ORGANOTIN CHEMISTRY
IX*. INVESTIGATIONS OF THE STRUCTURE OF SOME 1,3-DIFUNCTIONAL TETRAALKYL DISTANNOXANES BY MÖSSBAUER SPECTROSCOPY AND ^{119}Sn HETERONUCLEAR DOUBLE MAGNETIC RESONANCE

ALWYN G. DAVIES, LES SMITH AND PETER J. SMITH

Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H OAJ (Great Britain)

W. McFARLANE

Sir John Cass College, Jewry Street, Aldgate, London E.C.3 (Great Britain)

(Received December 21st, 1970)

SUMMARY

The ^{119m}Sn Mössbauer and ^{119}Sn NMR spectra of a series of functionally disubstituted symmetrical organostannoxanes, $XBu_2SnOSnBu_2X$, containing a range of substituents X, have been recorded. The results are compatible with a dimeric, ladder-type of structure for these compounds, in which the two tin atoms are both pentacoordinate and occupying very similar trigonal bipyramidal environments.

INTRODUCTION

Tetraorganodistannoxanes, $XBu_2SnOSnBu_2X$, may be regarded as resulting from the substitution of two organic groups in the 1,3-positions of the bis(triorgano-tin) oxides by anionic ligands X. In common with many other organotin compounds, this type of substitution produces a marked tendency towards association, and these distannoxanes have been shown to exist as dimers over a wide range of concentration in many organic solvents at room temperature[2-4]. The exact nature of the association in these oxides, however, has been a matter of some controversy.

Harada[5] argued the case for a cyclic oligomeric structure, $(R_2SnOR_2SnX_2)_m$ such as the dimer (I), where the tin atoms have coordination numbers of four, and of five.

(I)   (II)   (III)
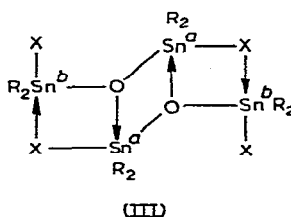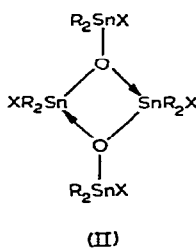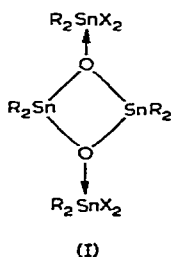
* For Part VIII see ref. 1.

It has been suggested, however[2,3], that an alternative dimeric four-membered ring structure (II), also containing both four- and five-coordinate tin atoms, is more probable.

The IR spectra of the compounds where $X = NCS$ show *two* bands in the $C=N$ stretching region at 2040 and 1960 cm^{-1}, which are indicative of non-bridging and bridging NCS groups respectively[6]. Okawara therefore proposed that these compounds had the "ladder" structure (III), in which all four tin atoms are 5-coordinate, and this has been confirmed in a preliminary report[7] of a partial X-ray structural analysis of the distannoxane where $R = Me$, and $X = OSiMe_3$.

To clarify the present situation, and obtain further information on the structure of these compounds both in the solid state and in solution, the Mössbauer parameters and ^{119}Sn NMR chemical shifts of a series of tetra-n-butyldistannoxanes containing a wide variety of X groups have now been recorded.

The Mössbauer spectra of compounds of structures such as (I) or (II), which contain both tetrahedral and trigonal bipyramidal tin atoms, would be expected to show two quadrupole split doublets of differing separations, or one pair of broadened peaks comprising the two overlapping doublets. If the configurations about the two types of pentacoordinate tin atoms in structure (III) were the same, the Mössbauer spectrum should consist of one doublet if the effect of the various groups X, and O, on the quadrupole splitting (ΔE_Q) is small, as is observed for many other organotin (IV) compounds[8]. Okawara's preliminary X-ray data, however, imply that, whereas the two alkyl groups on the terminal trigonal bipyramidal tin atoms (*b*) can adopt the diequatorial configuration which is usual in compounds R_2SnX_3[9], this configuration is not possible at the medial tin atoms (*a*) without some distortion*, and the effect that this would have on the magnitude of the quadrupole splitting is unknown.

The ^{119}Sn NMR spectrum of the dimer (II) would be expected to show a signal to low field of tetramethyltin for the 4-coordinate tin atoms, and one to high field for the 5-coordinate tin atoms[10]. The closest analogy that has been studied is the monomer–dimer equilibrium $[(IV) \rightleftarrows (V)]$ in dimethyltin methoxide chloride, where the chemical shift of the 4-coordinate tin is -126 ppm (with respect to Me_4Sn) and that for the 5-coordinate tin is $+90$ ppm[11].
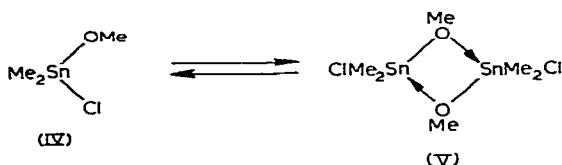
RESULTS AND DISCUSSION

The results are shown in Table 1.

The Mössbauer spectra for all the compounds, except that in which $X = Me_3SiO$ (which is discussed separately), consist of a symmetrical unbroadened doublet, with a value of ΔE_Q in the range 2.74–3.36 $mm \cdot s^{-1}$; the spectrum of the compound (NCS)-

---

* The three rings are not coplanar, and structure (III) might better be compared to a stair-case rather than to a ladder.

TABLE 1

MÖSSBAUER PARAMETERS AND ^{119}Sn CHEMICAL SHIFTS FOR $XBu_2SnOSnBu_2X$ COMPOUNDS

X	δ (mm·s^{-1})	ΔE_Q (mm·s^{-1})	^{119}Sn[a] (ppm)
F	1.14	2.99	+168±14
Cl	1.36	3.21	+145±5 and +94±5
	1.40[b]	3.24[b]	
Br	1.49	3.36	+141±5 and +87±5
NCS	1.34	3.30	+159±9[c]
OSiMe$_3$	1.08	2.46	+163±5[d]
OCOMe	1.32	3.22	+221±5[c,e]
	1.30[f]	3.24[f]	
OPh	1.17	2.81	+181±5[c]
OC$_6$H$_4$Me-4	1.16	2.86	+181±2
OC$_6$H$_4$OMe-4	1.13	2.74	+188±2
OC$_6$H$_4$Cl-4	1.24	2.80	+177±5[c]

[a] Relative to tetramethyltin; all NMR spectra were obtained on saturated solutions in benzene except when X = F or Cl, when the solvent was carbon tetrachloride. [b] Ref. 12. [c] Resonance very broad, suggesting two overlapping peaks separated by 9–14 ppm. [d] Dimethyltin compound (as saturated solution in CCl$_4$) shows two peaks at +137±2 and +153±2 ppm (ref. 17: +130 and +156 ppm). [e] Laurate shows a single broad resonance[2]. [f] Ref. 13.
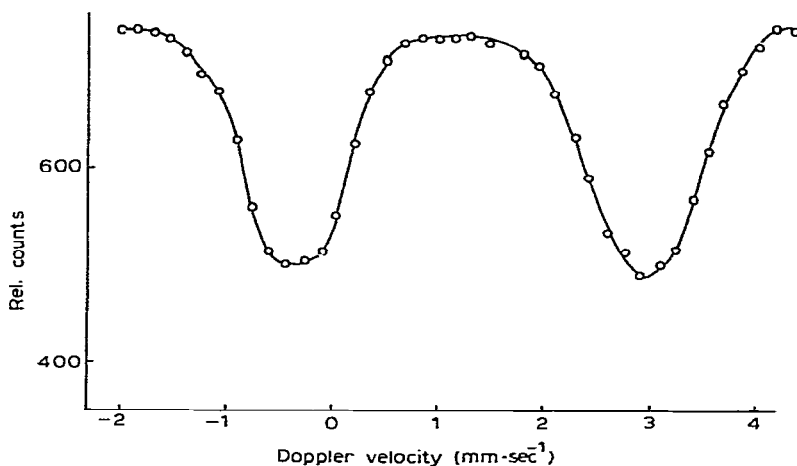
Fig. 1. Mössbauer spectrum of (NCS)Bu$_2$SnOSnBu(NCS)

Bu$_2$SnOSnBu$_2$(NCS), which is typical, is shown in Fig. 1. This is compatible with the ladder structure (III). The equivalent values of ΔE_Q in the compounds Me$_2$SnC$_3^-$ and Me$_2$SnCl$_2$·C$_6$H$_4$(OH)CHO-1,2, which are known by X-ray crystallography[14,15] to possess trigonal bipyramidal geometry with two equatorial alkyl groups, are 3.31[16] and 3.32[15] mm·s^{-1} respectively. Dimethyltin methoxide chloride, which is a closer molecular analogy to the difunctional tetraalkyldistannoxanes, and is believed, but not known, to have the structure (V) in the solid state, has a value of ΔE_Q of 3.35 mm·s^{-1} (ref. 11).

The ^{119}Sn NMR chemical shifts for the distannoxanes provide evidence for the existence of a ladder structure (III) in solution. In agreement with previous work[2], the

chloro- and bromodistannoxanes showed two well resolved tin signals separated by about 1000 Hz; the ^{1}H NMR spectra showed two distinct multiplets separated by ca. 20 Hz for the α-methylene groups, and these were associated (via the ^{119}Sn satellites) with the two different tin resonances. Whilst the observation of the two ^{119}Sn signals puts the lower limit to the lifetimes of the species involved at ca. 2×10^{-4} s, the result for the ^{1}H spectra shows that the lifetimes must exceed 10^{-2} s.

The other distannoxanes all give a single ^{119}Sn resonance which is often very broad, and the chemical shifts are situated upfield from tetramethyltin. Previous work assigned the tin signals which were found for the dichloro- and dibromotetrabutyl-distannoxanes[2], and also for the tetramethylbis(trimethylsiloxy)distannoxane[17] to the four- and five-coordinate tin atoms in the structure (II). However, it is now known that 4-coordinate alkyltin compounds [e.g.(IV)] usually display a ^{119}Sn signal which is well downfield from tetramethyltin[10,11], and the high-field shifts observed for all the distannoxanes can only be consistent with both the tin atoms occupying pentacoordinate environments. Any exchange involving appreciable amounts of 4-coordinate tin species can be excluded, since the resulting average chemical shift would occur at lower fields than those which are observed.

The observation of two ^{119}Sn signals for the chloro- and bromodistannoxanes [(III), X=Cl or Br] can be rationalised in terms of the large difference in the electro-negativity of the ligands X and O, which renders the tin atoms a (in the environment R_2SnO_2X) and b (in the environment R_2SnOX_2) nonequivalent. In the other distan-noxanes where the group X is bonded through oxygen (X = OCOR′, OC_6H_4Y, or $OSiMe_3$), or has an electronegativity near that of oxygen (X = F or NCS), the trigonal bipyramidal environments of the tin atoms a and b are so similar that their separate resonances are not distinguishable, or readily become merged by a relatively slow exchange process*.

The ^{19}F NMR spectrum of the fluorodistannoxane[(III), X = F] in toluene showed a single signal at $-32°$, which broadened at 23°, broadened considerably at 54°, and was lost at 100°. Two types of fluorine atoms (bridging and non-bridging) were not observed, but the broadening of the signal as the temperature is raised may indicate the onset of an exchange process involving a second species whose ^{19}F signal is too weak to be detected.

The IR spectra of the distannoxanes, however, as nujol mulls, can often show the existence of the two types of X group. The isothiocyanate exhibits both bridging and non-bridging C=N stretching bands[6], as mentioned above; the trimethylsiloxy com-pound shows two Si–O stretching bands[18] (at 910 and 980 cm^{-1}) due to bridging and non-bridging Me_3SiO groups; the acetoxy compound[19] shows two carbonyl absorp-tions at 1560 and 1418 cm^{-1} which are characteristic of symmetrical (bridging) car-boxylate groups, and also two bands at 1630 and 1362 cm^{-1} corresponding to the non-bridging groups[20]; and the phenoxy and substituted phenoxy compounds show two

---

* Tetramethyl-1,3-bis(trimethylsiloxy)distannoxane shows two ^{1}H singlets for the two types of Me_2Sn groups, separated by 12 Hz. If any exchange process which would render these two types of group equivalent does occur, the lifetimes of the species must therefore be greater than ca. 10^{-2} s. The observation of two *singlets* implies that the two methyl groups bonded to any one tin atom are magnetically equivalent on the NMR time scale, and argues against a static situation in which one is equatorial and one axial about trigonal bipyramidal tin.

types of C–O stretching bands at ca. 1250 and 1280 cm^{-1}, due to the bridging and non-bridging groups[19].

Within a generally consistent pattern of behaviour, the Mössbauer spectra of the bis(trimethylsiloxy)distannoxanes are anomalous. Although NMR, IR, and molecular weight measurements indicate that dimerisation is still taking place, tetrabutyl-1,3-bis(trimethylsiloxy)distannoxane show an unusually low quadrupole splitting value ($\Delta E_Q = 2.46$ mm·s^{-1}). Similarly we have found that the corresponding tetramethyldistannoxane, (which was found by X-ray crystallography to have the ladder structure[7]), and the tetraoctyldistannoxane, also show low values of ΔE_Q (2.42 and 2.45 mm·s^{-1} respectively).

We tentatively suggest that these low values of ΔE_Q result from a lengthening of the intermolecular Sn····O and Sn····X bonds in the structure (III), caused by the bulky trimethylsiloxy groups, while the trigonal bipyramidal environment about the tin atoms is preserved: in structure (III), when R = Me the intramolecular Sn–O bonds (2.2 Å) are considerably shorter than the intermolecular Sn····O distances (2.8 Å)[7]. We have observed a similar change in the value of ΔE_Q for trigonal bipyramidal compounds of the type R_3SnX_2, in which one of the axial Sn–X bonds is known, by X-ray crystallography, to be longer than the other.

EXPERIMENTAL

Mössbauer spectra were recorded with both $^{119m}SnO_2$ source (from the Radio-chemical Centre, Amersham, England) and absorber cooled to 77°K, using a constant velocity cam-driven spectrometer, which was calibrated periodically against a β-Sn standard. The values of δ and ΔE_Q are considered accurate to ± 0.08 mm·s^{-1}.

The tin-119 chemical shifts were obtained at 25° by the heteronuclear double magnetic resonance technique. Proton spectra were recorded in the field sweep mode throughout. The spectrometer used was a JEOL C-60-H instrument operating at a proton frequency of 60 MHz containing an extra coil within the probe. The ^{119}Sn frequency (22.37 MHz) was provided by a Schlumberger frequency synthesiser model FS 30.

Tetrabutyl-1,3-bis(trimethylsiloxy)distannoxane

A mixture of dibutyltin oxide (1.1 g; 4 mmoles) and trimethylsilanol (0.39 g; 4 mmoles) in benzene was refluxed in a Dean and Stark separator until no more water was collected (15 min). Removal of the solvent under reduced pressure left the required product, which was recrystallised from light petroleum (0.76 g; 53% yield) as white crystals, m.p. 107° (lit.[18] 107°).

Tetraoctyl-1,3-bis(trimethylsiloxy)distannoxane

This compound, which has not previously been reported in the literature, was prepared in a similar way from dioctyltin oxide and trimethylsilanol. The resulting white crystals (ca. 55% yield) had m.p. 48–51°. (Found: C, 51.44; H, 9.70. $C_{38}H_{86}O_3Si_2Sn_2$ calcd.: C, 51.58; H, 9.73%.)

The other distannoxanes were prepared by published methods[2,4,18,21]; the melting points were in good agreement with the reported values.

REFERENCES

1 A. G. DAVIES AND P. G. HARRISON, *J. Chem. Soc. B*, (1970) 2035.
2 D. L. ALLESTON, A. G. DAVIES, M. HANCOCK AND R. F. M. WHITE, *J. Chem. Soc.*, (1963) 5469.
3 R. OKAWARA, *Proc. Chem. Soc.*, (1961) 383.
4 W. J. CONSIDINE, J. J. VENTURA, A. J. GIBBONS AND A. ROSS, *Can. J. Chem.*, 41 (1963) 1239.
5 T. HARADA, *Bull. Chem. Soc. Jap.*, 43 (1970) 266.
6 R. OKAWARA AND M. WADA, *J. Organometal. Chem.*, 8 (1967) 261.
7 R. OKAWARA AND M. WADA, *Advan. Organometal. Chem.*, 5 (1967) 137.
8 B. W. FITZSIMMONS, N. J. SEELEY AND A. W. SMITH, *J. Chem. Soc. A*, (1969) 143.
9 E. L. MUETTERTIES AND R. A. SCHUNN, *Quart. Rev. Chem. Soc.*, 20 (1966) 245.
10 A. G. DAVIES, P. G. HARRISON, J. KENNEDY, T. N. MITCHELL, R. J. PUDDEPHATT AND W. MCFARLANE, *J. Chem. Soc. C*, (1969) 1136.
11 A. C. CHAPMAN, A. G. DAVIES, P. G. HARRISON AND W. MCFARLANE, *J. Chem. Soc. C*, (1970) 821.
12 V. V. KHRAPOV, Candidate Dissertation, Inst. of Chem. Phys., Acad. Sci. USSR, Moscow, 1965.
13 V. I. GOL'DANSKII, E. F. MAKAROV, R. A. STUKAN, V. A. TRUKHTANOV AND V. V. KHRAPOV, *Dokl. Phys. Chem.*, 151 (1963) 598.
14 F. W. B. EINSTEIN AND B. R. PENFOLD, *J. Chem. Soc. A*, (1968) 3019.
15 K. M. ALI, D. CUNNINGHAM, J. D. DONALDSON, M. J. FRAZER AND B. J. SENIOR, *J. Chem. Soc. A*, (1970) 913.
16 N. W. G. DEBYE, E. ROSENBERG AND J. J. ZUCKERMAN, *J. Amer. Chem. Soc.*, 99 (1968) 3234.
17 W. J. CONSIDINE, G. A. BAUM AND R. C. JONES, *J. Organometal. Chem.*, 3 (1965) 308.
18 R. OKAWARA, D. G. WHITE, K. FUJITANI AND H. SATO, *J. Amer. Chem. Soc.*, 83 (1961) 1342.
19 A. G. DAVIES, L. SMITH AND P. J. SMITH, unpublished.
20 B. F. E. FORD, B. V. LIENGME AND J. R. SAMS, *J. Organometal. Chem.*, 19 (1969) 53.
21 I. F. GRAHAM, Ph.D. Thesis, London, 1964.