Structural Studies in Main-group Chemistry. Part X.[1] Crystal and Molecular Structure of *catena*-(Cyclohexanone oximato)trimethyltin

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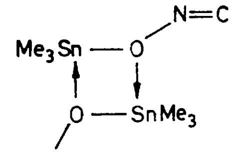
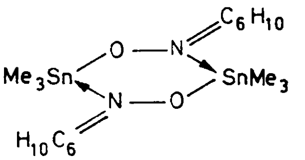
The crystal structure of the title compound has been determined from *X*-ray diffractometer data by Patterson and Fourier methods from 1 895 independent non-zero reflections to R 0.058. Crystals are monoclinic, space group $P2_1/c$ with a = 6.8244(12), b = 8.3786(18), c = 19.9490(22) Å, β = 92.37(2)°, Z = 4. Planar trimethyltin units [mean r(Sn–C) 2.133(7) Å] are bridged unsymmetrically by the oxygen atoms of the cyclohexanone oximate [r(Sn–O) 2.190(3), r(Sn · · · O) 2.481(3) Å] to form infinite zig-zag Sn–O–Sn–O– chains [O–Sn–O' 174.9(1), Sn–O–Sn' 128.03(15)°].

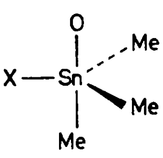
In a previous paper,[2] we concluded that *O*-trimethylstannylcyclohexanone oxime had one of the dimeric structures (I) and (II), involving either four-membered SnOSnO or six-membered SnONSnON rings, on the basis of the complex nature of the Sn–C stretching region in the i.r. spectrum and the observation of a large number of ditin-containing fragments in the mass spectrum. Both formulations involve five-co-ordinate tin and imply either the *cis* or *meridional* geometries, (III) or (IV), respectively. The large value of the tin-119m Mössbauer quadrupole splitting (2.96 mm s^{-1}) [2] serves to rule out the *cis*-configuration, and hence it was of interest to us to investigate this compound as an example of a triorganotin compound possessing the *meridional* geometry (IV) which is as yet unknown, although it has been postulated for several derivatives.[3] The value of the quadrupole splitting, however, is also not inconsistent with yet a third possibility, (V), the *trans* geometry, involving planar trimethyltin units. We now describe the results of an *X*-ray investigation.



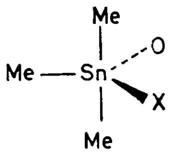
(I)



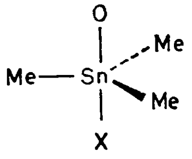
(II)



(III)



(IV)



(V)

X = O or N

EXPERIMENTAL

Crystal Data.—$C_9H_{19}NOSn$, M = 276.1, Monoclinic, a = 6.8244(12), b = 8.3786(18), c = 19.9490(22) Å, β = 92.37(2)°, U = 1 139.7 Å^3, Z = 4, D_c = 1.609, F(000) = 552. Space group $P2_1/c$ from systematic absences: $h0l$ for l odd, and $0k0$ for k odd. Mo-K_α radiation, λ = 0.71069 Å; μ(Mo-K_α) = 2.21 cm^{-1}.

Crystals were obtained by the equilibration *in vacuo* over a period of *ca.* 6 months of a sample prepared as reported previously.[2] The compound is moisture-sensitive, and a crystal of dimensions *ca.* 0.3 × 0.4 × 0.4 mm was mounted in a Lindemann capillary. The space group was deduced from oscillation and zero- and first-layer Weissenberg photographs. The intensities of 1 895 independent non-zero reflections were measured by use of a Hilger and Watts four-circle automatic diffractometer. Reflections with intensities $I < 3\sigma(I)$ were considered as unobserved and were not used further. 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.

Determination and Refinement of the Structure.—A three-dimensional Patterson synthesis gave approximate co-ordinates for the tin atom of 0,0,$\frac{1}{4}$. However, these co-ordinates, in a Fourier synthesis, revealed pseudo-mirror-plane symmetry. In order to destroy the pseudo-mirror plane, the position of the tin atom, initially placed at 0.0001, 0.0001, 0.25, was refined by two cycles of least-squares, and a Fourier synthesis using the refined positions yielded the positions of the non-hydrogen light atoms. Four cycles of full-matrix isotropic and two cycles of full-matrix anisotropic least squares reduced R to 0.077. At this stage the weighting scheme of the form $w = 1/\{1.0 + [(F_o - B)/A]^2\}$ was applied, where A = 20.00 and B = 4.00. Six further cycles of full-matrix least-squares refinement employing the weighting scheme, and two in which the rejection test $w\Delta F > 6.0$ was applied, resulting in the rejection of 10 reflections, gave a final R of 0.058. Scattering factors used were for neutral atoms.[4] Refinement was carried out by use of the '*X*-Ray' suite of

TABLE 1

Fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Sn	−0.010 84(5)	0.513 98(5)	0.242 91(2)
O	−0.061 68(6)	0.274 16(4)	0.202 10(2)
N	−0.005 58(6)	0.290 30(5)	0.134 64(2)
C(1)	−0.130 34(8)	0.239 56(6)	0.090 61(3)
C(2)	−0.078 00(10)	0.253 33(7)	0.018 55(3)
C(3)	−0.241 39(9)	0.334 16(8)	−0.022 56(3)
C(4)	−0.435 42(12)	0.247 86(9)	−0.014 70(4)
C(5)	−0.491 40(11)	0.246 88(10)	0.058 71(4)
C(6)	−0.329 48(9)	0.169 35(9)	0.104 16(3)
C(7)	0.156 88(10)	−0.049 54(7)	0.168 53(3)
C(8)	0.193 69(8)	0.127 54(7)	0.331 81(3)
C(9)	−0.297 05(10)	0.002 96(7)	0.272 51(4)

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[1] Part IX, J. Buckle, P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S. Dalton*, 1975, 1552.

[2] P. G. Harrison and J. J. Zuckerman, *Inorg. Chem.*, 1970, **9**, 175.

[3] G. M. Bancroft, V. G. Kumar Das, T. K. Sham, and M. G. Clark, *J.C.S. Chem. Comm.*, 1974, 236.

[4] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

programmes.[5] Atomic positions, anisotropic temperature factors, and structural data are listed in Tables 1—4.*

TABLE 2

Anisotropic thermal parameters ($\times 10^2$),* with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	3.30(3)	3.13(3)	3.24(3)	−0.07(1)	0.26(2)	−0.17(1)
O	4.6(2)	2.9(2)	2.8(2)	−0.6(1)	0.2(1)	−0.0(1)
N	3.8(2)	3.5(2)	3.3(2)	−0.0(2)	0.3(2)	−0.2(2)
C(1)	4.2(3)	2.5(2)	3.5(3)	0.1(2)	−0.2(2)	0.2(2)
C(2)	5.9(4)	4.8(3)	3.1(3)	1.0(3)	0.3(3)	−0.2(2)
C(3)	5.9(4)	5.0(3)	4.0(3)	0.2(3)	−0.2(3)	0.7(3)
C(4)	5.6(4)	7.4(5)	4.6(4)	−0.5(3)	−1.5(3)	0.9(3)
C(5)	5.0(4)	9.4(6)	5.8(4)	−1.1(3)	−1.2(3)	2.1(4)
C(6)	4.9(3)	7.0(4)	4.9(3)	−2.2(3)	−1.4(3)	2.2(3)
C(7)	6.4(4)	4.0(3)	4.2(3)	0.6(3)	2.2(3)	0.0(3)
C(8)	4.7(3)	3.8(3)	4.8(3)	−0.4(2)	−1.5(2)	−0.1(2)
C(9)	3.1(3)	5.4(4)	5.3(5)	−0.1(2)	1.1(3)	1.2(2)

* In the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})]$.

TABLE 3

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bond lengths

Sn–C(7)	2.132(7)	C(1)–C(2)	1.500(8)
Sn–C(8)	2.128(6)	C(2)–C(3)	1.516(9)
Sn–C(9)	2.138(7)	C(3)–C(4)	1.522(10)
Sn–O	2.190(3)	C(4)–C(5)	1.529(11)
Sn–O′	2.481(3)	C(5)–C(6)	1.543(10)
O–N	1.421(6)	C(6)–C(1)	1.515(8)
N–C(1)	1.271(7)		

(*b*) Bond angles

O–Sn–O′	174.9(1)	Sn–O–N	102.7(3)
C(7)–Sn–C(8)	114.3(2)	Sn–O′–N′	116.5(3)
C(7)–Sn–C(9)	127.2(3)	O–N–C(1)	115.1(4)
C(7)–Sn–O′	86.8(2)	N–C(1)–C(2)	117.2(5)
C(7)–Sn–O	90.4(2)	N–C(1)–C(6)	125.9(5)
C(8)–Sn–C(9)	118.0(2)	C(2)–C(1)–C(6)	116.9(5)
C(8)–Sn–O′	91.0(2)	C(1)–C(2)–C(3)	110.7(5)
C(8)–Sn–O	94.1(2)	C(2)–C(3)–C(4)	110.8(5)
C(9)–Sn–O′	85.5(2)	C(3)–C(4)–C(5)	110.7(6)
C(9)–Sn–O	92.8(2)	C(4)–C(5)–C(6)	111.3(6)
Sn–O–Sn′	128.03(15)	C(5)–C(6)–C(1)	110.9(6)

TABLE 4

Equation * of mean C_3Sn plane,† and deviations (Å) of relevant atoms from it

Plane: Sn, C(7)—(9)

$$0.1405x' - 0.9025y' + 0.4079z' = 1.8953$$

Sn −0.066, C(7) 0.022, C(8) 0.020, C(9) 0.023

* $x' = x + z\cos\beta$, $y' = y$, and $z' = z\sin\beta$. † According to V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

DISCUSSION

The title compound possesses neither of the two suggested cyclic dimeric structures (I) or (II). Instead, crystals consist of infinite chains of oxygen-bridged planar trimethyltin moieties with the $-N=C_6H_{10}$ groups pendant from the oxygen atoms. Figure 1 shows the repeat unit of the chain. Similar oxygen-bridged structures have been deduced for Me_3SnOMe,[6] Me_3SnNCO,Me_3SnOH,[7] and $(Me_3Sn)_3(OH)CrO_4$.[8] However, in these compounds both Sn–O bond distances

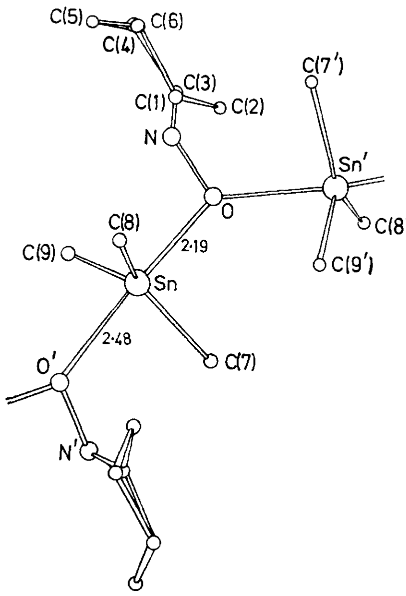

FIGURE 1 Atomic numbering in the repeating unit

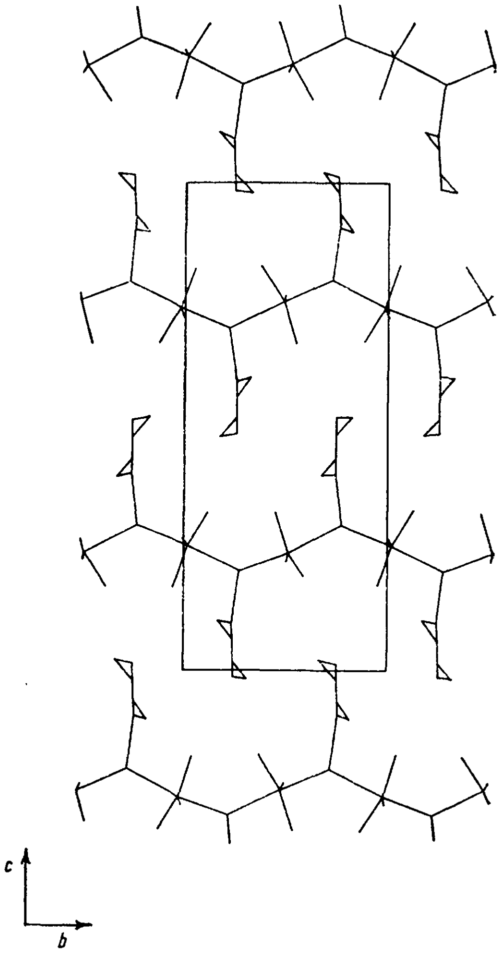

FIGURE 2 Projection on the *bc* plane

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* Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21407 (8 pp., 1 microfiche).

[5] '*X*-Ray' program system, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland Technical Report 67 58, 1967, revised version of 1970.

TABLE 5

Comparison of structural data (bonds in Å, angles in °) for $Me_3SnON{=}C_6H_{10}$ with those for related compounds

Compound	Mean *r*(Sn–O)	*r*(Sn–O)	*r* (Sn · · · O)	O–Sn–O	Sn–O–Sn
$Me_3SnON{=}C_6H_{10}$	2.133(7)	2.190(3)	2.481(3)	174.9(1)	128.03(15)
Me_3SnOMe [a]	2.14(2)	2.20(2)	2.26(2)	172.4(7)	131.2(12)
$(Me_3Sn)_3(OH)CrO_4$ [b]	2.13(6)	2.14(3), 2.17(4)		176(1)	136(2)
Me_3SnNCO,Me_3SnOH [c]	2.12(8), 2.15(8)	2.14(5), 2.15(5)		176(2), 178(2)	138(3)
Me_3SnO_2CMe [d]	2.129(5)	2.205(3)	2.391(4)	171.6(1)	
Me_3SnNO_3,H_2O [e]	2.11(2)	2.22(3)	2.47(2)	169.3(8)	
$(Ph_3PCHCOMe)Me_3SnCl$ [f]	2.133(9)		2.332(6)	177.8(2)	
$Ph_3SnONPhCOPh$ [g]	eq. 2.136(8) ax. 2.176(9)	2.091(5)	2.308(4)		

[a] A. M. Domingos and G. M. Sheldrick, *Acta Cryst.*, 1974, **B30**, 519. [b] A. M. Domingos and G. M. Sheldrick, *J.C.S. Dalton*, 1974, 477. [c] J. B. Hall and D. Britton, *Acta Cryst.*, 1972, **B28**, 2133. [d] H. Chih and B. R. Penfold, *J. Cryst. Mol. Struct.*, 1973, **3**, 285. [e] H. K. Drew and F. W. B. Einstien, *Acta Cryst.*, 1972, **B28**, 345. [f] J. Buckle, P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S. Dalton*, in the press. [g] P. G. Harrison and T. J. King, *J.C.S. Dalton*, 1974, 2298.

were approximately equal. The corresponding distances in the present case [2.190(3) and 2.481(3) Å] show a pronounced inequality. The shorter distance is similar to that in Me_3SnOMe [2.20(2)], but the intermolecular Sn · · · O distance is significantly longer [2.481(3) *vs.* 2.26(2) Å], probably owing to the greater steric bulk of the cyclohexanone oxime residue. The weakness of the co-ordinate bond is also reflected by the ease of solubility in non-polar solvents to afford monomeric species. Both distances are relatively long for covalent and co-ordinate Sn–O bond distances (Table 5). The mean Sn–C bond distance falls within the range found for compounds also containing planar trimethyltin groups, and may be considered normal. The O–Sn–O′ bond angle deviates only slightly from 180°, and Sn–O–Sn′ is 128.03(15)° [*cf.* 131.2(12)° for Me_3SnOMe (ref. 5)]. As can be seen from Figure 2, there is no interaction between adjacent chains, and there is a 'staggered' conformation of alternate C_3Sn units in the chain. No disorder of the trimethyltin group was apparent, as has been reported for Me_3SnOH and Me_3SnF.[9,10] The cyclohexane ring adopts the 'chair' conformation, and the endocyclic C–C and exocyclic N–O and C=N bond distances are as expected.

From consideration of the known structure, the method of formation of ditin-containing fragments in the mass spectrum becomes apparent: fission of the N–O bond leaving $-Me_3SnO{\cdot}Me_3SnO-$ chains is as important a primary fragmentation process as is Sn–O and Sn–C bond fission.

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[6] A. M. Domingos and G. M. Sheldrick, *Acta Cryst.*, 1974, **B30**, 519.

[7] J. B. Hall and D. Britton, *Acta Cryst.*, 1972, **B28**, 2133.

[8] A. M. Domingos and G. M. Sheldrick, *J.C.S. Dalton*, 1974, 477.

[9] N. Kasai, K. Yasuda, and R. Okawara, *J. Organometallic Chem.*, 1965, **3**, 172.

[10] H. C. Clark, R. J. O'Brien, and J. Trotter, *J. Chem. Soc.*, 1964, 2332.