

similar parameters from the orthorhombic polymorph (see below).

**Related literature.** The structures of the orthorhombic and trigonal polymorphs were originally determined by Britton & Dunitz (1965), who can be referred to for drawings of both polymorphs. The structure of the orthorhombic polymorph was redetermined by Barrick, Canfield & Giessen (1979). As shown in Table 2, the structural parameters for the fulminate ion are in complete agreement for the two polymorphs. The differences between the two

structures are confirmed; in particular the Ag—Ag distance in the cyclic hexamer of the trigonal form is significantly shorter than in the infinite polymer of the orthorhombic form and than in silver metal.

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## Structure of a New Form of Triphenyltin(IV) Isothiocyanate

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**Abstract.** Triphenyltin(IV) isothiocyanate,  $(C_6H_5)_3Sn.NCS$ ,  $M_r = 408.10$ , orthorhombic,  $Pna2_1$ ,  $a = 8.966$  (2),  $b = 14.552$  (5),  $c = 13.085$  (4) Å,  $V = 1707.4$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.587$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 16.6$  cm<sup>-1</sup>,  $F(000) = 808$ ,  $T = 294$  K,  $R_F = 0.042$  for 827 unique reflections. The complex features an infinite  $\mu$ -1,3-thiocyanato-bridged zigzag chain running along the  $2_1$  axis with the Sn atom in a trigonal bipyramidal  $NC_3S$ -coordination environment. The bond angles at various junctions along the  $[Ph_3SnNCS]_n$  polymeric chain in this orthorhombic form (I) are significantly different from those in the known form (II) belonging to space group  $P2_1$ , especially the Sn—N—C, C—S—Sn angles (by ca 10°); the bond lengths, the packing mode and the coordination geometry are all quite similar.

**Experimental.** To 4.1 g of crude triphenyltin isothiocyanate (m.p. 441–443 K) as prepared by Charland, Gabe, Khoo & Smith (1989) was added 1.1 g of sarcosine in 40 ml of ethanol (95%). The mixture was refluxed (20 min), cooled and kept in the freezer overnight. On filtration a solid (2.0 g, m.p. 465–467 K) was isolated. It was purified by repeated recrystallization (2 ×) in ethanol. Colorless needle-shaped crystals of triphenyltin isothiocyanate were obtained by slow evaporation of an ethanol solution.

A crystal of dimensions  $0.16 \times 0.22 \times 0.24$  mm was mounted on a Nicolet  $R3m/V$  diffractometer; data collected in the  $\omega$ -scan mode ( $3.0 \leq 2\theta \leq 50^\circ$ ) at room temperature (294 K); variable scan rate ( $1.51$ – $9.01^\circ$  min<sup>-1</sup>); graphite-monochromatized  $Mo K\alpha$  radiation; lattice parameters from a least-squares refinement of 25 reflections ( $10.3 \leq 2\theta \leq 16.6^\circ$ ); 1574 independent reflections measured ( $0 \leq h \leq 9$ ,  $0 \leq k \leq 17$ ,  $0 \leq l \leq 15$ ), of which 827 reflections were considered observed [ $|F_o| \geq 6\sigma(|F_o|)$ ]. Two standard reflections, 101 and 121, monitored after every 125 data measurements showed only random fluctuations within 1% of their mean values during data collection. Lorentz–polarization corrections and  $\psi$ -scan-based empirical absorption corrections (transmission factors 0.636–0.772) were applied. Structure solved by Patterson superposition and subsequent Fourier synthesis. The atoms of the tin and isothiocyanate group were refined anisotropically while the phenyl rings were handled as rigid groups. All H atoms were generated geometrically (C—H = 0.96 Å) and assigned the same isotropic temperature factor of  $U = 0.10$  Å<sup>2</sup> in structure-factor calculations. The quantity minimized was  $\sum w(F_o - F_c)^2$ , where  $w = [\sigma^2(F_o) + 0.0002|F_o|^2]^{-1}$ . Final  $R = 0.042$  and  $wR = 0.043$  for 71 parameters and 827 observed reflections,  $S = 1.318$ ,  $(\Delta/\sigma)_{max} = 0.001$ ; largest peaks in the final difference map lie in the range  $0.68$ – $-0.53$  e Å<sup>-3</sup>.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$  for Sn,  $10^3$  for other atoms)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{eq}/U$
Sn(1)	623 (1)	-5 (1)	0	457 (1)
S(1)	-2456 (4)	-51 (6)	-3171 (3)	84 (2)
C(1)	-1374 (15)	45 (15)	-2213 (12)	55 (6)
N(1)	-635 (14)	80 (16)	-1490 (10)	67 (5)
C(11)	-1118 (9)	684 (7)	783 (8)	43 (4)
C(12)	-1277	1633	679	50 (5)
C(13)	-2478	2081	1139	61 (5)
C(14)	-3519	1580	1703	65 (5)
C(15)	-3359	631	1807	58 (5)
C(16)	-2159	183	1347	55 (5)
C(21)	2424 (10)	732 (7)	-681 (8)	39 (4)
C(22)	2123	1391	-1427	60 (5)
C(23)	3294	1835	-1926	68 (5)
C(24)	4766	1619	-1680	66 (6)
C(25)	5068	960	-934	60 (5)
C(26)	3896	516	-435	55 (5)
C(31)	798 (12)	-1460 (6)	-81 (13)	50 (4)
C(32)	1542	-1809	-933	89 (7)
C(33)	1689	-2756	-1061	110 (9)
C(34)	1092	-3355	-336	81 (7)
C(35)	348	-3007	516	95 (8)
C(36)	201	-2059	644	75 (6)

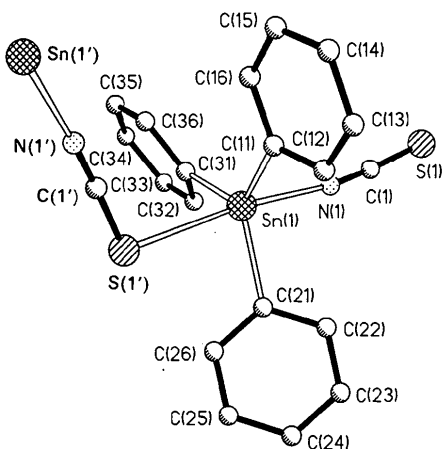


Fig. 1. Perspective view showing the coordination geometry of the Sn atom in orthorhombic  $\text{Ph}_3\text{SnNCS}$  (I) and the atom-numbering scheme. Symmetry code: (')  $-x, -y, \frac{1}{2} + z$ .

Table 2. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) in  $[\text{Ph}_3\text{SnNCS}]_n$

	(I)	(II)*
Sn(1)—C(11)	2.120 (9)	2.05 (5)
Sn(1)—C(21)	2.13 (1)	2.12 (5)
Sn(1)—C(31)	2.125 (9)	2.09 (5)
Sn(1)—N(1)	2.26 (1)	2.22 (2)
Sn(1)—S(1')	2.904 (4)	2.91 (1)
S(1)—C(1)	1.58 (2)	1.58 (7)
C(1)—N(1)	1.16 (2)	1.17 (8)
C(11)—Sn(1)—N(1)	91.3 (5)	93 (1)
C(21)—Sn(1)—N(1)	89.4 (5)	92 (1)
C(31)—Sn(1)—N(1)	92.8 (7)	96 (1)
C(11)—Sn(1)—C(21)	121.4 (4)	118 (3)
C(11)—Sn(1)—C(31)	123.3 (4)	126 (3)
C(21)—Sn(1)—C(31)	115.1 (4)	116 (3)
S(1')—Sn(1)—C(11)	90.3 (3)	98 (3)
S(1')—Sn(1)—C(21)	84.4 (3)	82 (3)
S(1')—Sn(1)—C(31)	91.6 (4)	94 (4)
S(1')—Sn(1)—N(1)	173.5 (5)	175 (3)
Sn(1)—S(1')—C(1')	107.6 (6)	97 (3)
S(1)—C(1)—N(1)	176 (2)	172 (3)
C(1)—N(1)—Sn(1)	172 (2)	161 (4)

Symmetry code: (')  $-x, -y, \frac{1}{2} + z$ .

\* Monoclinic form.

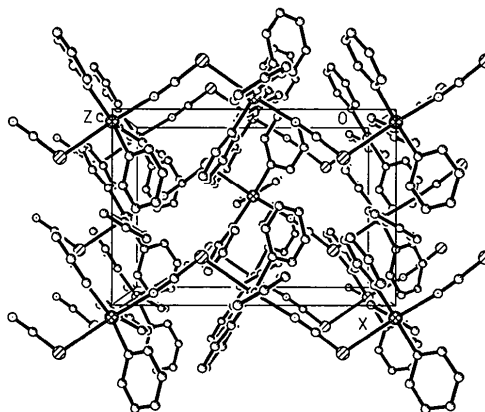


Fig. 2. Molecular packing in the crystal structure of form (I) showing the  $[\text{Ph}_3\text{SnNCS}]_n$  zigzag chains. The origin of the unit cell lies at the upper right corner, with  $a$  pointing downwards,  $b$  towards the reader, and  $c$  from right to left.

Computations were performed on a DEC MicroVAX II computer with the *SHELXS86* program package (Sheldrick, 1982, 1985). Analytic expressions of atomic scattering factors were employed, and anomalous-dispersion corrections were incorporated [*International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 55, 99 and 149)]. Table 1\*

\* Lists of structure factors, anisotropic thermal parameters, some additional bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54399 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lists the atomic parameters, and Table 2 compares selected bond lengths and angles of  $[\text{Ph}_3\text{SnNCS}]_n$  in the present orthorhombic form (I) and the monoclinic form (II) as determined by Domingos & Sheldrick (1974). Fig. 1 illustrates the coordination geometry about the Sn atom in (I), and Fig. 2 shows the molecular packing.

**Related literature.** The title compound is of interest in view of its coordination geometry as compared to that of its trimethyl analogue,  $[\text{Me}_3\text{SnNCS}]_n$  (Forder & Sheldrick, 1970). Domingos & Sheldrick (1974) determined the crystal structure of the monoclinic form of  $\text{Ph}_3\text{SnNCS}$  (II) [space group  $P2_1$ ,  $a =$

19.02 (2),  $b = 11.67$  (2),  $c = 15.49$  (2) Å,  $\beta = 95.6$  (1)°,  $V = 3421$  Å<sup>3</sup>,  $Z = 8$ ;  $R_F = 0.149$  for 3638 Cu  $K\alpha$  Weissenberg data], which consists of four independent chains of similar molecular dimensions along the screw diads. The same type of polymeric structure has been found in Ph<sub>3</sub>SnNCO (Tarkova, Chuprunov, Simonov & Belov, 1977). In the presence of another ligand such as a Schiff base, Ph<sub>3</sub>SnNCS can form monomeric complexes exhibiting trigonal bipyramidal coordination geometry, for example, [L<sub>2</sub>H]<sup>+</sup>[Ph<sub>3</sub>Sn(NCS)<sub>2</sub>]<sup>-</sup> [ $L = 1$ -(salicylideneamino)-2-methoxybenzene] (Charland *et al.*, 1989) and Ph<sub>3</sub>Sn(NCS)L [ $L = 1$ -[(4'-methylphenylimino)methyl]-2-naphthol] (Khoo, Charland, Gabe & Smith, 1987).

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## Structure of Dimeric Lithium 2,6-Di-*tert*-butylphenoxide–Diethyl Ether (1/1)

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**Abstract.** {Li[OC<sub>6</sub>H<sub>3</sub>(C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>][O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]}<sub>2</sub>,  $M_r = 572.77$ , triclinic,  $P\bar{1}$ ,  $a = 10.188$  (8),  $b = 11.202$  (9),  $c = 9.220$  (5) Å,  $\alpha = 99.92$  (6),  $\beta = 113.39$  (5),  $\gamma = 68.31$  (7)°,  $V = 897.02$  Å<sup>3</sup>,  $Z = 1$  (one dimer),  $D_x = 1.06$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.61$  cm<sup>-1</sup>,  $F(000) = 316$ ,  $T = 230$  (5) K,  $R = 0.063$  for 1467 observed reflections with  $I > 2\sigma(I)$ . The structure is that of a centrosymmetric dimer, the phenoxide-O act as bridging atoms and the Li<sub>2</sub>( $\mu$ -O)<sub>2</sub> unit is planar. Each Li atom carries an additional ether ligand and thus shows the unusual coordination number of three.

**Experimental.** Reaction of [Lu(CH<sub>3</sub>)<sub>6</sub>][Li(TMEDA)]<sub>3</sub> (TMEDA = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>) with cyclopentadiene and 2,6-di-*tert*-butylphenol in toluene at 195 K gave the title compound and other Lu-containing products. Crystals were obtained by extracting the white residue of the reaction mixture with ether/pentane (1/4) and keeping the extract at 253 K. As the compound rapidly loses ether at room temperature, all crystal manipulations had to be carried out at low temperature in a cold nitrogen stream.

Colourless crystal (0.42 × 0.28 × 0.25 mm) mounted on glass fibre and transferred to Enraf–Nonius

CAD-4 diffractometer equipped with low-temperature device. Lattice parameters derived from setting angles of 25 reflections,  $12 \leq 2\theta \leq 24^\circ$ . Intensity data were collected in the  $\omega$ - $2\theta$  scan mode with  $\Delta\omega = (0.90 + 0.35\tan\theta)^\circ$ , using graphite-monochromated Mo  $K\alpha$  radiation. Three reference reflections recorded every two hours showed only random variations. Intensity data for 3368 reflections with  $2\theta \leq 50^\circ$  ( $-11 \leq h \leq 12$ ,  $-13 \leq k \leq 13$ ,  $-10 \leq l \leq 0$ ); 2525 unique reflections ( $R_{\text{int}} = 0.018$ ), 1467 reflections with  $I > 2\sigma(I)$  used for refinement. Corrections for Lorentz and polarization effects. Structure solved with direct methods using *SHELXS86* (Sheldrick, 1986) and refined on  $F$  by full-matrix least squares with *SHELX76* (Sheldrick, 1976); non-H atoms refined with anisotropic thermal parameters, H atoms located from a difference Fourier map and refined isotropically, except the H atoms of the ether CH<sub>3</sub> groups. The C atoms of the ether methyl groups showed rather high temperature factors, indicating a small degree of disorder; therefore these CH<sub>3</sub> groups were treated as rigid groups with C—H bond lengths of 0.95 Å and a common isotropic temperature factor  $U = 0.08$  Å<sup>2</sup> for the H atoms. 290 parameters were refined,  $R = 0.063$ ,  $wR = 0.082$ ,  $w^{-1} = [\sigma^2(F_o) + 0.0027 F_o^2]$ ,  $S = 0.67$ ,  $(\Delta/\sigma)_{\text{max}} = 0.014$ ;  $|\Delta e| <$