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GROUP IVB ORGANOMETALLIC SULPHIDES

IV*. CRYSTAL STRUCTURE OF TRIPHENYLTIN *p*-tert-BUTYLPHENYL SULPHIDE

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SUMMARY

The crystal structure of $Ph_3SnSC_6H_4$-t-Bu-*p* has been determined using three dimensional X-ray diffractometer data. The crystals are monoclinic, $P2_1/c$, $a = 13.65$, $b = 9.42$, $c = 19.71$ Å, $\beta = 105° 15'$, $Z = 4$. The structure was refined by least squares to an R index of 0.061. The coordination of the tin atom is tetrahedral with a Sn–S bond of length 2.413 Å and an average Sn–C bond of 2.126 Å.

INTRODUCTION

Organotin sulphides have been extensively studied[2,3]. In particular, the physical and chemical properties of organotin sulphides of the type, R_3SnSR', have been variously reported[1a,b,2,3]. The nature of the bonding between tin and sulphur in these compounds has often been questioned without any definite conclusions being reached about the extent of the contribution, if any, from $d\pi \leftarrow p\pi$ interaction in these bonds. Very recently[4], it was concluded from a ^{13}C-NMR and $S2p_{\frac{3}{2}}$ ESCA study that a $d\pi \leftarrow p\pi$ contribution was in fact an important feature of the tin–sulphur bond. The results of other spectral studies, in agreement with this finding, include the measurement of ^{119}Sn–^{1}H coupling constants[5,6] of the series $Me_{4-n}Sn(SMe)_n$; $n = 1$–4; and examination of UV spectra[7,8], of $Bu_{4-n}Sn(SBu)_n$[7], $n = 1, 2$ and of a series[8] of Me_3SnSAr compounds.

Determinations of the crystal structures of organotin sulphides are few. The structures of triphenyltin triphenyllead sulphide[9], $Ph_3SnSPbPh_3$, and trimeric diphenyltin sulphide[10], $(Ph_2SnS)_3$, are the only ones reported in the most recent review[2] We now wish to report the first structure determination study of an organotin sulphide of the type R_3SnSR', namely triphenyltin *p*-tert-butylphenyl sulphide, $Ph_3SnSC_6H_4$-t-Bu-*p*. The Sn–S bond length in this sulphide was compared with the published bond lengths in $Ph_3SnSPbPh_3$ and in $(Ph_2SnS)_3$ as well as with the sum of the covalent radii of tin and sulphur.

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* For Part III see ref 1a

EXPERIMENTAL

Triphenyltin *p*-tert-butylphenyl sulphide was prepared from the metathetical reaction of triphenyltin chloride and *p*-tert-butylthiophenol in the presence of triethylamine. It was recrystallised from ethanol, m.p. 112–113°.

Crystal data

$C_{28}H_{28}SSn$, mol.wt. 515.3, monoclinic, $a = 13.65(2)$, $b = 9.42(1)$, $c = 19.71(3)$ Å, $\beta = 105° 15' \pm 10'$, U 2461 Å^3, d_m 1.37 g/cm^3 measured by flotation, d_c 1.39 g/cm^3 for $Z = 4$, $F(000) = 1048$, Mo-K_α ($\lambda = 0.7107$ Å), Systematic absences: $h0l$, $l = 2n+1$; $0k0$, $k = 2n+1$ are consistent with space group $P2_1/c$.

A crystal of approximate dimensions (0.27 × 0.40 × 0.49 mm), was mounted about the *b* axis (0.40 mm edge). Intensity data for layers $h0l$ to $h10l$ inclusive were collected on a Hilger and Watts Y190 automatic linear diffractometer using Mo-K_α radiation with balanced filters. Each reflection in one half of reciprocal space was measured twice giving, after averaging, 2931 independent observed reflections. An empirical check showed that absorption errors were not likely to be serious and no correction was applied; the linear absorption coefficient for Mo-K_α radiation is 12.8 cm^{-1}, the mean cross sectional radius of the crystal was 0.19 mm. The unit cell parameters were determined from $0kl$ and $hk0$ precession photographs.

STRUCTURE SOLUTION AND REFINEMENT

The position of the tin atom was readily determined from a 3-D Patterson synthesis and a Fourier synthesis calculated on the resulting heavy atom phases revealed all of the remaining non-hydrogen atoms. From this point the structure was refined by least squares using the block diagonal approximation*, assuming isotropic thermal motion for all atoms. After several cycles of least squares it became apparent from an error analysis that interlayer scaling was necessary to increase the contribution from the higher layers. Convergence of the isotropic model was reached at an *R* index of 0.083. The tin, sulphur and terminal carbon atoms [C(26), C(27), C(28)] of the tert-butyl group were allowed anisotropic thermal motion, and the refinement converged at an *R* index of 0.061. In the latter stages of refinement a weighting scheme of the form $w = 1/\{1 + [(F-b)/a]^2\}^{\frac{1}{2}}$ was used ($a = 110$, $b = 40$) which was shown to be satisfactory from an analysis of F_o against $\langle w(F_o - F_c)^2\rangle$. A final difference Fourier map showed no electron density outside the range ±1 e/Å^3. Atomic scattering factors for neutral atoms were used as given in the International Tables[11].

RESULTS AND DISCUSSION

Tables 1 and 2 give respectively the intramolecular distances (Part A bonded, Part B selected non-bonded), and bond angles. Figure 1 shows a view of the molecule perpendicular to the plane containing C(7), C(13), C(19), and Fig. 2 shows the packing

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* The computing programmes used were mainly those supplied by Dr F R. Ahmed and collaborators, of the National Research Council of Canada, and adapted by Mr J S Knowles of the Department of Computing, University of Aberdeen.

TABLE 1

INTRAMOLECULAR DISTANCES (Å)

A Bonded					
Sn–S	2 413(3)[a]		*C–CH$_3$ bonds*		
Sn–C(7)	2 122(10)	2 126[b]	C(4) –C(25)	1 544(14)	1 548
Sn–C(13)	2 132(9)		C(25)–C(26)	1 565(17)	
Sn–C(19)	2 124(9)		C(25)–C(27)	1 523(19)	
S –C(1)	1 784(9)		C(25)–C(28)	1 559(18)	
Phenyl groups					
C(1)–C(2)	1 380(15)	1 391	C(7) –C(8)	1 412(13)	1 397
C(1)–C(6)	1 376(14)		C(7) –C(12)	1 401(14)	
C(2)–C(3)	1 406(14)		C(8) –C(9)	1 395(16)	
C(3)–C(4)	1 396(15)		C(9) –C(10)	1 399(17)	
C(4)–C(5)	1 383(14)		C(10)–C(11)	1 414(16)	
C(5)–C(6)	1 405(14)		C(11)–C(12)	1 362(17)	
C(13)–C(14)	1 405(14)	1 401	C(19)–C(20)	1 376(16)	1 397
C(13)–C(18)	1 388(15)		C(19)–C(24)	1 397(15)	
C(14)–C(15)	1 406(15)		C(20)–C(21)	1 427(17)	
C(15)–C(16)	1 396(17)		C(21)–C(22)	1 354(18)	
C(16)–C(17)	1 392(17)		C(22)–C(23)	1 394(19)	
C(17)–C(18)	1 420(16)		C(23)–C(24)	1 431(17)	
B Selected non-bonded distances					
Sn–C(1)	3 35		S–C(7)	3 81	
Sn–C(8)	3 08		S–C(13)	3 77	
Sn–C(12)	3 09		S–C(19)	3 44	
Sn–C(14)	3 11		S–C(24)	3 46	
Sn–C(18)	3 05				
Sn–C(20)	3 06				
Sn–C(24)	3 08				

[a] The estimated standard deviation in parentheses applies to the least significant digit

[b] Mean values.

of the molecules in the unit cell. Tables of observed and calculated structure factors may be obtained from the authors

The coordination of the tin is approximately tetrahedral with three phenyl groups and a *p*-tert-butylphenylthio group as ligands. The Sn–C bond lengths are all in good agreement with each other and the mean value of 2.126 Å compares with values of 2.144(14) in Ph_4Sn[12], 2.114(6) in Ph_2SnCl_2[13], and 2.13 in $(CO)_3Mn{-}C_5Ph_4{-}OSnPh_3$[14]. The greatest distortion from regular tetrahedral geometry involves the S–Sn–C bond angles which have a range of 98–114° ; the distribution of the C–Sn–C bond angles being much closer to the mean tin valence bond angle of 109.5°. In particular there is a marked contraction of the S–Sn–C(19) bond angle which results in an approach between S–C(19) of 3.44 Å compared to 3.81 and 3.77 Å for C(7) and C(13) respectively. Distortion of tin valence angles is not unusual and has commonly been attributed to crystal packing requirements[14]. The present structure is not exceptional, since it is noted (Table 3) that most of the shortest intermolecular contacts, while being of the Van der Waals type, are between atoms in the tert-butylphenyl

(*Continued p* 284)

TABLE 2

BOND ANGLES (°)

S-Sn-C(7)	114.0(3)	109 5[a]	C(4) -C(25)-C(26)	110.1(9)	109 5
S-Sn-C(13)	112 0(3)		C(4) -C(25)-C(27)	111 9(10)	
S-Sn-C(19)	98 5(3)		C(4) -C(25)-C(28)	108 5(9)	
C(7)-Sn-C(13)	108.6(4)		C(26)-C(25)-C(27)	106 9(10)	
C(7)-Sn-C(19)	111 6(4)		C(26)-C(25)-C(28)	108 9(10)	
C(13)-Sn-C(19)	112 0(4)		C(27)-C(25)-C(28)	110 5(11)	
Sn-S-C(1)	105 0(3)				
S-C(1)-C(2)	120 8(7)				
S-C(1)-C(6)	119.0(7)				
C(2)-C(1)-C(6)	119 8(9)		Sn-C(7)-C(8)	120 3(7)	
C(1)-C(2)-C(3)	120 0(9)		Sn-C(7)-C(12)	121.1(7)	
C(2)-C(3)-C(4)	120.4(9)	120 0	C(8)-C(7)-C(12)	118 4(9)	120 0
C(3)-C(4)-C(5)	118 9(9)		C(7)-C(8)-C(9)	120 3(9)	
C(4)-C(5)-C(6)	120 3(9)		C(8)-C(9)-C(10)	120 9(10)	
C(1)-C(6)-C(5)	120 6(9)		C(9)-C(10)-C(11)	117 9(11)	
C(3)-C(4)-C(25)	119 5(8)		C(10)-C(11)-C(12)	121 5(11)	
C(5)-C(4)-C(25)	121.6(8)		C(7)-C(12)-C(11)	121 0(10)	
Sn-C(13)-C(14)	121 5(7)		Sn-C(19)-C(20)	120 6(8)	
Sn-C(13)-C(18)	118 4(7)		Sn-C(19)-C(24)	120 6(7)	
C(14)-C(13)-C(18)	120 1(9)	120 0	C(20)-C(19)-C(24)	118.8(10)	120 0
C(13)-C(14)-C(15)	120 3(9)		C(19)-C(20)-C(21)	120.7(11)	
C(14)-C(15)-C(16)	119 8(11)		C(20)-C(21)-C(22)	120 3(12)	
C(15)-C(16)-C(17)	120.0(11)		C(21)-C(22)-C(23)	120 7(12)	
C(16)-C(17)-C(18)	120 5(11)		C(22)-C(23)-C(24)	118 8(12)	
C(13)-C(18)-C(17)	119 4(10)		C(19)-C(24)-C(23)	120 6(10)	

[a] Mean values.

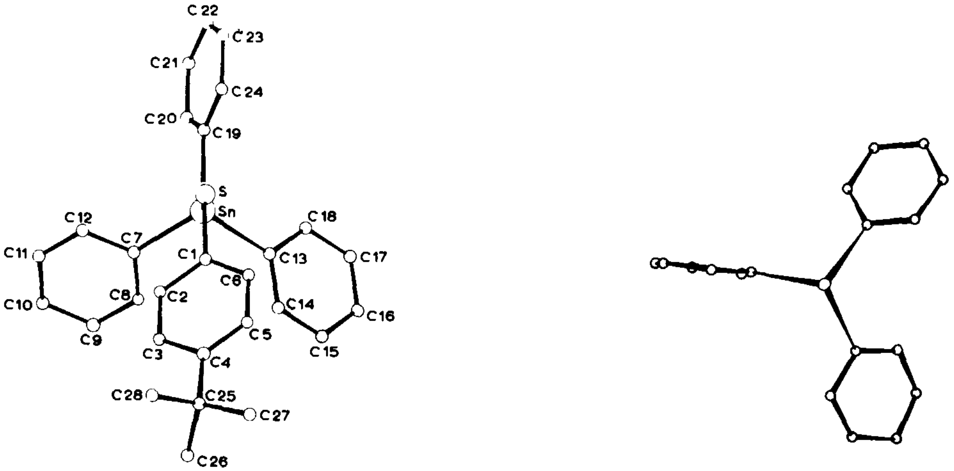

Fig 1 View of the molecule perpendicular to the plane containing C(7), C(13), C(19) The insert shows a comparable view of part of Ph_4Sn

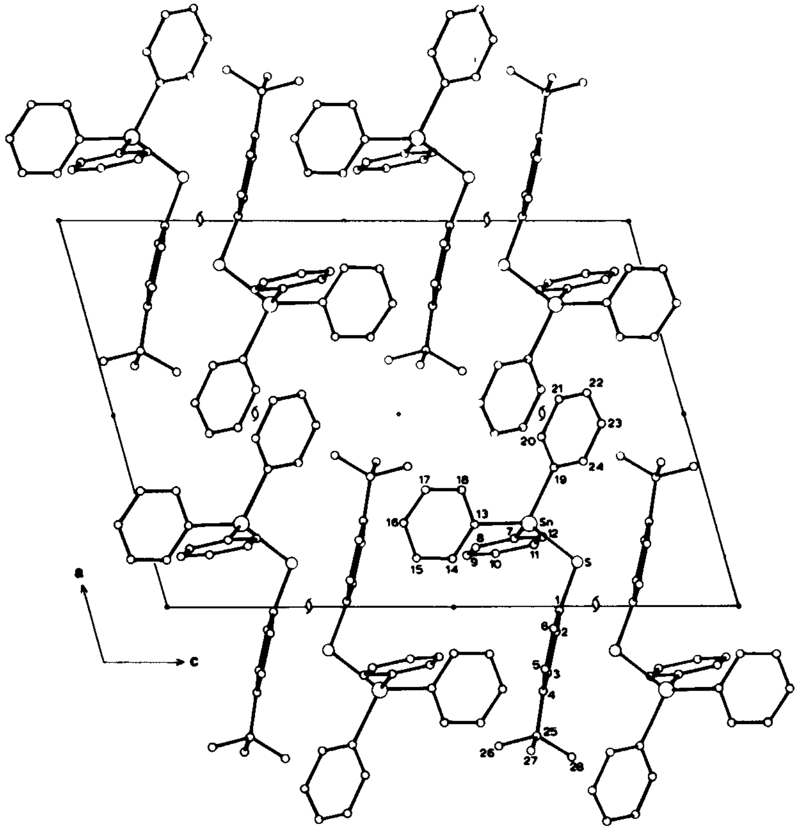

Fig 2 The molecular packing as viewed down the *b* axis

TABLE 3

INTERMOLECULAR DISTANCES LESS THAN 3.70 Å

Atom 1	*Atom* 2	*Position*	*Distance* (*Å*)
C(2)	C(15)	$\bar{x}, 1-y, \bar{z}$	3.69
C(3)	C(15)	$\bar{x}, 1-y, \bar{z}$	3.51
C(5)	C(9)	$\bar{x}, 1-y, \bar{z}$	3.67
C(5)	C(12)	$\bar{x}, y-\frac{1}{2}, \frac{1}{2}-z$	3.67
C(6)	C(12)	$\bar{x}, y-\frac{1}{2}, \frac{1}{2}-\bar{z}$	3.69
C(9)	C(15)	$\bar{x}, 1-y, \bar{z}$	3.54
C(28)	C(21)	$x-1, y, z$	3.67

group bonded to the sulphur atom.

The Sn–S bond length of 2.413(3) Å compares with other reported single covalent Sn–S bonds; namely 2.42(2) Å in $(Ph_2SnS)_3$[10] and 2.442 Å in $Ph_3SnSPbPh_3$[9] but it is significantly shorter than those in the dimethyldithiocarbamato compounds, $Me_3Sn{-}S{-}C(S)NMe_2$, [2.47(1) Å][15], and $Me_2ClSn{-}S{-}C(S)NMe_2$, [2.48(1) Å and 2.79(1) Å][16] (for further discussion see below). The angle at the sulphur of 105.0(3)° is that expected for normal sp^3 hybridisation of the sulphur atom and further the S–C bond length of 1.784(9) is within the range of reported S–C single bonds; 1.81 Å[17] and 1.81 and 1.79 Å in $(PhS)_2$[18].

It is of interest to compare the arrangement of the phenyl groups with that of Ph_4Sn (Fig. 1). In the present structure no symmetry constraint is imposed on the phenyl groups which allows rotation of the C(19)–C(24) ring about the C(19)–Sn bond to maintain normal Van der Waals contacts with C(28) of the neighbouring molecule. Three-fold rotational symmetry would be obtained if the phenyl rings were rotated by equal amounts about their respective Sn–C bonds with respect to the normal to the plane containing the three atoms C(7), C(13), C(19). In the present structure these rotations are 126°, 123° and 157° for C(7)–C(12), C(13)–C(18), C(19)–C(24) rings respectively; corresponding rotations for Ph_4Sn are 126°, 124° and 173°.

$d\pi \leftarrow p\pi$ Bonding in tin–sulphur bonded compounds

Our study shows that $Ph_3SnSC_6H_4$-t-Bu-*p* contains an essentially sp^3-hybridised 4-coordinate tin atom with a Sn–S bond length of 2.413(3) Å comparable to that in $Ph_3SnSPbPh_3$ (2.442 Å), and in $(Ph_2SnS)_3$ (2.42(2) Å). Furthermore, the sum of the covalent radii of Sn and S (2.43 Å)[19] is only slightly greater than the measured Sn–S bond length in $Ph_3SnSC_6H_4$-t-Bu-*p*. (The Sn–S bond lengths in the binary tin sulphides are however significantly larger; in SnS, with 3-coordinate Sn^{II}, the Sn–S bond lengths[20] are 2.62 and 2.68 Å; in Sn_2S_3, with 3-coordinate Sn^{II}, and 6-coordinate Sn^{IV}, the Sn^{II}–S bond lengths are 2.741 and 2.644 and the Sn^{IV}–S bond lengths are between 2.497 and 2.611 Å[21], and in SnS_2, with 6-coordinate Sn^{IV}, the bond length[22] is 2.55 Å.)

As already stated, the distortion of the tin from a regular tetrahedron is due to crystal packing factors rather than to some electronic or bonding effect. We conclude that no evidence for any significant $d\pi \leftarrow p\pi$ contribution to the overall tin–sulphur bonding can be extracted from our data; if such bonding is present, it can play only a minor role. The question of whether or not the small deviation of the measured Sn–S bond length from the value of the sum of the covalent radii is significant, cannot be answered with any certainty. It would be extremely helpful to have a reliable value for a tin–sulphur double bond length. The best available value is an estimated one (2.24 Å)[19a]. Using this value with our measured bond length of 2.413(3) Å and assuming the covalent bond radii (2.43 Å) to be accurate to ±0.01 Å, extreme values are found for the bond order of Sn–S in $Ph_3SnSC_6H_4$-t-Bu-*p* of 1.02 and 1.14. Considering the size of the errors involved in this calculation, the values should not be taken too seriously.

If $d\pi \leftarrow p\pi$ bonding in Sn–S compounds plays at the outside a small part in the solid state, it is most unlikely that this bonding would be anymore significant in solution. The evidence generally put forward for $d\pi \leftarrow p\pi$ bonding ought to be carefully assessed; too often, any slight deviation of a particular property from an anticipated value is automatically assumed to arise from some double bond character in the Sn–S bond.

Pignataro *et al.*[4] in their report of ^{13}C-NMR and $S2p_{\frac{3}{2}}$ ESCA data for Me_3MSPh; M = C, Si, Ge, Sn and Pb, state that as the atomic number of M increases, so overlap of the *d* orbitals of M with the sulphur *p* orbitals should increase to make the $d\pi \leftarrow p\pi$ contribution more important. This is quite wrong. As the atomic number of M increases, the "size" of the *d* orbitals increases and this should result in less overlap of the sulphur *p* orbitals with the increasingly diffuse metal *d* orbitals.

A ^{119}Sn Mössbauer study of the series of compounds, $Ph_3SnSC_6H_4X$-*p*; X = NH_2, OMe, t-Bu, Me, H, Cl, Br, NO_2 clearly indicated the whole series to be simple four-coordinate species; the isomer shifts were in the range -1.20 to -1.26 mm/sec relative to β-tin and quadrupole splittings were 1.50, 1 34, 1.41, 1.54, 1.41, 1.52, 1.44 and 1.72 mm/sec respectively. No symmetric trend in the quadrupole splittings is apparent. This also seems to point against much $d\pi \rightarrow p\pi$ bonding[23].

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