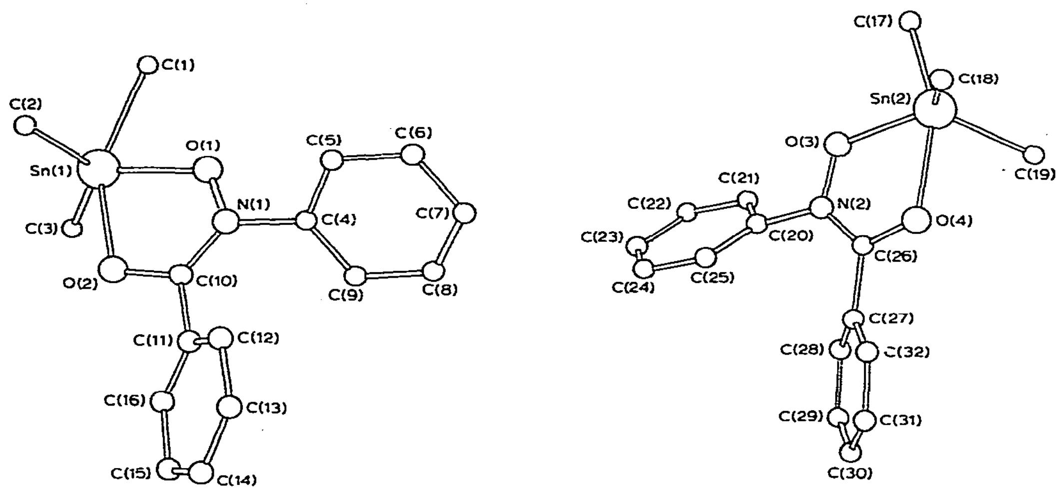


Fig. 1. Views of the two crystallographically independent molecules of $Me_3Sn[ON(Ph)COPh]$ showing the atomic numbering; left molecule 1, right molecule 2.

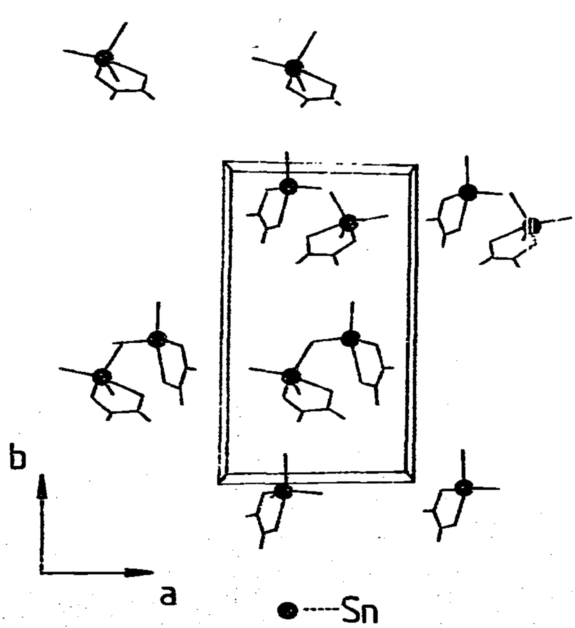


Fig. 2. Projection of the unit cell of $Me_3Sn[ON(Ph)COPh]$ onto the *ab* plane.

TABLE 4

COMPARISON OF BOND PARAMETERS OF $ME_3Sn[ON(Ph)CO \cdot Ph]$ AND RELATED COMPOUNDS

Compound	C_{ax}—Sn—O_{ax} (deg)	r(Sn—C) (Å)	r(Sn—O) (Å)	r(Sn—O) (Å)	O—Sn—O (deg) [d]	Ref.
$Me_3Sn[ON(Ph)CO \cdot Ph]$	151.9(5) 157.8(3)	ax : 2.220(10) [a] eq : 2.110(10) [a]	2.108(6) [a]	2.328(6) [a]	71.1(2) 70.7(2)	This work
$Ph_3Sn[ON(Ph)CO \cdot Ph]$	157.2(2)	ax : 2.176(9) eq : 2.136(8)	2.091(5)	2.308(4)	71.3(2)	3
$Me_2Sn[ON(Me)CO \cdot Me]_2$ [b]		2.105(8) 2.113(6)	2.107(4) 2.126(4)	2.374(5) 2.384(4)	71.6(1) 71.1(2)	7
$Cl_2Sn[ON(Ph)CO \cdot Ph]_2$ [c]		2.05(2) 2.04(2)	2.10(1) 2.11(2)		76.3(5) 76.6(6)	8
$Me_2Sn[ON(H)CO \cdot Me]_2$ [c]		2.144(6)	2.106(4)	2.228(4)	88.3(2)	12
$Me_2Sn[ON(H)CO \cdot Me]_2 \cdot H_2O$ [b,c]		2.16(2) 2.17(2) 2.16(2) 2.14(2)	2.15(1) 2.15(1) 2.17(1) 2.16(1)	2.35(1) 2.49(1) 2.36(2) 2.43(1)	72.1(4) 70.7(4) 71.7(5) 61.5(4)	12

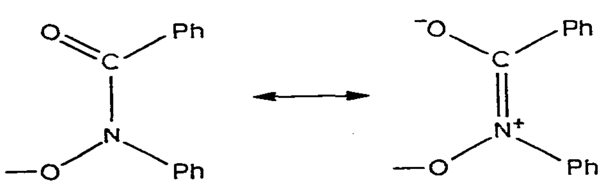
[a] Mean value of bonds in both molecules of the asymmetric unit. [b] Distorted *trans*-$[SnX_2Y_4]$ octahedral geometry at tin. [c] Distorted *cis*-$[SnX_2Y_4]$ octahedral geometry at tin. [d] Where several O—Sn—O angles are present, data refers to the angle of 'bite' of the (substituted) hydroxylamine ligand. [e] The asymmetric unit consists of two crystallographically independent molecules.

R_3SnXY trigonal bipyramidal geometry at the tin. The structure is, however, heavily distorted from that of a regular trigonal bipyramid, so that the C_{ax}—Sn—O_{ax} angle is closed from 180° to 157.8(3)° or 151.9(5)°, and the three equatorial bond angles range from 105.7(7)° to 126.7(8)° in the two molecules, rather than the ideal value of 120°. The overall geometry of each of the two independent molecules is, however, very similar; moreover, correlation of bond parameters with other organotin hydroxylamine derivatives is, not surprisingly, good (Table 4).

The bond lengths of atoms bonded directly to tin require careful examination. It has been noted [11] that in five-coordinate trigonal bipyramidal complexes, axial bond are longer than the corresponding equatorial bonds e.g. $Ph_3Sn[ON(Ph)COPh]$: Sn—C_{eq} = 2.136(8) Å; Sn—C_{ax} = 2.176(9) Å [12]. The relative lengths of the equatorial and axial Sn—C bonds in the title compound, are different in each of the two crystallographically independent molecules, and can be related to the length (and hence strength) of the Sn—O coordinate bond. Thus in molecule 1, Sn—C_{ax} > Sn—C_{eq} (2.220(20) and 2.060(20), 2.020(10) Å respectively) as expected, while in molecule 2 the converse is true i.e. Sn—C_{ax} = 2.155(9) Å, Sn—C_{eq} = 2.180(10), 2.170(10) Å.

Two distinct Sn—O bonds are observed in both molecules, and, as expected, the covalent bond (2.152(6) and 2.064(6) Å) is shorter than the corresponding coordinate bond length (2.263(6) and 2.392(6) Å). The very short Sn—O coordinate bond in molecule 1 (2.263(6) Å) can be thought of as increasing the electron density at the tin, which is removed by a lengthening of the Sn—C_{ax} bond. In molecule 2, the near equivalence of the Sn—C bond lengths (2.155(9), 2.180(10), 2.170(10) Å) is consistent with a much longer Sn—O coordinate bond (2.392(6) Å), i.e. a lengthening of the Sn—O_{ax} bond results in a shortening of the Sn—C_{ax} bond and vice versa.

The two SnONCO rings are essentially planar, deviations from the mean plane through the five atoms lying in the ranges 0.014—0.035 Å (molecule 1) and 0.023—0.074 Å (molecule 2). Inspection of the bond distances within the hydroxylamine residue reveals significant contribution of the canonical resonance (VII) to the overall electronic distribution, similar to that noted for other hydroxylamine derivatives [3,7,8].



(VI) (VII)

Structural parameters for the unsubstituted hydroxylamine are not available, but those of the similar *N*-acetylhydroxylamine hemihydrate, HO · NH · COMe · $\frac{1}{2}$ H_2O [9] are compared with $Me_3Sn[ON(Ph) \cdot CO \cdot Ph]$ in Table 5. The endocyclic C—N bond lengths in both free (1.333(6) Å) and bonded ligand (1.320(10) Å) lie between that of a normal C—N single bond, as exemplified by the exocyclic C—N bond (1.43(10), 1.441(9) Å) and a C=N double-bond (1.27—1.29 Å [10]), indicating a significant amount of double bond character

TABLE 5

COMPARISON OF INTRALIGAND BOND DISTANCES IN (A) HO · NH · COMe · $\frac{1}{2}$ H_2O and (B) $Me_3Sn[ON(Ph)COPh]$

	(A)	(B1)	(B2)
N—O	1.400(5)	1.336(9)	1.383(8)
C(:O)—N	1.333(6)	1.320(10)	1.320(10)
C=O	1.245(6)	1.310(10)	1.252(9)
C—R	1.505(6) [a]	1.450(10) [b]	1.500(10) [b]
C—NR		1.430(10)	1.441(9)

[a] R = Me, [b] R = Ph.

TABLE 6

SHORTEST INTERMOLECULAR CONTACT DISTANCES (Å) IN $Me_3Sn[ON(Ph) \cdot CO \cdot Ph]$

Sn(1)—O(3)	5.67(4), 5.88(4), 6.92(3)
Sn(1)—O(4)	5.77(4), 5.97(4), 6.46(3)
Sn(1)—N(2)	5.20(4), 5.62(4)
Sn(2)—O(1)	5.53(5), 5.90(5), 7.11(3)
Sn(2)—O(2)	5.77(4), 5.85(4), 6.76(3)
Sn(2)—N(1)	5.23(4), 5.62(4)

in this bond. The C=O double-bond is lengthened from 1.245(6) Å in the free ligand to 1.310(10) and 1.252(9) Å, all of which are longer than analogous distances in esters, aldehydes and ketones (1.23 Å [11]), following the trend in known zwitterionic compounds such as DL-serine [11]), where the C=O distance is 1.26 Å.

No evidence for any intermolecular interaction can be found, the shortest non C—C or Sn—C intermolecular interaction being 5.20(4) Å (Sn(1)—N(2)). A more extensive list of nearest intermolecular contacts is given in Table 6. Thus, this compound is cautionary example of how the most careful interpretation of spectroscopic data may still lead to an erroneous structural conclusion.

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