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Metal–metal spin coupling through chalcogenides. Correlation of $^2J(^{119}Sn, ^{119}Sn)$ with molecular structure. Crystal structure of $[(2\text{-}MeC_6H_4CH_2)_3Sn]_2O$ and $[(2\text{-}MeC_6H_4)_3Sn]_2O$

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Abstract

The dependence of $^2J(^{119}Sn\ ^{119}Sn)$ on the molecular structure of compounds containing the Sn–X–Sn moiety (where X = 0, S, Se, Te) has been investigated using new and earlier ^{119}Sn solution and solid-state NMR and X-ray structural data for 46 linear and cyclic organotins. While $^2J(^{119}Sn, ^{119}Sn)$ is found generally to vary with the size of the Sn–X–Sn angle for the chalcogenides, there is considerable scatter of the data. A plot of $^2J(^{119}Sn, ^{119}Sn)$ (in Hz) vs. the angle Sn–X–Sn (in deg.) for compounds with X = O gives a straight line defined by the equation: angle Sn–O–Sn = 0.087 $^2J(^{119}Sn, ^{119}Sn) + 98.6$ with $r = 0.990$ and $n = 8$ (assuming no sign change in $^2J(^{119}Sn, ^{119}Sn)$). The quantity of data presently available does not permit regression analysis to be carried out for X = S, Se and Te. The range of Sn–X distances for a given X is small, and no meaningful relationships with $^2J(^{119}Sn, ^{119}Sn)$ or the Sn–X–Sn angle were found. The X-ray crystal structures of $[(2\text{-methylbenzyl})_3Sn]_2O$ and $(o\text{-tolyl}_3Sn)_2O$ are reported.

Introduction

The synthesis, structure and properties of main group and transition metal bimetallic μ-chalcogenide compounds M–X–M′ (X = O, S, Se, Te) are of consider-

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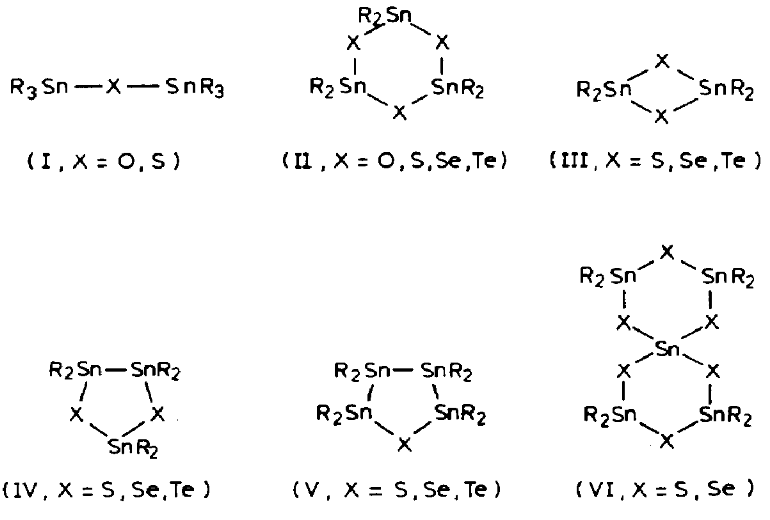
able interest in catalysis and bioinorganic chemistry studies. A number of reports of scalar J coupling constants $^{2}J(\mathrm{M, M'})$ have appeared [1–11] for compounds where both M and M′ contain spin $\frac{1}{2}$ nuclei. The observation of M–M′ spin coupling can provide evidence for the presence of the M–X–M′ linkage in a molecule [2,15] and may also offer a sensitive probe of molecular structure [4–6,9]. At a simple level of analysis, for a system M–X–M′ in which the Fermi contact term provides the largest contribution to the J coupling, the magnitude of $^{2}J(\mathrm{M, M'})$ will depend on the amount of s-character in the bonding orbitals. For a closely related group of compounds, changes in the hybridisation of the bridging chalcogenide X should be reflected by changes in the M–X–M′ angle and the M–X and M′–X distances. Thus comparison of $^{2}J(\mathrm{M, M'})$ values may provide information about these structural parameters. To date, however, the structural dependence of $^{2}J(\mathrm{M, M'})$ in bimetallic μ-chalcogenide compounds has not been examined in detail for any system M and M′. Limited data on the structural dependence of tungsten–tungsten coupling through oxygen, $^{2}J(^{183}\mathrm{W}, {}^{183}\mathrm{W})$ have been presented [4] for heteropolytungstates. Also, in a preliminary report [9], the effect of substituents and solvents on $^{2}J(^{119}\mathrm{Sn}, {}^{119}\mathrm{Sn})$ was examined for a number of hexaorganodistannoxanes; the values reported appeared consistent with a dependence of $^{2}J(^{119}\mathrm{Sn}, {}^{119}\mathrm{Sn})$ on the size of the Sn–O–Sn angle. Results on octaorganospirobis(cyclotristannachalcogenides) have however previously been interpreted [8] in terms of a correlation of $^{2}J(^{119}\mathrm{Sn}, {}^{119}\mathrm{Sn})$ with D(Sn–X).

In order to examine more fully the structural dependence of J coupling through oxygen and other chalcogenides, we have collected new and published ^{119}Sn NMR and X-ray structural data for a large number of organotins containing the linkage Sn–X–Sn, where X = O, S, Se and Te.

In all the compounds to be discussed the tin atoms have a coordination number of four, while that of the chalcogens is two. They fall into the following structural types, see Scheme 1.



Scheme 1.

In order to increase the amount of data available for compounds of type I we have determined the crystal structures of $[(2\text{-methylbenzyl})_3Sn]_2O$ and (*o*-$\text{tolyl}_3Sn)_2O$.

Results and discussion

Solution state, and in several cases high-resolution solid state, ^{119}Sn NMR data for 46 organotins are given in Table 1, together with key structural parameters; this table includes some solid state NMR data which are at present in the press [44]. Figure 1 shows a plot of $^2J(^{119}Sn, ^{119}Sn)$ vs. the angle Sn–X–Sn for those compounds for which these data are available. There is apparently a direct relationship between the two quantities; however, it is somewhat problematic to compare solid-state structural data with solution NMR data because of the possible structural changes accompanying crystallisation. Experiments have shown [9] that tin chemical shifts and $^2J(^{119}Sn, ^{119}Sn)$ values for certain hexaorganodistannoxanes can be very sensitive to solvent effects: for this reason compounds **1–4**, **6–10**, **18** and **19** have been studied in non-coordinating solvents. That solvents can have a very considerable influence on ^2J is shown by the following values [9]: ^2J for **6** in $CDCl_3$ is 621 Hz, in CH_2Cl_2 643 Hz, and in the solid state 991 Hz. The smaller coupling constants in solution indicate a bending of the molecule which results in a decrease of the Sn–O–Sn angle. In compounds for which such an angle change is not possible because of the size of the organic residues (e.g. $\text{t-Bu}_3Sn\text{–}O\text{–}Sn\text{-t-Bu}_3$) or because of the rigid molecular skeleton (e.g. $(\text{t-Bu}_2SnO)_3$) the solid state and solution NMR data are extremely similar.

Compounds containing dipolar Sn–X moieties sometimes associate strongly in solution [16]; however, the values for the tin–carbon coupling constants $^1J(^{119}Sn, ^{13}C)$ in the hexaalkyldistannoxanes and hexaalkyldistannthianes were ca. 400 Hz, indicative [17] of unassociated, tetracoordinated tin. Further, except for **16** (see Experimental), there was no evidence for dynamic effects in the NMR spectra of dilute solution ($< 30\%$ w/v) of the compounds studied. X-ray crystal structure determinations carried out on cyclic tristannoxanes (see Table 1) show them to be unassociated in the solid state, so that it seems reasonable to rule out their association in solution.

If only the oxygen compounds are considered and the solid-state NMR data included, there appears to be a linear relationship between ^2J and the angle Sn–O–Sn: a regression analysis of the angle Sn–O–Sn and the $^2J(^{119}Sn, ^{119}Sn)$ data for the distannoxanes **1**, **3**, **6**, **14**, **16** (solid-state data for **1**, **3** and **6**) and **18–20** (solid-state value for **19**) gives the following equation:

$$\text{angle (Sn–O–Sn)} = 0.086\ ^2J(^{119}Sn, ^{119}Sn) + 98.6;\ r = 0.990\ (n = 8)$$

This indicates that $^2J(^{119}Sn, ^{119}Sn)$ will change sign at an Sn–O–Sn angle of ca. 99°, rather than as suggested by Wrackmeyer [18] at ca. 110°. It should be noted that the structural parameters for **16** were obtained by electron diffraction [32*]. The danger of such a statistical treatment is, however, seen for compound **9**: while the crystal structure shows clearly that the angle Sn–O–Sn is 180°, the solution NMR J value

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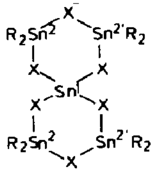
* Reference numbers with asterisks indicate notes in the list of references.

Table 1

NMR and structural data for organotins containing the Sn–X–Sn structural unit

Compound	^2J(Sn, Sn) [a]	δ(^{119}Sn) [b]	NMR ref.	Sn–X–Sn angle [c]	*D*(Sn–X) [d]	X-ray ref.
(t-Bu$_3$Sn)$_2$O (1)	910[932]	−37.1	[e]	180.0	195.4	18
		[−39.1]		180.0 [k]	193.6 [k]	43
(t-Bu$_2$PhSn)$_2$O (2)	841	−53.9	[e]			
(2-MeBz$_3$Sn)$_2$O (3)	721[895]	22.5				
		[6.5]	[e]	180.0	189.3	[e]
(s-Bu$_3$Sn)$_2$O (4)	681	24.7	9			
(cyclo-Hex$_3$Sn)$_2$O (5)	649	−7.6	10			
(Bz$_3$Sn)$_2$O (6)	646[991]	9.2				
		[11.1]	9[[e]]	180.0	191.9	33
(i-Pr$_3$Sn)$_2$O (7)	643	20.7	9			
(Ph$_2$t-BuSn)$_2$O (8)	629	−67.5	[e]			
(*o*-Tol$_3$Sn)$_2$O (9)	564	−120.2	[e]	180.0	192.2	[e]
(Neophyl$_3$Sn)$_2$O (10)	558	57.7	9[[e]]			
		[56.0 [f]]				
(Bu$_3$Sn)$_2$O (11)	473	84.8	9			
(Pr$_3$Sn)$_2$O (12)	467	83.7	9			
(i-Bu$_3$Sn)$_2$O (13)	463	77.7	[e]			
(Ph$_3$Sn)$_2$O (14)	440	−83.1	9	137.3	195.5	24
	[g] [h]	[−76.3, −81.7 [h]]	[[e]]			
(*p*-Tol$_3$Sn)$_2$O (15)	440	−73.2	[e]			
(Me$_3$Sn)$_2$O (16)	418 ± 10	109.5	[e]	140.8	194.0	32
(Et$_3$Sn)$_2$O (17)	377	94.6	[e]			
(t-Am$_2$SnO)$_3$ (18)	412	−72.9	7	134(av.)	196(av.)	7
(t-Bu$_2$SnO)$_3$ (19)	395[396]	−84.3				
		[−85.8]	7[[e]]	133.1	196.5	7
(Mes$_2$SnO)$_3$ (20)	320	−104.0	[e]	120.8	196	34
(Bz$_3$Sn)$_2$S (21)	227	28.0	[e]	105.2	240.8(av.)	1
				104.2 [k]	239.9(av.) [k]	43
(Ph$_3$Sn)$_2$S (22)	223	−51.7	[e]	107.4	239(av.)	35
	[g]	[−50.0, −53.2]	[[e]]			
(Bu$_3$Sn)$_2$S (23)	213	83.0	[e]			
(Mes$_2$SnS)$_2$ (24)	168	−25.8	11			
(t-Bu$_2$SnS)$_2$ (25)	114[g]	124.0				
		[116.2 [i]]	[e][[e]]	85.8	244	27
(Ph$_2$SnS)$_3$ (26)	207[197]	16.2				
		[28.2]	12[44]	104.7	240	12
((CH$_2$)$_5$SnS)$_3$ (27)	205	99.5	13	100.3	241	13
(Me$_2$SnS)$_3$ (28)	194[193]	131.0				
		[125.2]	3[44]	103(av.)	241(av.)	36
((CH$_2$)$_6$SnS)$_3$ (29)	174	132.0	13	101.8	240	13
t-Bu$_6$Sn$_3$S$_2$ (30)	220	115.3, 182.3 [j]	[e]	108.3	242	14
t-Bu$_8$Sn$_4$S (31)	217		[e]	116.5	242(av.)	28
(C$_6$F$_5$Sn)$_4$S$_6$ (32)	275	46.4	11	103.7(av.)		11
(Ph$_2$SnSe)$_3$ (33)	250	−44.9	12			
(Me$_2$SnSe)$_3$ (34)	237[202]	42.0				
		[32.6]	3[44]	100.8	253	3
t-Bu$_6$Sn$_3$Se$_2$ (35)	205	122.6, 161.6 [j]	[e]	105.9	252	14

Table 1 (continued)

Compound	^{2}J(Sn, Sn)[a]	δ(^{119}Sn)[b]	NMR ref.	Sn–X–Sn angle[c]	D(Sn–X)[d]	X-ray ref.
$Me_6Sn_3Se_2$ (**36**)	150	21.0, 82.0[j]	3	95.3	253	3
$(t\text{-}Bu_2SnSe)_2$ (**37**)	37	51.2	[e]	82.5	255	27
$t\text{-}Bu_8Sn_4Se$ (**38**)	196		[e]	112.5	254	28
$(Ph_2SnTe)_3$ (**39**)	264	−204.3	12	97.5	273	12
$(Me_2SnTe)_3$ (**40**)	250	−195.0	3	96(av.)	275	37
$(tBu_2SnTe)_2$ (**41**)	29	−125.2	[e]	80.1		27
$t\text{-}Bu_6SnTe_2$ (**42**)	159	−106.9, 63.9[j]	[e]	101.9	275	14
$t\text{-}Bu_8Sn_4Te$ (**43**)	158		[e]	107.4	274.6	28
						
R = i-Pr; X = S (**44**)	295 (Sn1–Sn2)	89.9	8	104.4	238.4, 242.8	8
	137 (Sn2–Sn2′)	116.4		103.5	239.3	
R = t-Bu; X = S (**45**)	348 (Sn1–Sn2)	84.1	8	109.8(av.)	237, 242(av.)	8
	113 (Sn2–Sn2′)	108.4		109.4	241(av.)	
R = i-Pr; X = Se (**46**)	310 (Sn1–Sn2)		8	102.5	250.7, 255.1	8
	156 (Sn2–Sn2′)	87.1		101.1	251.2	

[a] ^{2}J(^{119}Sn, ^{119}Sn) in Hz. [b] In ppm vs. Me_4Sn. Solvent benzene except for **16** (n-heptane), **1**, **13**, **17**, **18**, **20**, **25–30**, **35–38**, **40–46** ($CDCl_3$). NMR data in square brackets are solid-state values. [c] In deg. [d] In pm. [e] This work. [f] Lit. [44] 57.3 ppm. [g] Not observed. [h] Lit. [44] ^{2}J 421 Hz, δ(Sn) −75.2, −80.5 ppm. [i] Lit. [44] 117.3, 119.4 ppm. [j] The first value is for the Sn–Sn unit, the second for the isolated tin. [k] At 190 K. [l] Abbreviations used: neophyl = $PhMe_2CCH_2$, t-Am = $EtMe_2C$, Mes = Mesityl, Bz = benzyl.

of 564 Hz indicates an angle of ca. 155° when the regression equation is used. Clearly, as in the case of **6** and to a lesser extent **3**, the *J*-value (i.e. bond angle Sn–O–Sn), though apparently not the chemical shift, changes considerably when the sample is dissolved. This is perhaps the first case in tin NMR where the coupling constant rather than the chemical shift serves as a probe for structural differences between the solid state and a solution.

The statistical basis for carrying out such regression analyses for the other couplings ^{2}J(^{119}Sn–X–^{119}Sn) (X = S, Se, Te) is at present too small. It is further narrowed by the fact that many of the compounds whose structures are known are of a cyclic nature. In molecules for which multiple spin coupling pathways are possible, the observed couplings are equal to the algebraic sum of the individual couplings [19]. For four-membered rings there are two identical pathways, while in 5- or 6-membered rings there are two different routes (^{2}J and ^{3}J or ^{4}J respectively). The assumption that the ^{4}J pathway can be neglected seems reasonable in the present state of knowledge, but this is certainly not the case for ^{3}J(Sn, Sn): thus in

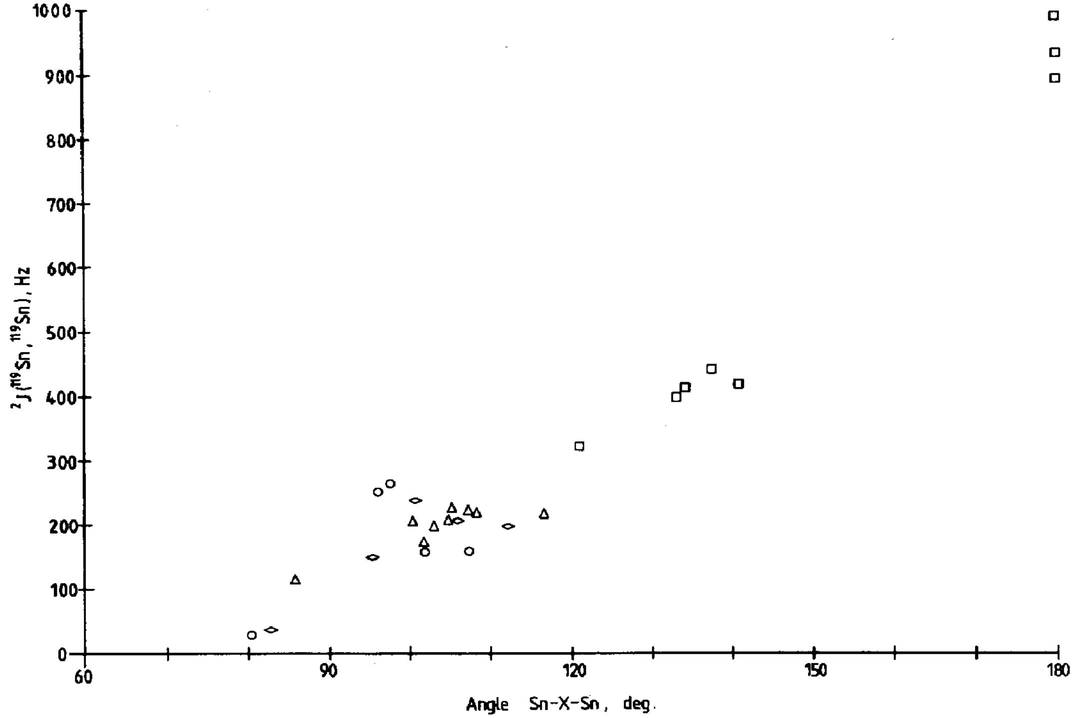


Fig. 1. Plot of $^2J(^{119}Sn\text{-}X\text{-}^{119}Sn)$ vs. angle Sn–X–Sn; X = O (□), S (△), Se (◇), Te (○).

linear $Bu_{10}Sn_4$ and $Bu_{12}Sn_5$ $^3J(Sn, Sn)$ is 233 and 220 Hz respectively [20] and in $X(t\text{-}Bu_2Sn)_4X$ the values are 284 Hz (X = Br) [21] and 307 Hz (X = 1) [22]. It is thus at present not possible in the case of the five-membered rings IV and V to determine the contribution of ^2J to the measured coupling. Because of the identical coupling paths, the observed value in the four-membered rings III must be divided by two to obtain ^2J.

A statistical evaluation is also made more difficult by the fact that in the case of the six-membered rings $(R_2SnX)_3$ the bond angle Sn–X–Sn becomes smaller on going from the sulfides to the tellurides although the coupling constant increases. The values for the spirocyclic tin atoms in **44**–**46** are also atypical since these atoms bear four electronegative substituents.

When it becomes feasible to deal with these problems, it should be possible to obtain regression analysis equations connecting other tin–chalcogenide–tin bond angles and the corresponding ^2J values. Such equations should be of some value for the qualitative prediction of Sn–X–Sn angles, but should be most reliable for evaluating relative changes in the structure of a given compound resulting from medium effects. It must be remembered that investigations of the dependence of solution NMR parameters on molecular structures determined for crystalline solids suffer from inherent uncertainties about the retention of the solid state structure in solution [23], and that specific solvent effects and solid-state packing effects provide additional sources of error.

Glidewell has argued [24] that electronic, rather than steric, factors normally determine the amplitude of the M–X–M angle for a variety of elements M and X, with greater electron donation by ligands on M leading to an increase in the angle.

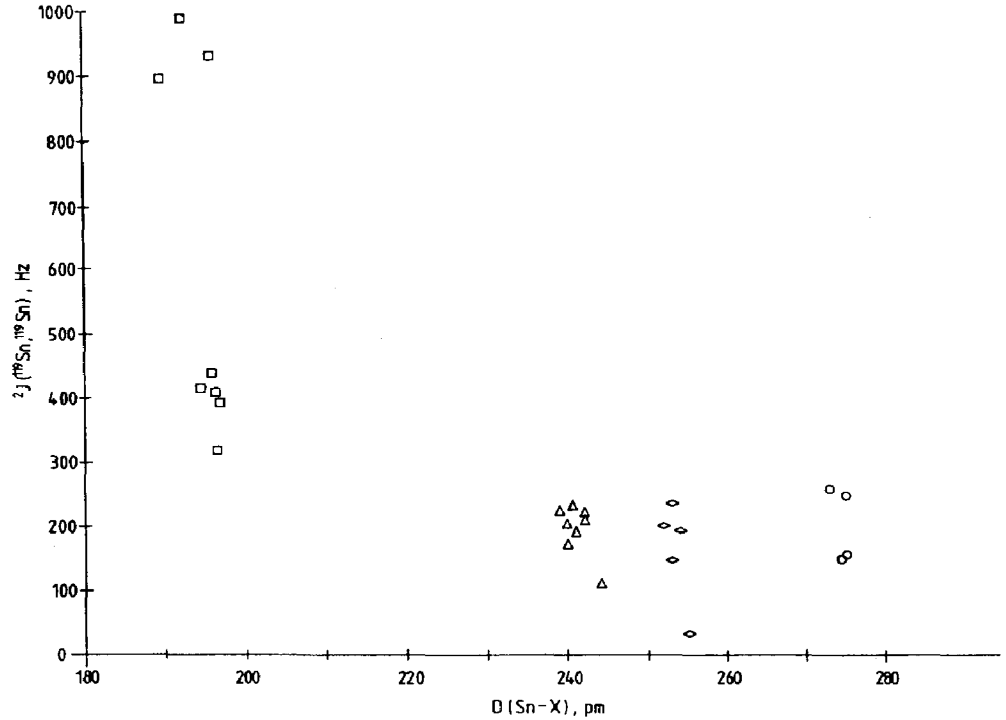


Fig. 2. Plot of $^{2}J(^{119}Sn-X-^{119}Sn)$ vs. Sn–X bond length; X = O (□), S (△), Se (◇), Te (○).

Following these arguments, an increase in the electron-donating ability of the organic substituents in a hexaalkyldistannoxane should result in an increase in the Sn–O–Sn angle. This appears to be the case, as can be seen from a consideration of the $^{2}J(^{119}Sn, ^{119}Sn)$ values for the distannoxanes **4**, **6**, **8**, **10–12** and **14–16**, all measured in benzene solvent.

The lack of X-ray data for distannoxanes with Sn–X–Sn angles between 140 and 180° led us to prepare hexa(*p*-tolyl)distannoxane (**15**) which would, it was hoped, have a larger Sn–O–Sn angle than the hexaphenyl derivative **14** due to the presence of the six electron-donating methyl groups [24]. However, neither the tin chemical shift nor ^{2}J changed appreciably. Comparison with the *o*-tolyl derivative suggests that steric effects are most important in determining the size of the Sn–X–Sn angle in the latter (which also shows a considerable high-field shift of the tin resonance). The utility of the tin–tin coupling constant as a diagnostic for the Sn–X–Sn moiety [9] was again demonstrated during the preparation of the *p*-tolyl derivative. The literature procedure followed [25] identifies $(p\text{-tolyl})_3SnOH$ as the reaction product; however, the presence of tin–tin J coupling in the tin NMR spectrum of this product (which has the same m.p. as that reported [25,26] for $(p\text{-tolyl})_3SnOH$) in a variety of solvents strongly implies that the earlier structural assignment is incorrect.

We had also expected that the Sn–X distance, D(Sn–X), which like the Sn–X–Sn angle should depend on the *s*-orbital character in the Sn and X bonding orbitals, would be simply related to $^{2}J(^{119}Sn, ^{119}Sn)$. However, a plot of $^{2}J(^{119}Sn, ^{119}Sn)$ vs. D(Sn–X) for 26 compounds (Fig. 2) clearly breaks down into individual groups for each chalcogenide, reflecting the fact that the variation of D(Sn–X) for each chalcogenide is small relative to the difference in D(Sn–X) between chalcogenides.

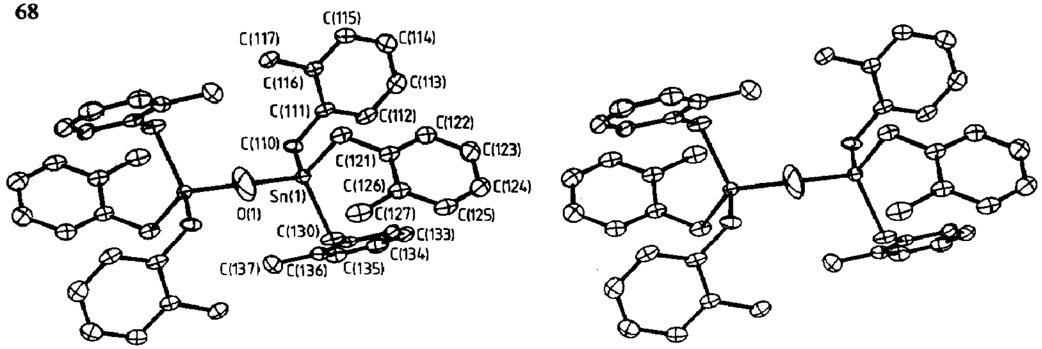


Fig. 3. Stereoscopic view of the hexa(2-methylbenzyl)distannoxane molecule. Thermal parameters are drawn at the 50% probability level.

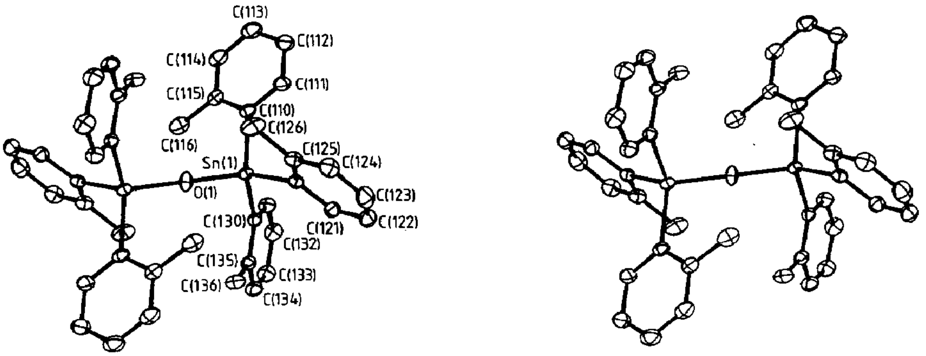


Fig. 4. Stereoscopic view of the hexa(*o*-tolyl)distannoxane molecule. Thermal parameters are drawn at the 50% probability level.

Table 2

Structural data [39*]

	[(2-Methylbenzyl)$_3$Sn]$_2$O	(*o*-Tolyl$_3$Sn)$_2$O
	$C_{48}H_{54}OSn_2$	$C_{42}H_{42}OSn_2$
molecular weight (g mol^{-1})	884.34	800.18
crystal system	triclinic	triclinic
space group (no.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
unit cell		
a (pm)	995.9(1)	919.4(2)
b (pm)	1025.3(2)	1060.1(4)
c (pm)	1077.7(2)	1162.0(5)
α (°)	89.59(1)	64.67(3)
β (°)	72.55(1)	63.94(3)
γ (°)	85.88(1)	68.95(3)
V (nm^3)	1.047	0.899
formula units *Z*	1	1
μ (cm^{-1})	11.18	12.98
number of reflexions	2361	3232
with $\sigma(I)/I <$	0.5	0.5
R-value	0.034	0.037
distances (pm)		
Sn–O	189.3(1)	192.2(1)
Sn–C	215.9(6)–217.2(7)	213.5(4)–214.3(6)
angles (°)		
Sn–O–Sn	180.0(1)	180.0(1)
O–Sn–C	104.7(2)–108.2(2)	107.0(1)–108.2(1)
C–Sn–C	109.7(2)–113.4(3)	110.7(2)–112.0(2)

Table 3

Atomic coordinates, thermal parameters [a] and their e.s.d.'s of $[(2\text{-methylbenzyl})_3Sn]_2O$

Atom	x	y	z	U_{eq}
Sn(1)	−0.06265(4)	0.12374(4)	0.13851(4)	0.043(1)
O(1)	0	0	0	0.216(16)
C(110)	−0.2893(6)	0.1544(6)	0.1869(7)	0.058(5)
C(111)	−0.3314(5)	0.2970(6)	0.1962(6)	0.051(5)
C(112)	−0.3350(6)	0.3680(6)	0.0855(6)	0.051(5)
C(113)	−0.3709(6)	0.5033(7)	0.0980(7)	0.062(6)
C(114)	−0.3980(7)	0.5682(8)	0.2153(8)	0.076(7)
C(115)	−0.3931(7)	0.4984(9)	0.3239(7)	0.075(7)
C(116)	−0.3603(6)	0.3653(8)	0.3146(6)	0.063(6)
C(117)	−0.3009(7)	0.3031(7)	−0.0465(6)	0.064(6)
C(210)	0.0435(6)	0.2982(7)	0.0625(6)	0.062(5)
C(211)	0.1023(6)	0.3539(6)	0.1607(6)	0.054(5)
C(216)	0.0295(7)	0.4597(7)	0.2391(7)	0.066(6)
C(215)	0.0755(9)	0.5128(8)	0.3345(8)	0.081(7)
C(214)	0.2008(10)	0.4601(9)	0.3524(8)	0.084(8)
C(213)	0.2757(7)	0.3570(8)	0.2776(8)	0.071(7)
C(212)	0.2285(6)	0.3009(7)	0.1811(7)	0.060(5)
C(217)	0.3115(7)	0.1847(8)	0.0991(7)	0.081(7)
C(310)	−0.0061(6)	0.0437(7)	0.3038(6)	0.068(6)
C(311)	−0.1328(6)	0.0537(6)	0.4244(6)	0.052(5)
C(312)	−0.2291(7)	−0.0437(6)	0.4539(6)	0.060(6)
C(313)	−0.3460(7)	−0.0286(8)	0.5661(7)	0.072(6)
C(314)	−0.3677(9)	0.0800(9)	0.6449(8)	0.082(7)
C(315)	−0.2741(9)	0.1745(8)	0.6156(7)	0.081(7)
C(316)	−0.1562(8)	0.1620(7)	0.5055(6)	0.063(6)
C(317)	−0.2097(10)	−0.1613(7)	0.3683(8)	0.095(8)

[a] $U_{eq} = \frac{1}{3}[\Sigma_i \Sigma_j u_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j] \times (10^{-2}\ \text{nm}^2)$.

Table 4

Atomic coordinates, thermal parameters [a] and their e.s.d.'s of $(o\text{-tolyl}_3Sn)_2O$

Atom	x	y	z	U_{eq}
Sn(1)	−0.13531(3)	−0.07654(2)	0.18440(2)	0.039(1)
O(1)	0	0	0	0.067(6)
C(110)	−0.3499(5)	0.0850(4)	0.2322(4)	0.043(4)
C(111)	−0.3928(6)	0.1177(5)	0.3464(5)	0.054(5)
C(112)	−0.5275(6)	0.2215(5)	0.3842(6)	0.064(6)
C(113)	−0.6205(7)	0.2981(6)	0.2997(7)	0.083(8)
C(114)	−0.5842(6)	0.2659(6)	0.1885(6)	0.070(7)
C(115)	−0.4503(5)	0.1615(5)	0.1494(5)	0.053(5)
C(116)	−0.4095(8)	0.1319(7)	0.0205(7)	0.082(9)
C(120)	0.0073(5)	−0.1358(4)	0.3108(4)	0.042(4)
C(121)	0.0223(6)	−0.2747(5)	0.4003(5)	0.056(5)
C(122)	0.1116(7)	−0.3221(6)	0.4862(5)	0.067(6)
C(123)	0.1909(6)	−0.2255(6)	0.4779(5)	0.068(7)
C(124)	0.1799(6)	−0.0909(6)	0.3898(5)	0.061(6)
C(125)	0.0852(5)	−0.0417(5)	0.3065(4)	0.048(5)
C(126)	0.0718(7)	0.1097(5)	0.2132(5)	0.064(7)
C(130)	−0.1974(6)	−0.2602(4)	0.1983(4)	0.047(5)
C(131)	−0.3616(6)	−0.2670(6)	0.2509(5)	0.061(6)
C(132)	−0.4117(8)	−0.3830(7)	0.2624(5)	0.076(8)
C(133)	−0.2896(9)	−0.4917(6)	0.2158(6)	0.082(9)
C(134)	−0.1244(8)	−0.4857(5)	0.1634(5)	0.068(6)
C(135)	−0.0762(6)	−0.3715(4)	0.1544(4)	0.050(5)
C(136)	0.1023(7)	−0.3685(6)	0.0961(6)	0.072(7)

[a] See Table 3.

Also, unlike the ^2J(Sn–X–Sn) plot, no strong correlations are found for any of the individual chalcogenides.

Crystal structures [39]*

In each case the molecules of $[(2\text{-methylbenzyl})_3Sn]_2O$ (Fig. 3) and $(o\text{-tolyl}_3Sn)_2O$ (Fig. 4) have an inversion centre; the tin–oxygen–tin fragment is linear and the organic groups are staggered. The tin–oxygen distances (192.2 pm) in the tolyl compound are comparable with those in other stannoxanes (Table 1) and are shorter than the sum of the covalent radii (140 + 66 pm [27]): the methylbenzyl compound has even shorter Sn–O distances (189.3 pm). Since in addition large temperature factors are observed for the oxygen atom, it can be assumed that even in the solid state the linear Sn–O–Sn geometry is slightly distorted. This would agree with the observation that this compound shows the smallest tin–tin coupling observed for a linear distannoxane in the solid state (Table 1).

Crystal data, bond distances and bond angles are given in Table 2, while atomic coordinates and thermal parameters are to be found in Tables 3 and 4.

Experimental

(a) Materials

Distannoxanes were generally prepared either by literature procedures or by alkaline hydrolysis of the corresponding triorganotin chlorides or bromides. These were dissolved in toluene and the solutions heated for 4 h under reflux along with 7 *N* NaOH. After separation of the phases and evaporation of the organic phase the compounds were purified by recrystallisation from toluene. This method was also used to prepare $(Mes_2SnO)_3$ (**20**), instead of the literature method. $(p\text{-tolyl}_3Sn)_2O$ (**15**) was prepared from tetra-*p*-tolyltin by the procedures described by Luijten and Van der Kerk [25] and Krause [30]. Recrystallisation from a benzene/n-hexane solution gave precipitates, except when the solution was allowed to concentrate over a period of several weeks; m.p. 104–106 °C (lit. [26] 107–108 °). The solid product of the hydrolysis of tri-*p*-tolyltin bromide was previously identified as $p\text{-tolyl}_3SnOH$ [25,26]: the observation of tin–tin *J* coupling for this material in solution, however, strongly suggests that it was the oxide.

Compound **16** was prepared by the literature procedure [31] except that NaH was used as the dehydrating agent. As observed previously for $(Bu_3Sn)_2O$ [9], $^2J(^{119}Sn, ^{119}Sn)$ for $(Me_3Sn)_2O$ was very sensitive to solvent effects. Sharp resonances were obtained in more polar solvents (linewidths were 12–16 Hz, presumably due to reversible self-association on the NMR time scale). Because the ^{117}Sn and ^{119}Sn satellites were fused, $^2J(^{119}Sn, ^{119}Sn)$ was calculated from the centre of the satellites.

The distannthianes **21**, **22** and **23** were prepared by dissolving the corresponding chlorides or bromides in ethanol and heating the solutions under reflux for 6 h with an aqueous solution of sodium sulphide. Crude products were recrystallised from toluene.

The preparations of **24**, **37** and **41** [27], **31**, **38** and **43** [28] and **10** [29] have been described previously; a sample of $(\text{neophyl}_3Sn)_2O$ (**10**) was kindly provided by Dr. P.J. Smith (International Tin Research Institute, London).

(b) NMR spectroscopy

Solution ^{119}Sn spectra were obtained at ca. 305 K either with a Bruker WM 400 spectrometer at 149.21 MHz or with a Bruker WH 90 at 33.54 MHz. Inverse gated decoupling was used; repetition rates were typically 4 s. Solutions of the organotins in protio solvents (0.3 g/ml or less) were run with a concentric tube containing a deuterated lock solvent. The digital resolution was 2 Hz/pt or better; chemical shift values are accurate to at least ±0.1 ppm. High-resolution solid-state ^{119}Sn NMR spectra were recorded on a Bruker MSL-200 spectrometer under CP/MAS conditions (74.63 MHz, spinning speed ca. 3–4 kHz, contact time 5 ms, repetition rate 5–10 s). Isotropic chemical shifts were determined from spectra containing many sidebands by recording two spectra at different spinning speeds.

(c) Structure determinations [39]*

The reflections were measured using an Enraf–Nonius CAD-4 diffractometer, Mo-K_α-irradiation and a graphite monochromator. The positions of the tin atoms were determined from Patterson syntheses, those of the oxygen and carbon atoms from subsequent difference Fourier syntheses. Anisotropic temperature factors were used in the refinement calculations. Hydrogen atoms were taken into account with an ideal geometry and a common isotropic temperature factor. The calculations were carried out on an IBM 3081 K computer (Regional University Computing Centre, University of Bonn): the programmes SHELX [40], ORTEP [41] and KPLOT [42] were used. Structural data are given in Tables 2–4. Tables of thermal parameters and lists of observed and calculated structure factors are available from the authors.

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