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LONG-RANGE TIN–TIN COUPLING CONSTANTS

II *. TWO-BOND COUPLING VIA CARBON

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Summary

Tin-119 and carbon-13 NMR data for a total of 34 compounds containing the grouping Sn–C–Sn (C is either sp^3- or sp^2-hybridised) are presented and discussed. In organotin derivatives of alkanes, ^2J(Sn–C–Sn) can only be correlated with ^1J(Sn–C_2) if a sign change for the former coupling is assumed. In most of the compounds of this type studied, ^1J(Sn–CH_3) is, due to rehybridisation and in contrast to the usual situation, larger than ^1J(Sn–C_2); the same is true in some cases for distannylalkenes, the behaviour of which is complicated by changes in the torsional angle about the carbon–carbon double bond. Thus correlation of ^2J(Sn–C–Sn) with other spectral parameters is not possible in these cases. The total tin chemical shift range for compounds $Me_nSn(CH_2MMe_3)_{4-n}$ (M = C, Si, Ge, Sn; $n = 0$–4) is 140 ppm. Incorporation of a ditin fragment in a six-membered ring causes a downfield tin shift of 30 ppm.

Introduction

Although a large body of data is available on tin–carbon coupling constants [2], the amount of information on tin–tin couplings is still relatively small. Studies of compounds containing two to five tin atoms have yielded values of ^1J(Sn–Sn) [3–5] and ^2J(Sn–X–Sn), where X = C [1,6–8], Si [6], Sn [4,6], N, P, As [6], S, Se and Te [9]. Wrackmeyer [6] has determined the sign of ^2J(Sn–Sn) in $(Me_3Sn)_3CH$ as negative.

This paper presents a more comprehensive collection of data on two-bond couplings via sp^2- and sp^3-hybridised carbon atoms, including compounds which

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* For Part I see Ref. 1.

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show the effect of substitution by electronegative atoms on the former coupling. It also includes tin and carbon chemical shifts and tin–carbon coupling constants.

Results and discussion

The ^{119}Sn NMR parameters are contained in Tables 1 and 3. Tables 2 and 4 give the corresponding ^{13}C data. Since we are only concerned with coupling constants via carbon, reduced coupling constants have not been calculated.

Tin–tin and Tin–carbon coupling constants

(a) In organotin derivatives of alkanes. In the following discussion we shall make the almost certainly justified assumption that all values of ^1J(SnC) are negative: a sign determination has been carried out by Wrackmeyer [6] for this coupling in $(Me_3Sn)_3CH$. The magnitude of ^2J(SnSn) varies in an apparently unsystematic

TABLE 1

TIN-119 CHEMICAL SHIFTS AND TWO-BOND TIN–TIN COUPLINGS VIA sp^3-HYBRIDISED CARBON

(Positive signs in parentheses are proposed, all others being assumed negative. The coupling in compound **14** has been found to be negative [9].)

Compound	Structure	$\delta(^{119}Sn)$ (ppm) [a]	^2J(Sn-Sn) (Hz) [b]	Linewidth (Hz)
1	$(Me_3Sn)_2CH_2$	23.3	287	⩽ 4
2	$(Me_2ClSn)_2CH_2$	160.9	253	9
3	$(MeCl_2Sn)_2CH_2$	99.4	266(+)	40
4	$Me_2ClSn^aCH_2Sn^bMeCl_2$	157.3(a)	358	36
		131.0(b)		84
5	$(Me_2BrSn)_2CH_2$	137.6	255	25
6	$(Me_3Sn)_2CHMe$	27.5	162	⩽ 4
7	$(Me_2ClSn)_2CHMe$	171.0	76	5
8	$(MeCl_2Sn)_2CHMe$	109.0	[c]	94
9	$(Me_3Sn)_2CHEt$	19.5	157	⩽ 4
10	$(Me_3Sn)_2CHPh$	17.8	173	⩽ 4
11	$(Me_3Sn)_2CMe_2$	30.9	19(+)	3
12	$(Me_2ClSn)_2CMe_2$	165.3	150(+)	24
13	$(MeCl_2Sn)_2CMe_2$	98.5	625(+)	70
14	$(Me_3Sn)_3CH$	41.0	−309	⩽ 4
15	$(Me_3Sn)_3CEt$	34.1	230	⩽ 4
16	$(Me_3Sn)_3CC_5H_{11}$	35.0	229	⩽ 4
17	$(Me_3Sn)_3CCH_2Ph$	34.7	229	⩽ 4
18	$(Me_3Sn)_3CCH_2OPh$	30.9	220	⩽ 4
19	$(Me_3Sn)_3CCH_2CH_2OPh$	37.8	235	⩽ 4
20	$(Me_3Sn)_4C$	49.8	325	⩽ 4
21	$\overline{CH_2SnMe_2SnMe_2CH_2SnMe_2Sn}Me_2$	−78.5	157 [d]	⩽ 4
22	$(Me_3Sn^aCH_2)_2Sn^bMe_2$	22.2(a)	285	⩽ 4
		45.5(b)		⩽ 4
23	$(Me_3Sn^aCH_2)_3Sn^bMe$	22.5(a)	281	⩽ 4
		67.7(b)		⩽ 4
24	$(Me_3Sn^aCH_2)_4Sn^b$	20.9(a)	281	⩽ 4
		87.4(b)		⩽ 4

[a] vs. Me_4Sn. [b] $^2J(^{119}Sn-^{119}Sn)$. [c] Not measurable. [d] $^1J(^{119}Sn-^{119}Sn)$ 4245 Hz, $^3J(^{119}Sn-^{119}Sn)$ 102 Hz.

TABLE 2

CARBON-13 NMR DATA FOR COMPOUNDS CONTAINING THE Sn–C(sp^3)–Sn RESIDUE (δ vs. TMS in ppm, J in Hz)

Compound	$\delta(Me_3Sn)/^1J(SnC)$		$\delta(C(1))/^1J(SnC)$		$\delta(C(2))/^2J(SnC)$		$\delta(C(3))/^3J(SnC)$	
1	−7.9	320	−14.8	272				
2	1.5	400	4.2	295				
3	9.2	547	19.3	403				
4	1.1	409	10.2	261				
	9.7	508		385				
5	1.0	364	2.5	272				
6	−9.8	314	−1.7	307	14.7	25		
7	0.9	369	17.2	316	12.6	28		
8	7.7	476	33.2	422	11.7	32		
9	−8.6	310	10.9	288	24.4	23	19.7	45
10	−8.5	324	18.1	261	146.7	34		
11	−10.8	299	10.1	341	26.3	18		
12	−1.8	340	29.8	361	23.8	24		
13	6.9	430	49.2	466	22.6	24		
14	−5.9	323	−20.0	−192				
15	−6.4	304	7.9	223	29.5	20	20.4	46
16	−6.4	304	6.0	222	36.7	22	36.1	44
17	−5.9	304	8.0	[a]	41.4	23	144.5	[a]
18	−6.8	318	6.0	[a]	75.3	[a]	158.6	
19	−6.0	309	0.1	[a]	35.7	23	71.6	46
20	−3.4	318	−25.7	107				
21	−8.4[b]	229[c]	−14.4	174[d]				
22	−7.8[e]	328	−12.9	272/282[g]				
23	−8.3[f]	311	−11.7	238/258[g]				
24	−8.2	314	−10.6	250/268[g]				

[a] Not determined. [b] Me_2Sn. [c] ^2J(Sn–Sn–C) 56 Hz. [d] ^2J(Sn–Sn–C) 62 Hz. [e] $\delta(Me_2Sn)$ −6.5 ppm. [f] δ(MeSn) −6.0 ppm. [g] For assignment see text.

manner: as indicated in Table 1, the accuracy of the values is in some cases poor, due to the line width of the tin signals. However, in only one case were we unable to determine ^2J(SnSn). The expected correlation of ^2J(SnSn) with $^1J(Sn_2C)$ (the litera-

TABLE 3

TIN-119 CHEMICAL SHIFTS AND TWO-BOND TIN–TIN COUPLINGS VIA sp^2-HYBRIDISED CARBON IN COMPOUNDS $RCH{=}C(Sn^aMe_3)(Sn^bMe_3)$

(Chemical shifts in ppm vs. Me_4Sn, coupling constants in Hz. Sn^a is *cis* with respect to R.)

Compound	R	$\delta(Sn^a)$	$\delta(Sn^b)$	^2J(Sn–Sn)
25	H	−19.3	−19.3	608
26	Me	−45.0	−15.7	671
27	Bu	−45.6	−15.8	693
28	cyclo-Hex	[a]	[a]	[a]
29	t-Bu	−46.8	−1.1	684
30	Ph	−38.0	−9.6	580
31	CH_2Ph	−44.0	−14.2	643
32	CH_2OMe	−43.9	−9.9	603
33	CH_2OPh	−40.5	−9.4	540
34	OPh	−28.3	−7.2	277

[a] Not measured.

TABLE 4

CARBON-13 NMR DATA FOR COMPOUNDS RCH=C$(SnMe_3)_2$ CONTAINING THE Sn–C(sp^2)–Sn RESIDUE

(Chemical shifts vs. TMS in ppm, coupling constants in Hz. The assignments of the Me_3Sn carbons as a and b are tentative. Except for compound **34**, C(1) shows only one one-bond coupling.)

Compound	$\delta(Me_3Sn^a)/^1J(SnC)$		$\delta(Me_3Sn^b)/^1J(SnC)$		$\delta(C(1))/^1J(SnC)$		$\delta(C(2))/^2J(SnC)$		$\delta(C(3))/^3J(SnC)$	
25	−9.2	330	−9.2	330	157.6	298	142.5	23		
26	−7.4	324	−8.7	329	144.3	400	151.6	22	24.6	79/106
27	−7.1	323	−8.5	323	142.6	399	158.0	26	39.9	73/98
28	−7.0	323	−8.5	327	140.2	319	163.9	18	49.6	69/95
29	−4.5	334	−7.3	327	136.8	320	168.7	25	37.7	41/96
30	−6.7	334	−8.2	329	150.8	404	155.6	26	143.1	55/100
31	−7.1	325	−8.5	330	144.8	[a]	155.5	23	46.1	76/103
32	−6.7	334	−8.5	332	141.1	412	152.2	27	76.4	64/105
33	−7.0	318	−8.5	318	141.1	430	151.1	[a]	71.8	73/110
34	−7.5	348	−8.4	348	113.4	275/307	152.7	18	157.1	–

[a] Not determined.

TABLE 5

NMR DATA FOR MISCELLANEOUS COMPOUNDS REFERRED TO IN THE DISCUSSION

(Chemical shifts in ppm vs. Me_4Sn or TMS, coupling constants in Hz. The preparation of these compounds is described in ref. 21 except for Me_3Sn^tBu, which was first described in ref. 22.)

Compound	$\delta(^{119}Sn)$	$\delta(Me_3Sn)/^1J(SnC)$		$\delta(CH_2)/^1J(SnC)$	
Me_3Sn^tBu	19.5	−12.1	295	21.1	437
$Me_3SnCH_2CMe_3$	−14.4	−8.4	317	31.3	368
$Me_2Sn(CH_2CMe_3)_2$	−27.5	−6.8	297	32.0	346
$MeSn(CH_2CMe_3)_3$	−40.5	−4.7	278	32.8	325
$Sn(CH_2CMe_3)_4$	−53.3	–	–		
$Me_3SnCH_2SiMe_3$	7.6	−8.1	331	−3.9	250
$Me_2Sn(CH_2SiMe_3)_2$	14.1	−8.0	325	−3.9	246
$MeSn(CH_2SiMe_3)_3$	19.2	−5.0	322	−1.0	241
$Sn(CH_2SiMe_3)_4$	23.0	–	–	−0.7	239
$Me_3SnCH_2GeMe_3$	11.6	−8.1	330	−8.1	279
$Me_2Sn(CH_2GeMe_3)_2$	22.3	−6.9	322	−3.6	269
$MeSn(CH_2GeMe_3)_3$	31.9	−7.0	323	−3.7	269
$Sn(CH_2GeMe_3)_4$	40.6	–	–	−1.6	258

ture contains many examples of correlations of this type) cannot be found unless the assumption is made that there is a sign change for $^2J(SnSn)$. On the basis of this assumption, a regression analysis for compounds **1–3**, **5–7** and **9–13** yields (using the signs given in Table 1) the following relation:

$$^2J(SnSn) = -0.221\ ^1J(Sn_2C) - 332\ (r = 0.977)$$

The value for compound **4** is anomalous, possibly due to the differences in effective nuclear charge on the two tin atoms. The data points for compounds **1**, **14** and **20** lie on a completely different straight line: however, the $^1J(Sn_2C)$ values for **14** and **20** are extremely low, perhaps because the tin–carbon bond length is larger.

A further anomalous value is that for the tetrastannacyclohexane **21**: since this is at present the only polystannacycloalkane which has been studied it is perhaps not advisable to speculate on the reasons for the anomaly. However, it seems possible that a four-bond contribution to the coupling is involved.

It is perhaps interesting to note that analysis of the data for related tri- and tetra-tins indicates that the value of $^2J(Sn{-}Sn{-}Sn)$ reported by Wrackmeyer [6] for dodecamethylpentatin (a compound also prepared by us [10]) of 20 Hz may well be of opposite sign to those for the former.

The relationship between the two tin–carbon one-bond coupling constants $^1J(Sn{-}CH_3)$ and $^1J(Sn_2{-}C)$ shows an unexpected trend: in all the compounds investigated except for **11–13**, the former is larger than the latter. This does not correspond to the usual behaviour for compounds, Me_3SnR, Me_2ClSnR or $MeCl_2SnR$ [11], the tin–methyl coupling in which was found to be the smaller of the two (as predicted on the basis of Bent's postulate [12]). Steric factors are apparently not involved: the coupling constants in trimethylneopentyltin (Table 5) which shows a large upfield tin shift (see below) are very similar to those in trimethylethyltin. Replacement of the t-butyl carbon of the neopentyl group by silicon shifts the tin resonance downfield by 22 ppm, while the $Sn{-}CH_2$ coupling decreases by 108 Hz: further downfield shifts occur on replacing silicon by germanium or tin, the behaviour of both values of $^1J(SnC)$ being irregular. The tin chemical shift of **1** corresponds approximately to that of trimethyl-t-butyltin.

The rehybridisation which accompanies substitution in an organotin molecule is obviously complex, as shown by the following data:

	$Me_3Sn-\overset{\star}{C}H_2-SnMe_3$	$Me_3Sn-\overset{\star}{C}H_2-H$	$Me_3Sn-\overset{\star}{C}H_2-Cl$
$^1J(Sn-CH_3)$	320	336	356
$^1J(Sn-\overset{\star}{C}H_2)$	272	336	324
$^1J(\overset{\star}{C}-H)$	124	125	145.6
$^2J(Sn-\overset{\star}{C}-H)$	60	54	19
$\Sigma\, ^1J(Sn-C)$	1232	1344	1392

Replacement of a proton in tetramethyltin by an electronegative residue leads to a large increase in $^1J(\overset{\star}{C}H)$ and a small decrease in $^1J(Sn\overset{\star}{C})$, while replacement by an electropositive residue leads to a small decrease in $^1J(\overset{\star}{C}H)$ but a large decrease in $^1J(Sn\overset{\star}{C})$. Various correlations with electronegativity are possible, including that of the sum of the one-bond tin–carbon couplings with substituent electronegativity. The behaviour of ^2J(SnH) has been rationalised by de Poorter [13] on the basis of Pople's [14] theory.

The "crossover" in the magnitudes of ^1J(SnC) on going from compound **10** to compound **11** is merely the result of rehybridisation, since the coupling constant trends in for example compounds **1–3**, **6–8** or **1**, **6**, **11** are clearly linear.

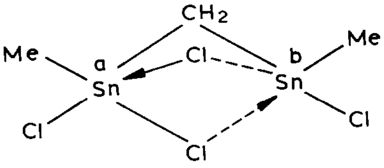
(b) In organotin derivatives of alkenes. Though no sign determination for ^2J(SnSn) has been carried out, it seems likely that all the couplings measured are positive. This can be argued both on the basis of precedent (^2J(HH) is negative in methane, positive in ethylene, ^2J(SnCH) positive in tetramethyltin [15] but negative in tetravinyltin [16]) and on the basis of the magnitude of $^1J(Sn-C(sp^2))$. The value of ^2J(SnSn) shows no clear correlation with the spectral parameters: the presence of an electronegative oxygen residue decreases the coupling greatly, while Wrackmeyer [8] has shown that an intermediate value of 443 Hz is observed in a 1,1-distannylallenyl fragment. One factor obviously involved, but difficult to quantify, is the torsional angle about the C=C double bond.

The two values of ^1J(SnC) for the trimethyltin residues in each compound are very similar, differing by a maximum of 7 Hz. In principle two values of ^1J(Sn–C=) should be observed, but this is in fact only the case for the distannyl vinyl ether **34**: this probably results from the electronegativity difference between hydrogen (and carbon) and oxygen.

The *cis*- and *trans*-tin–carbon coupling constants over three bonds show the general behaviour that the *trans* coupling is larger, though in several cases by only 35–40%. In the same compounds, the *trans*-tin–proton coupling is generally ca. 70–80% larger than the *cis* coupling. It is also interesting to note that the *trans*-tin–carbon coupling varies only over a small range (95–110 Hz) while the range for the *cis*-coupling is much larger (41–79 Hz).

Tin and carbon chemical shifts

(a) In organotin derivatives of alkanes. The distannyl compounds **1–8** and **11–13** can be considered as derivatives of methane, ethane and propane. There is a difference between the behaviour of the tin shifts in the group **1**, **6**, **11** (steady downfield shift) on the one hand and **2**, **7**, **12** and **3**, **8**, **13** on the other hand: here a downfield shift of 10 ppm (**2** → **7**, **3** → **8**) is followed by an upfield shift (**7** → **12**, **8** → **13**). In compound **4** the shift for Sn^b is clearly anomalous within this group of compounds, but is in fact comparable to that of Me_2SnCl_2, while the other dichlorotin shifts are 20–30 ppm to higher field. This indicates a tendency to intramolecular pentacoordination (which is no longer favourable in compound **4**) as shown.



(**4**)

The slightly smaller values for $^1J(Sn–C(1))$ in **4** (compared with **2** and **3**) tend to support this hypothesis. The line widths of the signals for the halogenotin compounds vary in an unsystematic manner: we have previously shown [17] that the linewidth for diisopropyltin dibromide is temperature-dependent while that of triisopropyltin bromide is not.

Compound **21**, the tetrastannacyclohexane, shows a downfield shift of ca. 30 ppm when compared with Me_6Sn_2, though the coupling constant $^1J(Sn–Sn)$ is comparable in magnitude [3]. Gielen [18] has observed a similar downfield shift for the corresponding octaphenyltetrastannacyclohexane.

The tin chemical shifts for compounds of the type $Me_nSn(CH_2MMe_3)_{4-n}$ ($M = C$, Si, Ge, Sn; $n = 0–4$) (Tables 1 and 5) show a systematic upfield shift (presumably due to steric compression) for $M = C$ with decreasing n, while for $M = Si$ and Sn a systematic downfield shift is observed: thus for these compounds (all formally tetraalkyltins) a total shift range of 140 ppm is observed. We have so far been unable to prepare the corresponding compounds with $M = Pb$.

(b) In organotin derivatives of alkenes. The tin chemical shifts in $RCH{=}C(Sn^aMe_3)(Sn^bMe_3)$ vary over a range of ca. 27 ppm for the tin *cis* to R (Sn^a) and ca. 18 ppm for that *trans* to R (Sn^b). Assignments were checked in some cases by studying the products of deuterostannation and measuring $^3J(SnD)$. These results, together with some as yet unpublished, suggest that tin chemical shifts in distannyl alkenes can be assigned using increment values obtained from monostannyl alkenes.

The carbon chemical shifts lie in the expected ranges and require no further comment: the assignments of the methyltin carbons in Table 4 are as yet only tentative.

Experimental

The NMR spectra were recorded with Bruker FT NMR spectrometers (WM-250 and HFX-90 for ^{119}Sn, WP-80 for ^{13}C) in 10 mm tubes using $CDCl_3$ as solvent and lock substance. Probe temperatures were ca. 30°C. The preparation of most of the compounds has been described elsewhere: compounds **1**, **6**, **9**, **10**, **11** and **14** in ref. 4; compounds **15**–**19** and **25**–**34** in ref. 19; compounds **1**–**4**, **6**–**8**, **11**–**13** in ref. 20. The preparation of compounds **5** and **21**–**24** will be described in ref. 21. In each case pure compounds, characterised by elemental analysis as well as spectroscopic techniques, were used.

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