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Triphenylstannyl derivatives of isothiazol-3(2*H*)-one 1,1-dioxides. Crystal structures of 2-triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide $[(C_6H_5)_3Sn\overline{NC(O)C_6H_4S}O_2]$ and 2-triphenylstannyl 4,5-dimethylisothiazol-3(2*H*)-one 1,1-dioxide $[(C_6H_5)_3Sn\overline{NC(O)C(CH_3)C(CH_3)S}O_2]$

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Abstract

2-Triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide forms crystals belonging to the orthorhombic $P2_12_12_1$ space group, with $a = 9.333(1)$, $b = 12.329(2)$ and $c = 19.348(3)$ Å. Owing to a weak (2.885(5) Å) tin–oxygen$_{\text{sulfonyl}}$ interaction that connects the molecules to form a helical chain, the tin is five-coordinate in a distorted *trans*-trigonal bipyramidal environment. The molecules of 2-triphenylstannyl 4,5-dimethylisothiazol-3(2*H*)-one 1,1-dioxide, which also crystallizes in the $P2_12_12_1$ ($a = 10.288(3)$, $b = 12.187(1)$, $c = 17.542(4)$ Å) space group, are similarly connected (2.742(5) Å) into a chain along the *b*-axis

Introduction

2-Triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide, an *N*-stannylimide, forms stable adducts even with weak oxygen-donor ligands [1–4]. Its crystal structure and that of 2-triphenylstannyl 4,5-dimethylisothiazol-3(2*H*)-one 1,1-dioxide are described below.

Experimental

2-Triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide was obtained by refluxing equimolar amounts of triphenyltin hydroxide and saccharin in toluene with azeotropic distillation of the water formed [5]. Large crystals of the analytically pure compound were obtained from the filtered solution upon slow cooling.

2-Triphenylstannyl 4,5-dimethylisothiazol-3(2H)-one 1,1-dioxide [4] was recrystallized from ethanol.

Diffraction data were collected on a Nicolet R3m/V four-circle diffractometer using graphite-monochromated Mo-K_α ($\lambda = 0.71069$ Å) radiation. The crystal of 2-triphenylstannyl 1,2-benzisothiazol-3(2H)-one 1,1-dioxide measured 0.36, 0.42, 0.46 mm. The unit-cell dimensions were obtained from 25 strong reflections scattered throughout reciprocal space, and intensities were collected ($h = 0$–13, $k = 0$–17, $l = 0$–26) up to $2\theta_{max} = 60°$. The data set comprised 2664 reflections obeying the $(I) \geqslant 3\sigma(I)$ criterion. Direct phase determination gave the position of the Sn atom, and the remaining non-H atoms were derived by successive difference Fourier syntheses. The weighting scheme, $w = [\sigma(F)^2 + (0.02F)^2 + 1]^{-1}$ [6], was used in the refinement. The H-atoms were located in later difference Fourier maps, and were refined with a B temperature factor of 5 Å^2. Full-matrix least-squares refinement based on F converged at $R = 0.034$, $R_w = 0.039$; 337 variables were refined. Computations were performed by using the MOLEN structure deter-

Table 1
Positional parameters for 2-triphenylstannyl 1,2-benzisothiazol-3(2H)-one 1,1-dioxide

Atom	x	y	z	B (Å^2) [a]
Sn	0.45571(4)	0 01865(3)	0 80186(2)	3 478(5)
S	0.2916(1)	−0 2211(1)	0 75776(7)	3 68(2)
O1	0.4075(4)	−0 2750(4)	0 7224(2)	4 57(8)
O2	0.1879(5)	−0 1678(4)	0.7158(2)	5 29(9)
O3	0.3776(7)	−0 1289(5)	0 9338(2)	6 8(1)
N	0.3570(5)	−0 1387(4)	0 8168(2)	3 85(9)
C1	0.4345(5)	0.0276(5)	0.6930(2)	3 74(9)
C2	0.5250(7)	−0.0280(8)	0.6517(3)	6 6(2)
C3	0.510(1)	−0.024(1)	0 5795(4)	10.2(3)
C4	0.4022(9)	0.039(1)	0.5507(3)	7.8(2)
C5	0.314(1)	0 088(1)	0.5911(4)	9.5(2)
C6	0.3293(9)	0 0872(8)	0 6624(3)	8 2(2)
C7	0.6647(5)	−0.0190(5)	0.8381(3)	3 84(9)
C8	0.7272(7)	−0 1133(6)	0.8181(4)	6 7(2)
C9	0 8682(8)	−0 1366(8)	0 8357(6)	8 8(2)
C10	0.9459(7)	−0.0657(7)	0 8735(5)	7 4(2)
C11	0 8843(7)	0.0289(7)	0 8944(4)	6 5(2)
C12	0 7452(7)	0 0530(6)	0 8766(3)	4 7(1)
C13	0.3266(5)	0.1221(4)	0 8640(3)	3 55(9)
C14	0 2177(8)	0.1831(7)	0 8370(4)	6 4(2)
C15	0.1377(9)	0 2510(8)	0.8771(5)	8 4(2)
C16	0 1647(8)	0.2638(6)	0.9445(5)	7 3(2)
C17	0.270(1)	0.2013(8)	0 9738(4)	8 1(2)
C18	0 3488(9)	0 1318(8)	0.9338(4)	7.3(2)
C19	0.3339(8)	−0.1756(6)	0.8836(3)	5.0(1)
C20	0 2435(8)	−0 2749(6)	0.8834(3)	5 4(1)
C21	0.2101(6)	−0 3093(5)	0.8175(3)	4.5(1)
C22	0.1202(7)	−0 3966(5)	0 8046(4)	5.7(1)
C23	0.0647(9)	−0 4492(7)	0.8609(5)	8.2(2)
C24	0.096(1)	−0 4154(8)	0 9277(5)	10 3(2)
C25	0 184(1)	−0.3288(7)	0 9386(4)	8.0(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B = 4/3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$

Table 2
Positional parameters 2-triphenylstannyl 4,5-dimethylisothiazol-3(2*H*)-one 1,1-dioxide

Atom	*x*	*y*	*z*	*B* (Å^2) [a]
Sn	0.42853(4)	0.12091(3)	0.77371(2)	2.993(6)
S	0.4716(2)	−0.1337(1)	0.86978(9)	3.10(2)
O1	0.5415(5)	−0.1903(4)	0.8094(3)	4.0(1)
O2	0.5496(5)	−0.0988(5)	0.9337(3)	4.9(1)
O3	0.1732(5)	0.0106(5)	0.8189(4)	5.2(1)
N	0.3875(5)	−0.0329(4)	0.8348(3)	3.2(1)
C1	0.6337(5)	0.1280(5)	0.7839(4)	3.3(1)
C2	0.6904(7)	0.2277(6)	0.8042(4)	4.0(1)
C3	0.8243(8)	0.2372(7)	0.8137(5)	5.1(2)
C4	0.9026(7)	0.1477(8)	0.8026(6)	5.6(2)
C5	0.8501(8)	0.0483(7)	0.7823(7)	6.1(2)
C6	0.7155(8)	0.0374(6)	0.7711(7)	5.5(2)
C7	0.3418(7)	0.2321(5)	0.8527(4)	3.7(1)
C8	0.2299(9)	0.2914(7)	0.8362(6)	5.8(2)
C9	0.175(1)	0.3584(8)	0.8926(8)	8.0(3)
C10	0.234(1)	0.3679(8)	0.9633(6)	8.2(2)
C11	0.345(1)	0.3109(9)	0.9790(5)	7.7(3)
C12	0.399(1)	0.2411(7)	0.9230(5)	5.9(2)
C13	0.3393(7)	0.0705(5)	0.6695(4)	3.5(1)
C14	0.4002(9)	−0.0038(6)	0.6233(5)	4.9(2)
C15	0.337(1)	−0.0430(7)	0.5573(5)	6.1(2)
C16	0.214(1)	−0.0068(7)	0.5410(5)	6.1(2)
C17	0.156(1)	0.0674(9)	0.5852(6)	6.6(2)
C18	0.2150(9)	0.1044(8)	0.6500(5)	6.0(2)
C19	0.2555(7)	−0.0526(6)	0.8423(4)	3.6(1)
C20	0.2267(7)	−0.1580(6)	0.8803(4)	3.8(1)
C21	0.3361(8)	−0.2110(6)	0.9002(4)	3.8(1)
C22	0.354(1)	−0.3169(7)	0.9394(6)	5.8(2)
C23	0.091(1)	−0.1936(9)	0.8938(6)	6.5(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B = 4/3[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

mination system on a DEC MicroVax II minicomputer [7]. The atomic coordinates are listed in Table 1.

Crystal data: $(C_6H_5)_3Sn\overline{NC(O)C_6H_4SO_2}$, $M = 532.19$, orthorhombic, $P2_12_12_1$, $a = 9.333(1)$, $b = 12.329(2)$, $c = 19.348(3)$ Å, $V = 2226.3(9)$ Å^3, $\mu = 12.64$ cm^{-1}, $D_c = 1.588$ g cm^{-3} for $Z = 4$.

The data set for the crystal of 2-triphenylstannyl 4,5-dimethylisothiazol-3(2*H*)-one 1,1-dioxide (0.36, 0.42, 0.62 mm) consisted of $2917(I) \geqslant 3\sigma(I)$ reflections (collection range: $h = 0–13$, $k = 0–16$, $l = 0–24$; $2\theta_{max} = 50°$). Direct methods again gave only the position of the heavy atom. The non-H atoms were obtained from difference Fourier syntheses. All non-H atoms were refined anisotropically and the H-atoms isotropically. The structure was refined to unweighted *R* and weighted R_w indices of 0.038 and 0.050, respectively; 325 variables were refined. Fractional atomic coordinates are listed in Table 2.

Crystal data: $(C_6H_5)_3Sn\overline{NC(CH_3)=C(CH_3)SO_2}$, $M = 510.18$, orthorhombic, $P2_12_12_1$, $a = 10.288(3)$, $b = 12.187(1)$, $c = 17.542(4)$ Å, $V = 2199(1)$ Å^3, $\mu = 12.79$ cm^{-1}, $D_c = 1.541$ cm^{-1} for $Z = 4$.

The absolute structures [8] of the compounds were not determined.

Results and discussion

2-Triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide was synthesized by condensing triphenyltin hydroxide with saccharin in toluene since use of ethanol as solvent gave the ethanol adduct [1]. However, ethanol-free 2-triphenylstannyl 4,5-dimethylisothiazol-3(2*H*)-one 1,1-dioxide was obtained by treating triphenyltin hydroxide with 4,5-dimethylisothiazol-3(2*H*)-one 1,1-dioxide in ethanol [4].

The 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide anion is covalently bonded to the triphenyltin cation through a short tin–nitrogen bond (2.167(5) Å) in the 2-triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide molecule (Fig. 1). The three carbon–tin–carbon angles (115.2(2), 117.7(2), 118.5(2)°) are opened up, whereas the three nitrogen–tin–carbon angles (98.0(2), 98.7(2), 102.8(2)°) are compressed from the 109.5° angle expected for an idealized tetrahedral structure. The sulfonyl oxygen atom of an adjacent (symmetry transformation: $1-x$, $\frac{1}{2}+y$, $1\frac{1}{2}-z$) molecule is located at a distance of 2.885(5) Å from the tin atom. This interaction, albeit weak, links the molecules into a stretched helical chain running parallel to the *b*-axis, so that the coordination polyhedron around the tin atom approaches a *trans*-trigonal bipyramid. This description is also supported by the magnitude of the tin-119*m* Mössbauer quadrupole splitting (2.99 mm s^{-1}), which falls at the lower limits of the range found for five-coordinate triphenyltin compounds [9]. The tin–oxygen bond distance compares well with that (2.822(3) Å) found in 2-trimethylstannyl 1,3,5-trithia-2,4,6-triazine 1,1-dioxide [10], which has been described as a weakly bridged polymer.

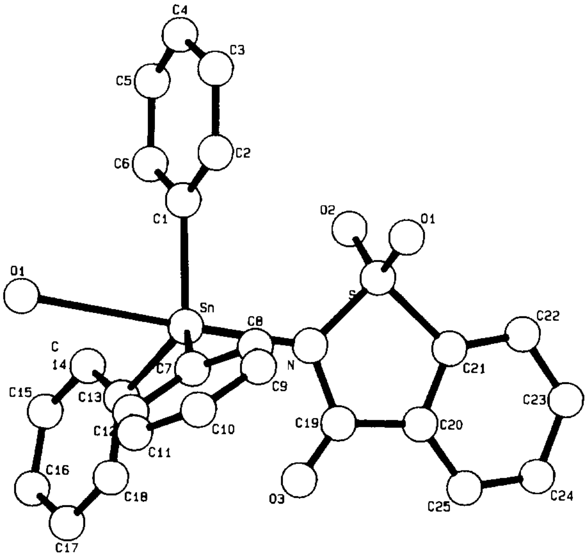

Fig. 1. The asymmetric unit of 2-triphenylstannyl 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide. Selected distances and angles Sn–O1′ 2 885(5), Sn–N 2.167(5), Sn–C1 2 118(5), Sn–C7 2 124(5), Sn–C13 2.127(6) Å, O1′–Sn–N 177.9(2), O1′–Sn–C1 80.4(2), O1′–Sn–C7 80.8(2), O1′–Sn–C13 79.3(2), N–Sn–C1 98.0(2), N–Sn–C7 98.7(2), N–Sn–C13 102 8(2), C1–Sn–C7 115.2(2), C1–Sn–C13 118.5(2), C7–Sn–C13 117.7(2)°

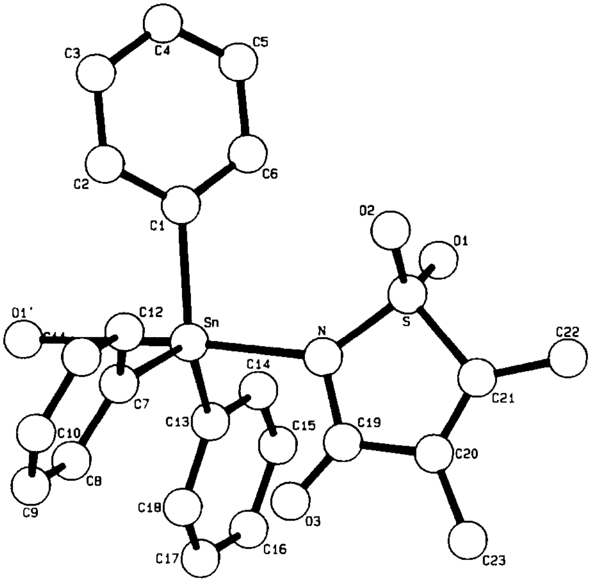

Fig 2. The asymmetric unit of 2-triphenylstannyl 4,5-dimethylisothiazol-3(2H)-one 1,1-dioxide. Selected distances and angles: Sn–O1' 2.742(5), Sn–N 2.200(5), Sn–C1 2.120(5), Sn–C7 2 133(7), Sn–C13 2.136(7) Å; O1'–Sn–N 174.7(2), O1'–Sn–C1 84.2(2), O1'–Sn–C7 81.9(2), O1'–Sn–C13 80.5(2), N–Sn–C1 100.6(2), N–Sn–C7 98 3(3), N–Sn–C13 95.1(2), C1–Sn–C7 109.6(3), C1–Sn–C13 120 8(3), C7–Sn–C13 123.9(3)°.

The weak interaction in 2-triphenylstannyl 1,2-benzisothiazol-3(2H)-one 1,1-dioxide is replaced by a formal dative bond in its oxygen-donor adducts. The bond distances in the adducts fall in the 2.376(7) to 2.413(7) Å range.

The effective bulk of the anionic group in 2-triphenylstannyl 4,5-dimethylisothiazol-3(2H)-one 1,1-dioxide (Fig. 2) is smaller than that in the 1,2-benzisothiazol-3(2H)-one 1,1-dioxide, so that the nearest neighboring (symmetry transformation: $1-x$, $\frac{1}{2}+y$, $1\frac{1}{2}-z$) sulfonyl oxygen atom can be expected to be closer to the tin atom in the crystal structure. This is indeed observed, the tin–oxygen distance being 2.742(5) Å. The close approach of the sulfonyl oxygen atom causes the axial nitrogen atom to be displaced further away (Sn–N = 2.200(5) Å). A further consequence is the widening (123.9(3)°) of one of the three carbon–tin–carbon angles. The geometry at the tin atom is a less distorted *trans*-C_3SnNO trigonal bipyramid.

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