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FOURIER TRANSFORM NMR INVESTIGATIONS OF ORGANOTIN COMPOUNDS

IX *. TIN-119 NMR SPECTRA OF ORGANOTIN CHALCOGENIDES OF THE TYPE $R_6Sn_3X_2$ AND $R_6Sn_3X_3$ (X = S, Se, Te)

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Summary

NMR spectra have been obtained for fifteen title compounds, mainly with R = Me. Tin chemical shifts were found to lie within the expected ranges, but to vary little with R or, apparently, with change in ring size. While the magnitude of ^1J(Sn—Se) was as predicted, that of ^1J(Sn—Te) was more than twice as large as that previously observed for $(Me_3Sn)_2Te$. In compounds $Me_6Sn_3X_3$, ^2J(Sn—M—Sn) varied systematically with variations in X, but within relatively narrow limits (195—250 Hz); a much more drastic variation was observed for $Me_6Sn_3X_2$, possibly due to bond angle changes at Sn and X.

Introduction

Though a great deal is known about tin-119 spectra of organotin compounds which can be classified as acyclic [2], comparatively few data are available for those in which the tin atom forms part of a ring. Data can be found in the literature for a number of stannacycloalkanes [3], stannadioxa- and stannadithiacycloalkanes [3,4], while only isolated values are available for other types of compound. The availability of the title compounds [5—8] thus provided a valuable opportunity to study the influence of structural changes on the various

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TABLE 1

^{119}Sn CHEMICAL SHIFTS [a] AND TIN—ELEMENT COUPLING CONSTANTS [b] IN COMPOUNDS OF THE TYPE $R_6Sn_3X_nX'_{3-n}$ (X = S, Se, Te; n = 2, 3) [c]

Compound	R	X	n	X'	$\delta(Sn^a)$	$\delta(Sn^b)$	$^1J(Sn^a—X)$	$^1J(Sn^n—X)$	$^1J(Sn^b—X')$	$^2J(Sn—X—Sn)$	$^2J(Sn—X'—Sn)$
I	Me	S	3		131					195	
II	Et	S	3		134					165	
III	i-Pr	S	3		119					155	
IV	t-Bu	S	*d*		123					*e*	
V	Me	Se	3		42		1228			237	
VI	Me	Te	3		—195		3098			250	
VII	Me	S	2	Se	137	84			1238	204	220
VIII	Me	Se	2	S	34	91	1220	1245	—	229	212
IX	Me	S	2	Te	148	—32			3198	223	223
X	Me	Te	2	S	—225	—9	3021	3278		247	232
XI	Me	Se	2	Te	55	—79	1244	1196	3174	244	244
XII	Me	Te	2	Se	—213	—64	3049	3220	1211	250	242

[a] In ppm, $\delta(Me_4Sn) = 0$. [b] In Hz. ^1J values are for $^1J(^{119}Sn—X)$, ^2J values those for $^2J(^{119}Sn—X—^{119}Sn)$; [c] Unsymmetrical compounds (VII—XII) are labelled as follows: $\overline{Sn^a—X—Sn^b—X'—Sn^b—X}$. [d] $t\text{-}Bu_4Sn_2S_2$. [e] Not observed (see text). Chemical shift values were measured to ± 0.2 ppm, coupling constant values to ±3 Hz.

spectral parameters; in some cases ^1H and ^{13}C data have been presented previously [5—8], but the ^{119}Sn data of tin as a ring component is of more interest.

Experimental

(a) Preparation of compounds studied

The preparation of compounds I [9], V [10] and VI [8] has been described previously. Compounds II—IV were prepared by a modification of the method used by Reichle [9] to prepare compound I:

$R_2SnO + CS_2 \rightarrow 1/n\ (R_2SnS)_n + COS$

We refluxed the correponding oxides with excess CS_2: dissolution was complete for t-Bu_2SnO within 2 h, for i-Pr_2SnO within 5 h and for Et_2SnO incomplete after 12 h. Compound IV, a white solid, m.p. 465—466 K, was found to have $n = 2$ rather than 3: it was identical with that prepared by Puff et al. [11] using two independent methods (as shown by m.p. and spectral data).

Compounds VII—XII were not isolated, but were obtained when compounds I and V, I and VI or V and VI were mixed and allowed to equilibrate [12].

The preparation of compounds XIII—XV has also been described previously [5,6].

(b) Spectroscopic measurements

^{119}Sn spectra were recorded in the pulse Fourier transform mode with proton noise decoupling as described in earlier papers of this series using a Bruker—Physik HFX-90 spectrometer. The digital resolution of the transformed spectra was ca. 3 Hz at 33.546 MHz. Benzene was used as solvent: no concentration- or temperature-dependence studies were carried out. The operating temperature of the spectrometer was ca. 308 K.

Results and discussion

The data obtained are presented in Tables 1 and 2; the normal sign convention is used for chemical shifts (given with respect to internal Me_4Sn).

(a) ^{119}Sn chemical shifts

Our intention is not to discuss the entire range of chemical shift values but only the effects resulting from the structural changes. The values for compounds I—III show that the nature of the alkyl group attached to tin has little influence on the tin shift, as is the case for the stannadithiacycloalkanes [3,4] (but in contrast to the situation in, for example, hexaalkylditins [13]). It appears that the compound (t-$Bu_2SnS)_3$ is thermodynamically unstable with respect to (t-$Bu_2SnS)_2$, since three independent methods lead to its formation; by the same token, other compounds $(R_2SnS)_2$ appear to be unstable when R = alkyl, as their formation is as yet unreported. It is thus difficult to draw conclusions as to the effect of ring size on $\delta(Sn)$, particularly as the corresponding stannadithiacyclobutane has not been reported on.

The chemical shift ranges for tin in the SnX_2 fragment in the 6-membered rings (R = Me) are as follows: X = S, 131 to 148; Se, 34 to 55; Te, —195 to

TABLE 2

^{119}Sn CHEMICAL SHIFTS [a] AND COUPLING CONSTANTS [b] IN COMPOUNDS OF THE TYPE $Me_6Sn_3X_2$ [c]

Compound	X	$\delta(Sn^a)$	$\delta(Sn^b)$	^1J(Sn—Sn)	$^1J(Sn^a$—X)	$^1J(Sn^b$—X)	^2J(Sn—X—Sn)
XIII	S	44	176	3977			125
XIV	Se	21	82	3466	992	1263	150
XV	Te	−38	−164	2643 [d,e]	2554 [d]	3159	94

[a] In ppm, $\delta(Me_4Sn)$ = 0. [b] In Hz, ^1J(Sn—Sn) refers to $^1J(^{119}Sn—^{117}Sn)$. [c] Labelling is as follows: $\overline{Sn^a—Sn^a—X—Sn^b—X}$. [d] Assignment uncertain. [e] ^2J(Sn—Sn—Te) 385 Hz.

—225 ppm. In this series the bond angle X—Sn—X increases from 107.7° (S) to 112.6° (Te) [14]. These three sets allow the estimation of the ligand effect on the SnX_2 fragment, which exhibits a downfield shift as X′ in Sn—X′—Sn varies from S to Te due to the increasingly induced electron deficiency. In order to estimate the effect of ring size on the SnX_2 shift we can approximate the Sn—Sn group in the 5-membered rings by the Sn—Te—Sn fragment of the 6-membered rings, since these two may be expected to have similar electronegativities. Thus by comparison of compounds IX and XIII, XI and XIV, and VI and XV we obtain values for the net ring size effect of 28, 27 and 31 ppm respectively. This is somewhat less than the corresponding effect (41 ppm) [3] found for stannadithiacycloalkanes, as the contraction of the interbond angle at tin is not so large. In the corresponding stannacycloalkanes the shift difference is 90 ppm, again to low field [3]. In the case of compounds V and XIV the X—Sn—X angle contraction of 2.4° [15] must contribute to the shift difference of 40 ppm, as the Sn—Se bond length remains constant at 253 ppm [15].

The chemical shifts for tin in the SnXX′ fragments are unremarkable, corresponding closely to the mean of SnX_2 and SnX'_2.

The incorporation of Sn in SnX_2 into a 6-membered ring apparently has little effect on δ(Sn), as can be seen from the following values: $Me_2Sn(SMe)_2$ 137 [16], $Me_2Sn(SeMe)_2$ 57 ppm [17]. In compounds XIII—XV, the chemical shift of tin in X—Sn—Sn is found to be relatively insensitive to variation in X compared to that in X—Sn—X, though the expected high-field shift is found for both on going from S to Te; the relative shift variations are constant in both series. The effect of bond angle variation at tin in Sn—Sn—X cannot, unfortunately, be evaluated, as no model compounds are at present known.

(b) Tin—element coupling constants

Up to three coupling constants can be extracted from the decoupled spectra of the title compounds: ^1J(Sn—Sn), ^2J(Sn—Sn), ^1J(Sn—X). The couplings will be discussed in this order.

(i) ^1J(Sn—Sn) (compounds XIII—XV). Direct tin—tin coupling constants have been previously determined only for di- and polytins [13,18]. The tin—chalcogen ring compounds can be considered as functionally substituted ditins, in which case Me_6Sn_2 can be taken as the parent compound: in it, ^1J(Sn—Sn) is 4404 Hz [13]. Replacement of methyl groups by chalcogens thus decreases ^1J; it should be noted that the decrease on going from 13 to 15 is paralleled by decrease in ^1J(Sn—C) (259 → 218 Hz), ^2J(Sn—Sn—C) (75 → 57 Hz) and

^2J(Sn—H) (54 → 48 Hz); in Me_6Sn_2 ^1J(Sn—C) = 244, ^2J(Sn—Sn—C) = 56.5 and ^2J(Sn—H) = 49.5 Hz [13]. It is however known that in 14 the Sn—Sn bond length is 278 pm [15], almost exactly equal to the sum of the covalent radii; the value for Ph_6Sn_2 is 277 pm. Thus the exact reason for the variations in ^1J, while clearly connected with element electronegativity, is at present unclear.

(ii) ^2J*(Sn—Sn).* In general, the values observed are of the same magnitude as those found for ^2J(Sn—C—Sn) [19] (138—325 Hz). Chalcogen variation from S to Te (compounds I, V, VI) leads to an increase, while alkyl group variation (I, II, III) causes the expected decrease. Though we were unable to determine ^2J(Sn—Sn) for compound IV, Puff [20] has obtained a value of 114 Hz, again of the approximate magnitude expected, even without taking ring size variation into account.

While the values for compounds VII—XII show a monotonic increase with decreasing angle at X and electronegativity of X, those for XIII—XV are irregular, perhaps as a result of couplings via two different pathways, ^2J(Sn—X—Sn) and ^3J(Sn—X—Sn—Sn); the interaction across four bonds, which is the corresponding alternative pathway in 6-membered rings, is probably negligible. From the available X-ray data it seems that bond angle changes may play an important role: in $Me_6Sn_3Se_3$ $<$ SeSnSe is 109.2°, $<$SnSeSn 100.8°, while in $Me_6Sn_3Se_2$ $<$ SeSnSe decreases to 106.8°, $<$SnSeSn to 95.3° [14,15]. X-ray data on 13 and 15 should help to clarify the situation.

(iii) ^1J*(Sn—X).* McFarlane has determined values for this coupling in $(Me_3Sn)_2Se$ (+1060 Hz) and $(Me_3Sn)_2Te$ (—1385 Hz); while the former is of the same magnitude as our values (992—1263 Hz), the latter is not comparable with our data (2554 (or 2643) to 3278 Hz). The reason for this discrepancy is not clear.

The most extreme values are shown by the 5-membered rings. Where one compound gives two distinct values for a particular coupling, the larger value is that for the more electronegativity substituted tin atom, e.g. compound X, $^1J(Sn^a$—X) 3021, $^1J(Sn^b$—X) 3278 Hz; the variations are however small (max. 4% für Se, 9% für Te). In contrast, the variations in the 5-membered rings are ca. 25%. From X-ray data on compound XIV it seems likely that these variations reflect changes in bond length, since $d(Sn^a$—Se) is 257 pm, $d(Sn^b$—Se) 253 pm [15]. We have previously observed a value for ^1J(Sn—Sn) in $Me_4Sn_2(OAc)_2$ of 14980 Hz compared with 4404 Hz for Me_6Sn_2; though one factor involved is hybridisation at tin (coordination number in the diacetoxyditin 5), a second is, by analogy with the corresponding phenyltins, a bond length decrease (Ph_6Sn_2 277, $Ph_4Sn_2(OAc)_2$ 269 pm [22]).

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