Journal of Organometallic Chemistry, 332 (1987) 85–94
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Studies in aryltin chemistry

III *. Crystal and molecular structures of tetra(*p*-methoxyphenyl)tin(IV) and tetra(*p*-methylthiophenyl)tin(IV) **

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(Received January 5th, 1987)

Abstract

Tetrakis(*p*-methylthiophenyl)tin(IV) (**A**) and tetrakis(*p*-methoxyphenyl)tin(IV) (**B**) have been prepared and their vibrational spectra (400–100 cm^{-1}) and X-ray crystal structures are reported. Both compounds are tetragonal with space group $I\bar{4}$, $Z = 2$. For (**A**), $a = b = 13.553(4)$, $c = 7.442(2)$ Å, and for (**B**), $a = b = 14.180(4)$, $c = 6.303(2)$ Å, both at 173 K. Both structures were solved by the direct method and refined by full-matrix least squares calculations to $R = 0.040$, 767 observed reflections for **A**, and to $R = 0.019$, 721 observed reflections for **B**. Both molecules have $\bar{4}$ molecular symmetry with the CH_3S or CH_3O groups in the all-*exo* conformation almost coplanar with the phenyl rings. Increasing size of the *para*-substituent as CH_3 is replaced by CH_3O and then CH_3S causes a decrease in d(Sn–C) from 2.147(6) to 2.136(4) and 2.123(7) Å ascribed to increased intermolecular repulsions in these isomorphous close-packed structures.

Introduction

As part of our continuing study [1] of the effect of substitution at the benzene ring (e.g., *p*- or *m*-YC_6H_4) on the properties of triaryltin compounds, particularly

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* Part II, see ref. 1.

** Presented in part by M.G.S. at the 54th Congress of the 'Association canadienne-française pour l'avancement des sciences', Montréal, Canada, 1986, Recueil des résumés, p. 72.

with respect to their biocidal activity, it has been necessary to synthesise various tetraaryltins since these compounds are the precursors needed for the preparation of the required triaryltin compounds. However the tetraaryltins in the solid state are themselves of interest since those reported to date [2] use a variety of tetragonal space groups, $P\bar{4}2_1c$, $I\bar{4}$, or $I4_1/a$, depending on the type of packing in the crystal even though all have the same $\bar{4}$ molecular asymmetry. An early study [3] showed that tetrakis(*p*-anisyl)tin (*p*-anisyl ≡ *p*-methoxyphenyl) crystallises in the $I\bar{4}$ space group and it was concluded from steric considerations that the *p*-methoxy group must lie in the plane perpendicular to the benzene ring, a conclusion which is at variance with more recent structures [4,5] of *p*-anisyl derivatives where the methoxy group is almost co-planar with the benzene ring. To provide more definitive information on the methoxy group orientation in $(p\text{-}CH_3OC_6H_4)_4Sn$, a reinvestigation of its crystal structure was undertaken which we report here.

To date only one *p*-thioanisyltin (*p*-thioanisyl ≡ *p*-methylthiophenyl) compound has been reported [6], $(p\text{-}CH_3SC_6H_4)_2SnCl_2 \cdot$ dipy, although tetrakis(*p*-thioanisyl)-lead was synthesised many years ago [7]. No structural data are available for these or similar compounds. We therefore present herein the X-ray analysis of $(p\text{-}CH_3SC_6H_4)_4Sn$ for comparison with the structures of the *p*-anisyltin analogue and other tetraaryltin compounds.

Experimental

All reactions were carried out under nitrogen. Tin tetrachloride (J.T. Baker) and *p*-bromoanisole and *p*-bromothioanisole (Aldrich) were used as received. All solvents were stored over molecular sieves, except anhydrous ether (Fisher) and tetrahydrofuran which was distilled from sodium just before use. Other experimental details, e.g., micro-analyses, and Raman and far-infrared spectra (400–100 cm^{-1}) were as described elsewhere [8].

Preparations

Tetra(p-thioanisyl)tin. Tin tetrachloride (21.4 g, 0.082 mole) in benzene (100 ml) was slowly added to the well stirred, cooled Grignard reagent solution obtained by treating *p*-bromothioanisole (67.7 g, 0.333 mole) with excess magnesium (9 g) in tetrahydrofuran (450 ml). The mixture was refluxed for 1 h and then filtered. Evaporation under vacuum of the filtrate, followed by addition of acetone gave the product which was recrystallised from acetone to give white needles; yield 63%, m.p. 169–170 ° C. Anal. Found: C, 54.91; H, 4.80. $C_{28}H_{28}S_4Sn$ calcd: C, 55.00; H, 4.62%. Far-infrared (Nujol mull): 390w, 354wm, 284sm, 269m, 212m ($\nu_{as}(SnC_3)$), 191w, 175w, 166w, 148w cm^{-1}. Raman (powder); 392w, 355sm, 285wbr, 268wm, 210wbr, 162vs ($\nu_s(SnC_3)$), 140s cm^{-1}.

Tetra(p-anisyl)tin. This compound was prepared using the Grignard method as described above. The crude product was dissolved in hot benzene and reprecipitated with ethanol. Recrystallisation from ethanol gave fine white needles; m.p. 133–134 ° C (lit. 135 ° C [9], 130 ° C [10], 133–134 ° C [11]. Far-infrared (Nujol mull): 320vs, 303sm, 239m ($\nu_{as}(SnC_3)$), 214wm, 203vw, 183vw, 177vw, 159wbr, 151w, 139w, 115m cm^{-1}. Raman (powder): 324w, 243vw, 213vw, 177vs,sp ($\nu_s(SnC_3)$), 162m, 158sh cm^{-1}.

X-ray analysis of $(p\text{-}CH_3ZC_6H_4)_4Sn$ (Z = O, S)

For each compound a suitable crystal (Z = O, $0.04 \times 0.10 \times 0.46$ mm^3; Z = S, $0.15 \times 0.19 \times 0.54$ mm^3) was mounted on an Enraf–Nonius CAD-4 diffractometer and a set of 25 random reflection was picked in the Laue sphere using the SEARCH procedure from the Nonius package. After centring, the indexing routine yielded a triclinic reduced cell which was verified by recording long-exposure photographs about each of the axes. The Niggli parameters associated with this cell showed it could be transformed to a tetragonal *I*-centered cell. Laue $4/m$ symmetry was confirmed by comparing intensities of a set of equivalent reflections obtained by fast pre-collection which enabled the Laue $4/mmm$ symmetry also expected for tetragonal space groups, to be ruled out. The lack of systematic absences found, except those for the *I*-centred condition ($h + k + l = 2n + 1$) is consistent with three space groups, $I4$, $I\bar{4}$, and $I4/m$.

Crystal data

(a) $(p\text{-}CH_3OC_6H_4)_4Sn$. $C_{28}H_{28}O_4Sn$. $fw = 547.22$. Tetragonal, $I\bar{4}$, a 14.180(4), c 6.303(2) Å, V 1267.4 Å^3, D_c 1.434 g cm^{-3}, $Z = 2$, λ(Cu-$K_{\bar{a}}$) 1.54178 Å (graphite monochromator), μ(Cu-K_α) 84.4 cm^{-1}, T 173 K.

(b) $(p\text{-}CH_3SC_6H_4)_4Sn$. $C_{28}H_{28}S_4Sn$, $fw = 611.48$. Tetragonal $I\bar{4}$, a 13.553(4), c 7.442(2) Å, V 1367.0 Å^3, D_c 1.485 g cm^{-3}, $Z = 2$, λ(Cu-$K_{\bar{a}}$) 1.54178 Å (graphite monochromator), μ(Cu-K_α) 105.3 cm^{-1}, T 173 K.

Crystal data for the two compounds were also obtained at room temperature [12*,13*].

Data collection and structure determination

A suitable number (Z = O, 721; Z = S, 767) of independent *hkl* reflections ($2\theta < 140°$) was collected as described elsewhere [14]. Seven standards were monitored during the collection for orientation (every 100 reflections) and intensity (every hour) control and only small variations of their intensities ($\leqslant \pm 1.5\%$, Z = O; $\leqslant \pm 2.2\%$, Z = S) were observed. All measured reflections were retained for the structure resolution and refinement ($I \geqslant 5\sigma(I)$). These were corrected for both Lorentz, polarization and absorption (Gaussian integration grid $10 \times 10 \times 10$; transmission range Z = O, 0.42–0.73; Z = S, 0.11–0.30).

The structures were solved by the direct method (EEES) and refined by full-matrix least squares using the SHELX programme [15]. Two of the three possible space groups $I4$ and $I\bar{4}$, are compatible with Z = 2. Resolution of the structures using the latter space group ($I\bar{4}$) gave better refinement thus confirming the earlier report for tetrakis(*p*-anisyl)tin [3].

For the anisyl structure, the tin atom was introduced at 0,0,0 (equipoint *a*) and the difference Fourier (ΔF) map revealed all non-hydrogen atoms. Isotropic refinement of all non-hydrogen atoms gave $R = [\Sigma \| F_0 | - | F_c \|)/\Sigma | F_0 |] = 0.035$. All hydrogens were then found from a ΔF map and introduced in the refinement. At convergence, $R = 0.019$, $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w |F_0|^2]^{1/2} = 0.023$ with a goodness-of-fit of 2.90. The final ΔF map showed only a background below 0.25 e$^-$/Å^3 with only two peaks of 0.36 e$^-$/Å being at 1.3–1.6 Å from tin.

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* This and other references marked with asterisks indicate notes occurring in the list of references.

For the thioanisyl structure, the tin atom was introduced at the same position (equipoint *a*, space group $I\bar{4}$) but the difference Fourier (ΔF) map revealed a pseudo-higher symmetry. Introduction of the two strongest peaks due to sulphur and refinement of their occupancy factors permitted phasing of the model. The ΔF map then computed revealed all non-hydrogen atoms. Isotropic refinement converged to $R = 0.063$. Anisotropic refinement with introduction of all hydrogens at idealised positions (d(C–H) 1.08 Å) and refinement of their temperature factors gave $R = 0.048$. The weighting scheme $w = 1/[\sigma^2(F_0) + 0.0001(F_0)^2]$ was used to complete the refinement which converged at $R = 0.040$, $R_w = 0.052$, goodness-of-fit 4.71. The final ΔE map showed only two peaks of 0.65–0.40 e$^-$/Å at 1.2–1.3 Å from tin and sulphur with a general background below 0.33 e$^-$/Å^3.

Scattering curves were from standard sources [16] with the f' and f'' contributions to anomalous dispersion taken from Cromer [17]. Refined coordinates for all

Table 1

Refined coordinates ($\times 10^4$; H$\times 10^3$) and isotropic temperature factors ($U_{eq} \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq}(Å^2)
(a) (p-$CH_3OC_6H_4)_4$Sn				
Sn	0	0	0	25
O	3598(2)	−858(2)	5570(4)	39
C(1)	1207(2)	−334(3)	1884(6)	26
C(2)	1174(3)	−1012(3)	3495(6)	29
C(3)	1951(3)	−1209(3)	4769(13)	30
C(4)	2795(3)	−732(3)	4415(5)	28
C(5)	2852(3)	−70(3)	2779(7)	34
C(6)	2073(3)	119(3)	1556(7)	30
C(7)	3530(4)	−1402(4)	7459(9)	48
H(2)	44(3)	−137(3)	378(7)	50
H(3)	191(3)	−165(3)	585(6)	36
H(5)	345(3)	18(3)	247(8)	48
H(6)	216(3)	57(3)	59(8)	52
H(7A)	421(4)	−132(3)	814(9)	51
H(7B)	340(3)	−205(4)	715(9)	53
H(7C)	310(4)	−104(4)	838(11)	86
(b) (p-$CH_3SC_6H_4$)Sn				
Sn	0	0	0	35
S	3657(1)	−757(1)	5907(3)	43
C(1)	1217(5)	−299(5)	1712(10)	37
C(2)	1074(5)	−942(5)	3156(10)	39
C(3)	1794(5)	−1115(5)	4461(9)	37
C(4)	2704(4)	−634(4)	4320(10)	33
C(5)	2859(5)	0(5)	2871(12)	44
C(6)	2134(5)	165(5)	1626(10)	40
C(7)	3084(7)	−1413(8)	7706(17)	67
H(2)	38	−132	327	90
H(3)	165	−161	556	49
H(5)	356	37	273	90
H(6)	228	67	54	67
H(7A)	361	−153	877	104
H(7B)	282	−212	722	49
H(7C)	247	−99	821	136

Table 2

Bond distances and bond angles for $(p\text{-}CH_3ZC_6H_4)_4Sn$

(a) Bond distances (Å)	Z = O	Z = S	(b) Bond angles (°)	Z = O	Z = S
Sn–C(1)	2.136(4)	2.123(7)	C(1)–Sn–C(1) $(\bar{x}, \bar{y}, z)$	112.5(1)	106.2(3)
C(1)–C(2)	1.399(5)	1.397(10)	C(1)–Sn–C(1) $(y, \bar{x}, \bar{z})$	108.0(1)	111.1(3)
C(2)–C(3)	1.392(7)	1.397(10)	Sn–C(1)–C(2)	121.9(3)	118.2(5)
C(3)–C(4)	1.393(5)	1.399(9)	Sn–C(1)–C(6)	121.2(3)	125.4(5)
C(4)–C(5)	1.397(6)	1.395(10)	C(2)–C(1)–C(6)	116.8(3)	116.1(6)
C(5)–C(6)	1.373(6)	1.369(10)	C(1)–C(2)–C(3)	122.0(4)	122.9(6)
C(6)–C(1)	1.401(5)	1.394(9)	C(2)–C(3)–C(4)	119.4(4)	119.0(6)
C(4)–Z	1.363(4)	1.758(7)	C(3)–C(4)–C(5)	119.6(4)	118.5(6)
Z–C(7)	1.422(6)	1.785(12)	C(4)–C(5)–C(6)	119.9(4)	121.0(7)
			C(5)–C(6)–C(1)	122.2(4)	122.4(7)
			C(4)–Z–C(7)	117.5(3)	103.4(4)
			C(3)–C(4)–Z	124.6(4)	123.6(5)
			C(5)–C(4)–Z	115.7(3)	117.8(5)

atoms are listed in Table 1, with bond lengths and angles for the non-hydrogen atoms in Table 2. The atom labelling scheme adopted is shown in Fig. 1 together with the projection on the *ab* plane of the unit cell of $(p\text{-}CH_3OC_6H_4)_4Sn$ in Fig. 2. Lists of structure factors, thermal parameters, mean planes data as well as bond lengths and angles involving hydrogen atoms and stereo-views of the unit cells of both compounds are available on request from the authors (IW).

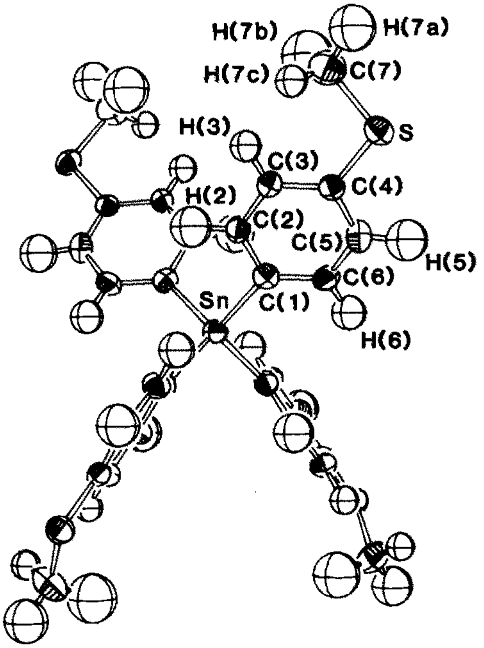

Fig. 1. The view of the $(p\text{-}CH_3SC_6H_4)_4Sn$ molecule perpendicular to the $\bar{4}$ axis.

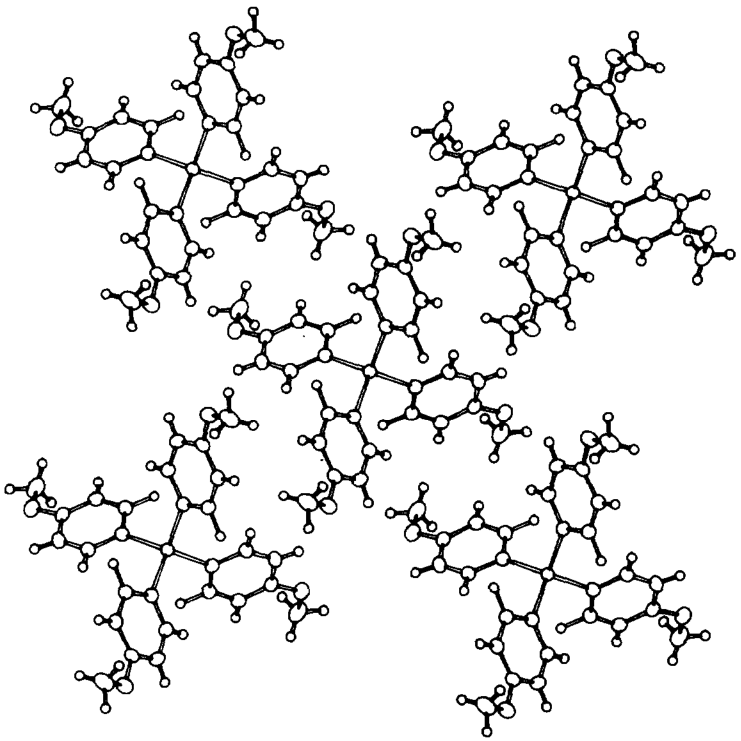

Fig. 2. A projection on the *ab* plane viewed along the $\bar{4}$ axis of the unit cell of (p-$CH_3OC_6H_4)_4Sn$.

Discussion

Tetrakis(*p*-anisyl)tin and tetrakis(*p*-thioanisyl)tin are isomorphous with exact $\bar{4}$ molecular symmetry in the crystalline state. As with tetrakis(*m*-tolyl)tin [18] this is achieved by the four aryl groups adopting an all-*exo* conformation (Fig. 1). The ring angles show the usual departure from D_{6h} symmetry found for a benzene ring σ-bonded to a metal [19]: av. C_{ortho}–C_{Sn}–C_{ortho} 116.5(5)°; av. C_{Sn}–C_{ortho}–C_{meta} 122.4(5)°; av. C_{ortho}–C_{meta}–C_{para} 119.8(5)°; av. C_{meta}–C_{para}–C_{meta} 119.0(5)°. The rings are planar within 1.0σ (0.007 Å) for the thiomethoxy compound and within 2.0σ (0.005 Å) for the methoxy analogue, but the tin atoms are significantly out of these planes (0.198(2) and 0.062(3) Å respectively).

The C–O and O–CH_3 distances (1.363(4), 1.422(6) Å, the C_{para}–O–CH_3 angle (117.5(3)°), and the deviation of the O atom from the phenyl ring plane (0.031(3) Å) are all typical of those for *p*-anisyl compounds [4,5]. For (p-$CH_3SC_6H_4)_4Sn$, the analogous values are, 1.758(7), 1.785(12) Å, 103.4(4)°, and 0.064(2) Å respectively which may be compared with similar data obtained for other systems where a methylthio group is attached to an aromatic ring [20,21], as well as that predicted on the basis of ab initio calculations for the planar conformation of thioanisole itself [22]. The O–CH_3 and S–CH_3 bonds are nearly completely eclipsed with respect to the adjacent C_{para}–C_{meta} bond with torsion angles C(3)–C(4)–O–C(7) −10.2(6)° and C(3)–C(4)–S–C(7) −9.2(7)° respectively.

Table 3

Shorter interatomic distances (Å) in $(p\text{-CH}_3\text{ZC}_6\text{H}_4)_4\text{Sn}$

	Z = O	Z = S [g]
Intramolecular		
H(2)–H(6) [a]	2.98(7)	3.14
H(7B)–C(3)	2.81(5)	2.83
H(7B)–C(4)	2.68(5)	2.96
H(7B)–H(3)	2.34(6)	2.13
H(7C)–C(3)	2.81(7)	2.94
H(7C)–C(4)	2.57(7)	2.95
H(7C)–H(3)	2.48(8)	2.41
Intermolecular		
H(2)–C(3) [b]	2.64(4)	2.71
H(2)–C(2) [b]	2.70(4)	–
H(2)–C(1) [b]	2.95(4)	–
H(2)–C(4) [b]	2.85(4)	2.94
H(2)–C(5) [b]	3.10(5)	–
H(3)–C(5) [b]	–	3.04
H(3)–C(6) [b]	3.08(4)	2.99
H(6)–Z [c]	–	3.01
H(6)–C(7) [c]	3.08(4)	–
H(7A)–Z [d]	2.48(5)	2.93
H(7A)–C(4) [d]	2.93(5)	–
H(7A)–C(5) [d]	3.08(5)	–
H(7B)–C(2) [e]	2.94(5)	3.10
H(7B)–C(3) [e]	3.01(5)	2.96
H(7C)–C(6) [f]	2.99(7)	3.02

[a] $y, \bar{x}, \bar{z}$. [b] $y, \bar{x}, 1-z$. [c] $\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}-z$. [d] $\frac{1}{2}-y, -\frac{1}{2}+x, \frac{3}{2}-z$. [e] $\frac{1}{2}-x, -\frac{1}{2}-y, \frac{1}{2}+z$. [f] $x, y, 1+z$.
[g] No errors given; hydrogen atoms placed in idealised positions with *d*(C–H) 1.08 Å.

Most intramolecular contacts are greater than Van der Waals, the exceptions involving the methyl group hydrogens (H(7B) and H(7C)) which are *cis* to the phenyl ring (Table 3). Although there are uncertainties associated with the location of hydrogen atoms using X-ray diffraction methods, the data reported here show that both molecules adopt the electronically preferred planar conformation for the anisyl and thioanisyl groups, notwithstanding the probable steric interactions of methyl group hydrogens with those on the ring which Ismailzade suggested would favour the perpendicular conformer. These interactions may however be the cause of the further phenyl group asymmetry seen in the *p*-anisyl and *p*-thioanisyl compounds reported here. Thus angles C(3)–C(4)–O (124.6(4)°); C(5)–C(4)–O (115.7(3)°) and C(3)–C(4)–S (123.6(5)°); C(5)–C(4)–S (117.8(5)°) clearly deviate from the 120° angles suggested for an sp^2 carbon atom. Moreover, ab initio calculations for the planar conformation of thioanisole [22] predict values for the angles very similar to those given here.

As with $(p\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$ [23] significant intermolecular contacts involve the methyl group hydrogens (Table 3) but ring hydrogens are also involved in the lattice interactions. Notably short interactions are H(7A) – – – O,S ($\frac{1}{2}-y$, $-\frac{1}{2}+x$, $\frac{3}{2}-z$), 2.48(5) or 2.93 Å; H(2) – – – C(3) (y, $\bar{x}$, $1-z$), 2.64(4) or 2.71 Å for the anisyl and thioanisyl compounds respectively with H(2)–C(2) (y, $\bar{x}$, $1-z$) 2.70(4)

Table 4

Crystal and molecular parameters for various tetra-aryltins

Compound (Space group)	Crystal angles (°) [a]		Molecular angles (°) [a]				d(Sn–C) (Å)	ν_{ave}(Sn–C) [b] (cm^{-1})
	ϕ	α	θ	β	γ	λ		
$(C_6H_5)_4Sn$ [c] ($P\bar{4}2_1c$)	7.1	56.5	110.5	108.9	121.7	119.8	2.143(5)	253 [d]
$(2\text{-}C_4H_3S)_4Sn$ [e] ($P\bar{4}2_1c$)	6.6 [f]	58.4	112.6	107.9	[g]	[g]	2.15(1)	[g]
$(p\text{-}CH_3C_6H_4)_4Sn$ [h] ($I\bar{4}$)	14.5	48.4	114.4	107.0	[g]	[g]	2.147(6)	228 [d]
$(p\text{-}CH_3OC_6H_4)_4Sn$ ($I\bar{4}$)	15.5	52.1	112.5	108.0	121.9	121.2	2.136(4)	224
$(p\text{-}CH_3SC_6H_4)_4Sn$ ($I\bar{4}$)	13.8	49.2	106.2	111.1	118.2	125.4	2.123(7)	200
$(m\text{-}CH_3C_6H_4)_4Sn$ [i] ($I4_{1/a}$)	37.5	40.7	109.3	109.5	121.7	119.8	2.150(3)	[g]
$(C_6F_5)_4Sn$ [j] ($I4_{1/a}$)	41.9	53.2	105.5	111.5	124.1	119.6	2.126(8)	[g]

[a] See text. [b] $\nu_{ave}(Sn\text{–}C) = 1/4(\nu_s(Sn\text{–}C) + 3\nu_{as}(Sn\text{–}C))$. [c] P.C. Chieh and J. Trotter, J. Chem. Soc. A, (1970) 911; L.M. Engelhardt, W.-P. Leung, C.L. Raston, and A.H. White, Austral. J. Chem., 35 (1982) 2383. [d] I. Wharf, unpublished data. [e] A. Karipides, A.T. Reed, D.A. Haller, and F. Hayes, Acta Cryst. B, 33 (1977) 950. [f] For $(2\text{-}C_4H_3S)_4Si$, A. Karipides, A.T. Reed, and R.H.P. Thomas, Acta Cryst., B, 30 (1974) 1372. [g] Data not available. [h] Ref. 23. [i] Ref. 18. [j] Ref. 29.

Å in the former compound as well. Notwithstanding the uncertainties associated with the location of hydrogen atoms using X-ray diffraction methods, the many short contacts within Van der Waals distances show the close packing in the crystals while those involving the methyl hydrogens require the methyl groups to be rigidly oriented in these lattices. Comparison of the projection of the structure of $(p\text{-}CH_3OC_6H_4)_4Sn$ on the *ab* plane (Fig. 2) with that given by Ismailzade [3] shows how the electronically preferred conformation of the methoxy group co-planar with the phenyl ring is retained in the solid state even though this causes considerable steric strain in both the molecular and crystal structure of this compound. Likewise, the planar conformation for the *p*-thioanisyl system suggests some $3p \cdots \pi$ conjugation occurs across the C–S bond, as does the C_{sp^2}–S bond length of 1.758 Å when compared with values for *d*(C–S), 1.80–1.82 Å [20,24–26], and *d*(C=S), 1.60–1.66 Å [27,28].

The effect of substitution at the phenyl ring on the structures of tetraaryltins is summarised in Table 4. As noted earlier [29] *para*-substituents cause a change in space group from $P\bar{4}2_1c$ to $I\bar{4}$, which are both close-packed arrangements, and the crystal packing as shown by changes in σ (the angle between the projection of the Sn–C(1) bond on the *ab* plane and the *a* axis, i.e., the angle of rotation of the molecule about the *c* axis) and α (the angle between the aryl ring plane and the C(1)–Sn–C(1) $(\bar{x}, \bar{y}, z)$ plane). Increasing the size of the *para*-substituent causes a decrease in *d*(Sn–C) with the value for $(p\text{-}CH_3SC_6H_4)_4Sn$ significantly less than that for tetra(*p*-tolyl)tin. The thioanisyl compound shows the greatest change in the molecular parameters with θ (angle C(1)–Sn–C(1) $(\bar{x}, \bar{y}, z)$) smaller than β (angle C(1)–Sn–C(1) $(y, \bar{x}, \bar{z})$) and more distortion at C(1) as shown by the greater difference between γ (angle Sn–C(1)–C(2)) and δ (angle Sn–C(1)–C(6)), as compared with most of the tetraaryltin compounds in Table 4. The other exception in the Table is $(C_6F_5)_4Sn$ which even though it has a non-close-packed space group $(I4_1/a)$ to reduce intermolecular repulsions, has almost the same amount of distortion as $(p\text{-}CH_3SC_6H_4)_4Sn$, as well as the same, short tin–carbon bond. In contrast, tetra(*m*-tolyl)tin which has the same non-close-packed structure, shows the least deviation from the "ideal" tetrahedral bond angles expected for an isolated molecule and no shortening of the tin–carbon bond.

Substitution of the hydrogen at the *para*-position by a methoxy group causes a decrease in ν_{ave}(Sn–C) as shown in Table 4, which the earlier report [3] of *d*(Sn–C) 2.17 Å for tetra(*p*-anisyl)tin when compared with values for tetraphenyltin, implied might be due to some weakening of the tin–carbon bond on substitution of *para*-hydrogen by CH_3O. However, for $(p\text{-}FC_6H_4)_4Sn$ (ν_{ave}(Sn–C) 230 cm^{-1}) and $(p\text{-}ClC_6H_4)_4Sn$ (ν_{ave}(Sn–C) 210 cm^{-1}) [8] the similar decrease was ascribed to the increase in mass of the *para*-substituent (X) and/or coupling of ν(C–X) with ν(Sn–C). Our results show some tin–carbon bond shortening as *para*-hydrogen is replaced by CH_3O and then CH_3S. Thus the decreases seen for ν_{ave}(Sn–C) are more probably due to the above kinematic effects rather than to electronic changes in the tin–carbon bond. Indeed, this bond shortening as well as the accompanying molecular distortion is more likely caused by the increasing intermolecular "compression" in these close-packed structures due to the presence of larger *para*-substituents on the phenyl rings. The effect of a wider range of *para*-substituents, e.g. larger, less-symmetric, or ionic on the crystal structures of tetraaryltins will be of interest in this respect.

Acknowledgement

The financial support of the "Fonds FCAR Programme ACSAIR" of le Gouvernement du Québec is gratefully acknowledged as well as the Department of Chemistry, McGill University, where part of this work was carried out.

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