Structure of 10,10-Dimethylphenothiastannin, C₁₄H₁₄SSn

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Abstract. $M_r = 333.02$, orthorhombic, $Pca2_1$, $a = 7.712$ (1), $b = 11.538$ (1), $c = 15.080$ (1) Å, $V = 1341.8$ (3) Å^3, $Z = 4$, $D_x = 1.65$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 20.3$ cm^{-1}, $F(000) = 656$, $T = 294$ K. Final $R = 0.017$ for 1083 observed reflections. The 10,10-dimethylphenothiastannin structure represents the first report for a heterocyclic molecule of the 5,10-substituted anthracene template involving a non-carbon Group IV element in a central-ring position. The two nearly planar C₆H₄SnS 'halves' of the molecule form a dihedral angle of 126.95 (8)°. The Sn—C bond distances are 2.136 (3) Å, the S—C bond distances average 1.780 (7) Å, the C—Sn—C exocyclic bond angle is 112.6 (2)°, the endocyclic C—Sn—C bond angle is 97.1 (1)°, and the C—S—C bond angle is 105.1 (3)°.

Introduction. The title compound (I) presents several molecular features which have not been present in other heterocyclic molecules of general template (II) which have been subjected to structural study. The stannin molecule of this report is not only the first heterocyclic molecule of template (II) to have an Sn atom as one of the heteroatoms, it is also the first to possess a Group IV element other than carbon. The Sn and S atoms give this structure one of the largest heteroatom combinations for template (II) molecules, a feature of interest because of possible cross-ring interactions between the heteroatoms. The title molecule is also of interest because the Sn atom is bonded to two non-hydrogen exocyclic groups and has no lone-pair electrons, as opposed to the arsenic analogs which have been the subject of a number of structural studies.

(I)   (II)

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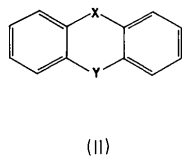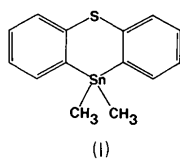
Experimental. Title compound prepared by general method reported by Meinema & Noltes (1973), suitable crystals obtained by slow cooling of a petroleum ether solution; colorless parallelepiped crystal used for data collection had dimensions $0.22 \times 0.23 \times 0.35$ mm, mounted with epoxy on a glass fiber; all data collected using an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; 25 reflections with 2θ between 20 and 34° used for a least-squares determination of cell constants; 1388 unique reflections measured using θ–2θ scans for 2θ from 2 to 50° ($h = 0$ to -9, $k = 0$ to -13, $l = 0$ to 17), scan range $(0.9 + 0.35 \tan\theta)$°, scan speeds varied from 2 to 20° min^{-1}; intensities of four reflections ($03\bar{8}$, $\bar{2}6\bar{2}$, $\bar{1}46$ and $\bar{2}60$) measured periodically during data collection varied less than 4.1% and thus indicated crystal and electronic stability; 310 reflections had $I < 3\sigma(I)$ and considered unobserved; systematic absences of $0kl$ for l odd and $h0l$ for h odd indicate space group $Pca2_1$ or (with an interchange of h and k) $Pbcm$; statistical tests of intensity distribution of data set indicated a non-centrosymmetric space group, and subsequent refinement failures using $Pbcm$ confirmed space group $Pca2_1$; analysis of the Patterson map gave positions of Sn and S atoms; final full-matrix least-squares refinement based on $(|F_o| - |F_c|)^2$ included 139 parameters (positional and anisotropic thermal parameters for all non-H atoms) for a parameter/reflection ratio of 1:7.8; H atoms included in calculation of structure factors, but neither their idealized positions (C—H = 0.95 Å) nor their assigned thermal parameters of $B = 5.0$ Å^2 refined; no absorption or secondary-extinction corrections made; 002 and 004 reflections given zero weight because of evidence of extinction problems; final $wR = 0.018$, $S = 0.83$, weighting scheme of unit weights gave no systematic variation of $\Delta F/\sigma$ as a function of either F or $\sin\theta$; in final cycle of refinement maximum shift/error 0.4; final difference map had maximum value of 0.16 e Å^{-3}; scattering factors for neutral atoms and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); computer programs

used were those of Enraf–Nonius (1979) *SDP* program package.

Discussion. Table 1 gives atom coordinates for the non-H atoms, and Table 2 gives derived distances and angles.* Fig. 1 shows the atom-numbering scheme used and Fig. 2 is a stereoview showing the crystal packing.

The endocyclic C—Sn—C angle of 97·1 (1)° is comparable to the 95–100° values found for the C—As—C angle in arsenic heterocycles (Pennington, Cordes, Graham & Jung, 1983*b*), and the C—S—C angle and S—C bond distances are comparable to

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* Lists of structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38404 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and* B_{eq} *values with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
Sn	0·18913 (3)	0·17658 (3)	0·25	3·280 (5)
S	0·4098 (2)	0·4068 (1)	0·1751 (1)	4·65 (4)
C(Me1)	0·1691 (6)	0·0064 (6)	0·3053 (4)	4·2 (1)
C(Me2)	−0·0581 (8)	0·2512 (5)	0·2214 (4)	4·7 (2)
C(1)	0·3656 (6)	0·1708 (5)	0·1409 (4)	3·6 (1)
C(2)	0·4562 (7)	0·2735 (4)	0·1196 (4)	3·7 (1)
C(3)	0·5788 (7)	0·2762 (6)	0·0527 (4)	4·6 (2)
C(4)	0·6132 (9)	0·1778 (8)	0·0050 (5)	5·7 (2)
C(5)	0·5303 (9)	0·0734 (5)	0·0256 (5)	5·3 (2)
C(6)	0·4077 (8)	0·0717 (4)	0·0928 (5)	4·5 (1)
C(7)	0·3388 (6)	0·2888 (4)	0·3324 (4)	3·3 (1)
C(8)	0·4358 (6)	0·3759 (5)	0·2895 (4)	3·8 (1)
C(9)	0·5402 (7)	0·4499 (5)	0·3378 (5)	4·6 (1)
C(10)	0·5504 (9)	0·4403 (6)	0·4298 (6)	5·6 (2)
C(11)	0·4605 (8)	0·3549 (6)	0·4724 (4)	5·2 (2)
C(12)	0·3556 (7)	0·2776 (5)	0·4242 (4)	4·1 (1)

$$* B_{eq} = \tfrac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2).$$

Table 2. *Bond distances* (Å) *and angles* (°)

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Sn—C(Me1)	2·139 (7)	Sn—C(Me2)	2·136 (6)
Sn—C(1)	2·136 (5)	Sn—C(7)	2·133 (5)
S—C(2)	1·787 (6)	S—C(8)	1·774 (6)
C(1)—C(2)	1·413 (8)	C(7)—C(8)	1·410 (7)
C(1)—C(6)	1·392 (8)	C(7)—C(12)	1·397 (9)
C(2)—C(3)	1·383 (8)	C(8)—C(9)	1·381 (8)
C(3)—C(4)	1·37 (1)	C(9)—C(10)	1·39 (1)
C(4)—C(5)	1·40 (1)	C(10)—C(11)	1·37 (1)
C(5)—C(6)	1·39 (1)	C(11)—C(12)	1·397 (9)
Sn···S	3·351 (1)		
C(Me1)—Sn—C(Me2)	112·6 (2)	C(Me1)—Sn—C(1)	108·5 (2)
C(Me1)—Sn—C(7)	111·7 (2)	C(Me2)—Sn—C(1)	115·2 (2)
C(Me2)—Sn—C(7)	110·8 (2)	C(1)—Sn—C(7)	97·1 (1)
C(2)—S—C(8)	105·1 (3)	Sn—C(1)—C(2)	117·6 (4)
Sn—C(1)—C(6)	125·2 (4)	C(2)—C(1)—C(6)	117·0 (5)
S—C(2)—C(1)	121·1 (4)	S—C(2)—C(3)	117·3 (4)
C(1)—C(2)—C(3)	121·5 (5)	C(2)—C(3)—C(4)	119·8 (6)
C(3)—C(4)—C(5)	120·6 (7)	C(4)—C(5)—C(6)	119·1 (6)
C(1)—C(6)—C(5)	121·9 (6)	Sn—C(7)—C(8)	116·9 (4)
Sn—C(7)—C(12)	124·8 (4)	C(8)—C(7)—C(12)	118·1 (5)
S—C(8)—C(7)	121·9 (4)	S—C(8)—C(9)	117·0 (4)
C(7)—C(8)—C(9)	120·6 (5)	C(8)—C(9)—C(10)	120·5 (6)
C(9)—C(10)—C(11)	119·9 (6)	C(10)—C(11)—C(12)	120·4 (6)
C(7)—C(12)—C(11)	120·5 (5)	S···Sn—C(Me1)	153·6 (2)
		S···Sn—C(Me2)	112·6 (2)
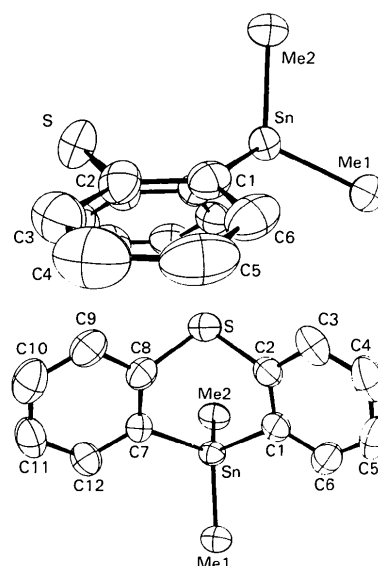
Fig. 1. Two views, and atom-numbering scheme, of $C_{12}H_8SSn(CH_3)_2$. Upper drawing: The view parallel to the longest dimension of the molecule, showing the orientation of the methyl groups with respect to the bent molecule. Lower drawing: A general view showing the atom-numbering scheme used.
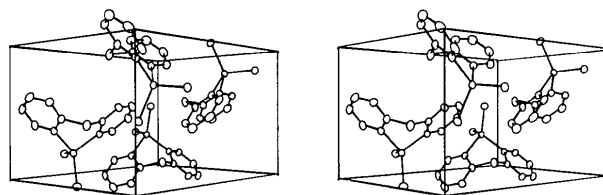

Fig. 2. Molecular packing of $C_{12}H_8SSn(CH_3)_2$. The z axis is vertical, the x axis horizontal and the origin is in the lower, left, rear corner.

values found in other S-containing heterocycles of template (II) (Pennington *et al.*, 1983*a,b*). The fact that the Sn—C distances of 2·136 (3) Å for the Sn—ring bonds are the same as the exocyclic Sn—methyl bonds and are equal to typical values found for trimethyl tin compounds implies there is little or no multiple-bond character in the Sn—C ring bonds.

The presence of two *exo*-groups on the Sn atom is of interest because of the significant structural differences noted for the axial and equatorial isomers of arsenic and antimony type (II) molecules (Pennington, Cordes, Graham & Jung, 1983*a,b*). The arsenic compounds are found most commonly as axial isomers and are characterized by molecular dihedral angles of 150–155°, relatively long As···*X* cross-ring distances, and central-ring carbon angles of 120–126°. In contrast, the two equatorial isomers reported [*X* = *Y* = AsMe by Kennard, Mann, Watson, Fawcett & Kerr (1968) and *X* = S, *Y* = SbCl by Pennington *et al.* (1983*a*)] have dihedral angles of 115–120°, shortened *X*···*Y* cross-

ring distances, and central-ring angles at carbon of 113–119°. The structural parameters of the present tin compound are similar to those of the equatorial isomers. Because of the poor overlap between the diffuse orbitals of Sn, As, or Sb and the compact π system of a phenylene group, the role of the lone-pair electrons of the heteroatoms is not likely to be the dominant factor in these structural differences. A more important factor may be the cross-ring interaction between heteroatoms. In the present tin structure the Sn···S distance is 3·35 Å, which is 0·65 Å shorter than the van der Waals separation. The equatorial heterocyclics with small dihedral angles also have short cross-ring distances: 0·73 Å shorter than van der Waals for the Sb···S distance in $C_{12}H_8SSbCl$, and 0·90 Å shorter for equatorial $C_{12}H_8(AsMe)_2$. Axial $C_{12}H_8SAsCl$, in contrast, has an As···S distance that is only 0·32 Å shorter than the van der Waals radii and it has a flattened structure with a dihedral angle of 152°. These cross-ring interactions may, of course, be either the cause or the result of the molecular folding.

One minor structural feature of interest involves the displacement of the heteroatoms from the planes of the phenylene groups (Table 3). Heterocyclic molecules of template (II) have invariably been found to have the heteroatoms displaced (0·03–0·10 Å) from the planes of the phenylene groups, so that the heteroatoms are on the outside of the fold of the molecule. The tin compound presents an exception to this generalization: while the S atom is displaced in the normal way, the Sn atom is displaced (0·05 and 0·09 Å) from the two phenylene planes on the inside of the fold angle.

Table 3. *Deviations* (Å) *from least-squares planes and dihedral angles* (°) *between planes*

	Plane 1	Plane 2		Plane 3	Plane 4
Sn	−0.0001 (2)	0.0904 (2)*	Sn	−0.0002 (3)	0.0503 (3)*
S	0.006 (2)	−0.052 (2)*	S	0.014 (2)	−0.182 (2)*
C(1)	0.048 (5)	−0.009 (5)	C(7)	0.031 (5)	−0.012 (5)
C(2)	−0.024 (6)	0.005 (6)	C(8)	−0.081 (5)	0.005 (5)
C(3)	−0.062 (6)	0.006 (6)	C(9)	−0.110 (6)	0.008 (6)
C(4)	−0.018 (7)	−0.018 (7)	C(10)	−0.018 (7)	−0.015 (7)
C(5)	0.011 (7)	0.009 (7)	C(11)	0.061 (6)	−0.002 (6)
C(6)	0.049 (7)	0.007 (7)	C(12)	0.071 (6)	0.016 (6)

Dihedral angles

(1)–(3)	126·95 (8)	(2)–(4)	128·4 (2)

* Atoms excluded from the plane calculation.

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(N,N-Dimethylformamide)tetrakis(8-quinolinolato)thorium(IV), [Th(C₃H₇NO)(C₉H₆NO)₄]

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Abstract. $M_r = 881·0$, triclinic, $P\bar{1}$, $a = 12·186$ (2), $b = 13·765$ (2), $c = 12·083$ (2) Å, $\alpha = 108·92$ (2), $\beta = 98·30$ (2), $\gamma = 112·92$ (1)°, $V = 1678·58$ Å³, $Z = 2$, $D_m = 1·755$ (4), $D_x = 1·743$ g cm⁻³, Mo $K\alpha$, graphite monochromator, $\lambda = 0·71069$ Å, μ(Mo $K\alpha$) = 51·84 cm⁻¹, $T = 295$ (2) K, $F(000) = 860$, R refined to 0·076 based on 6032 independent reflections. The four 8-quinolinolato ligands are bidentate, bonding to Th through O and N with an average Th—O distance of 2·341 (10) Å and Th—N distances ranging from 2·715 (10) to 2·800 (11) Å. The dimethylformamide ligand is bonded only through O with a Th—O distance of 2·48 (1) Å. The coordination polyhedron of the Th atom has been analysed in terms of the set of dihedral angles formed by the two faces meeting at each edge and has been identified as a slightly distorted tricapped trigonal prism.

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