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FOURIER TRANSFORM NMR SPECTROSCOPY OF ORGANOTIN COMPOUNDS

IX *. GEMINAL TIN—TIN COUPLING CONSTANTS OF THE TYPE ^2J(Sn—C—Sn)

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Summary

Geminal tin—tin coupling constants ^2J(Sn—C—Sn) are presented for a number of organotin compounds and discussed in terms of other coupling data. Chemical shift data have also been obtained; particularly noteworthy is the tin chemical shift difference of ca. 40 ppm between the two tin nuclei in 7,7-bis(trimethylstannyl)norcarane.

Introduction

The advent of Fourier transform NMR spectroscopy has made the study of magnetically active nuclei which are present in low abundance much easier. Of the organometallic compounds of Group IVB elements, organotins are especially interesting for the spectroscopist, since the presence of two magnetically active isotopes (^{117}Sn and ^{119}Sn) in similar amounts (7.65 and 8.68%, respectively) simplifies the problem of obtaining coupling constants of the type ^nJ(E—E) (E = element); for E = ^{13}C, ^{29}Si and ^{207}Pb this problem can become particularly intractable when the two E nuclei are isochronous.

We [1—3] and others [4—6] have previously determined values for ^1J(Sn—Sn); long-range tin—tin couplings have however as yet been studied but little, except in tri-, tetra- and pentatins [2,3]. The publication of isolated data [7] on long-range couplings ^nJ(Sn—Sn) (n = 2—5) has prompted us to publish some data on compounds containing the $(Me_3Sn)_2C=$ fragment; we intend shortly to present data on ^2J(Sn—X—Sn), where X = S, Se, Te [8] and on ^3J(Sn—C=C—Sn) [9].

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* For part VIII see ref. 15.

Experimental

^{13}C and ^{119}Sn spectra were recorded in the pulse Fourier transform mode with proton noise decoupling as described in earlier papers of this series using Bruker-Physik spectrometers (WP-80 for ^{13}C and HFX-90 for ^{119}Sn). Values of $^{1}J(C—H)$ were obtained using gated decoupling. The digital resolution of the transformed spectra under the conditions used was ca. 3 Hz for ^{119}Sn at 33.546 MHz and ca. 1 Hz for ^{13}C at 20.155 MHz.

The compounds studied (see Table 1) were prepared by the following methods:

(a) Compounds I, II, IV—VII and IX:

$$RR'CCl_2 + 2\ Me_3SnLi \xrightarrow{THF} (Me_3Sn)_2CRR' + 2\ LiCl$$

(b) Compound VIII:

$$CCl_4 + 4\ Me_3SnLi \xrightarrow{THF} (Me_3Sn)_4C + 4\ LiCl$$

In order to obtain $^{1}J(C—Sn_4)$ it was necessary to use ^{13}C-enriched CCl_4 as starting material: the sample taken contained ca. 18% ^{13}C.

(c) Compound III:

$$Me_3SnCH{=}CHMe + Me_3SnH \xrightarrow{AIBN} (Me_3Sn)_2CHCH_2CH_3 \text{ (sole product)}$$

Methods (a) and (b) are modifications of that previously used by Kuivila to prepare compounds I, VIII [10] and IX [11] *. A typical example is given below. All new compounds gave satisfactory elemental analyses.

Tris(trimethylstannyl)methane

To trimethyl(dichloromethyl)tin (8.8 g, 36 mmol) in abs. THF (50 ml) was added a THF solution of trimethylstannyllithium (75 ml, 72 mmol). The reaction was exothermic. The mixture was allowed to cool to room temperature, hydrolysed, and extracted with ether (100 ml). The ether layer was separated, dried, and the volatile compounds removed at the water pump. The remaining oil was subjected to a vacuum distillation; the main fraction was collected at 70°C/10^{-3} mmHg and solidified in the receiver. M.p. 32—34°C. Yield 8.1 g (45%). Anal. Found: C, 23.88; H, 5.74. $C_{10}H_{28}Sn_3$ calcd.: C, 23.81; H, 5.59%.

Results and discussion

The data obtained are presented in Tables 1 and 2. It can be seen from Table 1 that the range of variation of $^{2}J(Sn—Sn)$ is fairly large (as yet we have not been able to carry out any sign determinations for this coupling); however, only in the case of compound VIII can we be sure that the angle Sn—C—Sn is tetrahedral, so that we are obviously dealing with a combination of electronic

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* We are grateful to Prof. Kuivila for discussions and for making available to us his carbon-13 data on compound IX prior to publication.

TABLE 1

TIN—TIN, TIN—CARBON AND CARBON—HYDROGEN COUPLING CONSTANTS FOR COMPOUNDS OF THE TYPE $(Me_3Sn)_2CRR'$ (in Hz)

Compound	R	R'	$^2J(^{119}Sn—^{119}Sn)$ [a]	$^1J(^{119}Sn—\underline{C}H_3)$	$^3J(Sn—\underline{C}H_3)$	$^1J(^{119}Sn—\underline{C}RR')$	$^1J(Sn_2\underline{C}—\underline{H})$
I	H	H	287	320	10	272	124
II	H	Me [b]	161	314	*c*	307	125
III	H	Et [d]	157	310	8	288	124
IV	H	Ph [e]	173	324	*c*	261	
V	H	*p*-MeC_6H_4	160	322	*c*	267	*f*
VI	H	*p*-$MeOC_6H_4$	138	323	*c*	270	*f*
VII	H	$SnMe_3$	309	323	12	192	123
VIII	$SnMe_3$	$SnMe_3$	325	318	11	107 [g]	—
IX		*h*	324	318/318	*c*	332	—

[a] Calculated from $^2J(^{119}Sn—^{117}Sn)$, in compound IX also observed directly. [b] $^2J(Sn—CH_3)$ 25 Hz. [c] Not observed. [d] $^2J(Sn—CH_2)$ 23 Hz, $^3J(Sn—CH_3)$ 45 Hz [e] ^2J(Sn—C(1) (ring)) 34 Hz, ^5J(Sn—C(4) (ring)) 10 Hz; [f] Not measured. [g] This value was obtained for $\underline{C}(SnMe_3)_4$ containing 18% ^{13}C. [h] See text. Accuracy of measurement: $^2J(Sn—Sn)$ ± 1.5 Hz, $^nJ(Sn—C)$ and $^1J(H—C)$ ± 1 Hz.

TABLE 2

^{119}Sn [a] AND ^{13}C [b] CHEMICAL SHIFTS FOR COMPOUNDS OF THE TYPE $(Me_3Sn)_2CRR'$ (in ppm)

Compound	$\delta(^{119}Sn)$	$\delta(Me_3Sn)$	$\delta(\underline{C}Sn_2)$	Other shifts
I	23.3	−7.9	−14.8	—
II	27.5	−9.8	−1.7	CH_3 14.7
III	19.5	−8.6	10.9	CH_2 24.4, CH_3 19.7
IV	17.8	−8.5	18.1	ring: C(1) 146.7, C(4) 122.0
V	17.4	−8.5	17.7	
VI	17.0	−8.5	16.8	
VII	41.0	−5.9	−20.0	—
VIII	49.8	−3.4	−25.7	—
IX	36.8/−2.0	−5.9/−9.3	8.0	C(1) 17.7, C(2) 25.8, C(3) 21.1 [c]

[a] $\delta(Me_4Sn) = 0$. [b] $\delta(Me_4Si) = 0$. [c] Compound numbered as 7,7-distannylnorcarane. Lock substance or solvent C_6D_6 except for compounds III—VI ($CDCl_3$).

and steric effects when R and R′ are varied. Since compounds VII and VIII are solids, we hope to be able to obtain information on bond lengths and angles from X-ray studies of these.

The following discussion (of necessity brief) should be seen against the background of the following factors affecting tin and carbon chemical shifts and one-bond coupling constants: (a) carbon and tin chemical shifts are dominated by the paramagnetic term, which includes a dependence on ΔE, the mean electronic excitation energy, and $(r^{-3})_{2p}$, the inverse cube of the distance between a $2p$ electron and the nucleus.

(b) variations in ^1J(A—B) depend (apart from the magnetogyric ratios of A and B) on ΔE and on variations in element hybridisation (α^2), as well as on the electron densities in the *s* valence orbitals at the nuclei; a more exact treatment necessitates replacement of the α^2 and ΔE terms by π_{AB}, the mutual polarisability, which in its turn depends on β, the valence *s*-overlap integral between A and B.

More detailed treatments can be found in the literature [6,12]. Since a number of the compounds contain the fragment $\geqslant C{-}\overset{|}{Sn}{-}\overset{|}{C}H{-}Sn\leqslant$, a large amount of additional coupling information is available apart from ^2J(Sn—Sn). The influence of electronic factors can be seen most clearly in compounds IV—VI, electron-donating substituents at the *para*-position causing a decrease in ^2J(Sn—Sn) and a slight increase in ^1J(Sn—$\underline{C}$RR′). We hope to be able to extend this series of compounds.

The importance of steric factors is shown by the following trends: while ^2J(Sn—CH_3) remains approximately invariant, as does ^1J(Sn_2—C—H), ^1J(Sn—$\underline{C}$CR′) varies between 332 and 107 Hz (the lowest value of ^1J(Sn—C) observed in a purely covalent organotin compound). Thus there is no correlation between these two ^1J values, contrary to the situation in simple mixed tetraalkyltins [13]. This indicates that the decrease in ^1J(Sn—CRR′) is due to a decrease in β, the overlap integral.

Since there is no correlation between ^2J(Sn—Sn) and ^1J(Sn—CRR′), we can conclude that the two-bond coupling shows a complex dependence on steric and electronic factors, as is the case for other two-bond couplings. It is also of interest to note that there are no similarities between ^2J(Sn—C—Sn) and ^2J(H—

C—H) in related compounds; for example, ^2J(H—H) in compound I is —10.4 Hz (cf. CH_4, —12.4 Hz), in toluene —14.5 and in cyclopropane —4.3 Hz.

In compound IX, 7,7-bis(trimethylstannyl)norcarane, the long-range coupling constants are of particular interest as the stannyl groups are non-equivalent (*exo* and *endo*). While only one value of ^2J(Sn—C) could be determined (24 Hz), C(2) showed two sets of satellites with ^3J(Sn—C) equal to 34 and 44 Hz. Inspection of models showed that these are due to coupling with the *exo* and *endo* tins respectively, the agreement with Kuivila's Karplus curve [14] being extremely good (models indicated a dihedral angle for the *exo*-coupling of ca. 140°, for the *endo*-coupling of ca. 10°).

Compounds IX also shows clearly the steric effect on tin shielding, the chemical shift difference between the tin nuclei being 39 ppm, larger than the total shift range for compounds I—VIII. On the basis of the low-field shift in the series Me_4Sn, I, VII, VIII, it seems likely that the low-field signal in IX is due to the *endo*-tin. Using this hypothesis and the tin and carbon shifts in compound VII, we can tentatively assign the methyltin signals in IX as follows: —5,9 *endo*, —9,3 *exo*. In order to test this hypothesis we attempted to prepare a mixture of *exo*- and *endo*-7-trimethylstannylnorcaranes (starting from the appropriate mixture of 7-chloronorcaranes). However, we obtained only one isomer, apparently the *exo*-isomer (^3J(Sn—C) 30 Hz, corresponding to dihedral angle 130° or 35°), with a methyltin shift of —7.9 ppm, a rather inconclusive result.

The steady high-field carbon shift in the series Me_4Sn (—9.5), I, VII, VIII for the "central" carbon can be interpreted as an r_{2p}-effect due to the increasing number of electron-donating Me_3Sn groups attached to it; this seems likely in view of our earlier results on mixed tetraalkyltins [13]. A heavy-atom effect comparable to that shown by CI_4 is evidently not present.

There is in fact a correlation, when poor ($r = 0.856$) between δ(Sn) and $\delta(\underline{Me}_3Sn)$; there is naturally no correlation with $\delta(\underline{C}Sn_2)$. This would seem to confirm that both shifts are dominated by the same (paramagnetic) term, though it seems possible that ΔE is more important than (r_{2p}) for tin, the opposite being true for carbon. However, when we again consider the series Me_4Sn, I, VII, VIII, both carbon shifts can be correlated with one another and with the tin shift, with correlation coefficients better than 0.96. We feel that this is not a coincidence but a result of the regular changes along the series.

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