Tin-119 Mössbauer and Nuclear Magnetic Resonance Studies of Organotin Compounds. Part 1. Sterically Crowded Tetraorganotin Derivatives

Christopher S. Frampton, Roger M. G. Roberts,* Jack Silver,* Joanne F. Warmsley, and Bahrum Yavari
Department of Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, Essex

^{119}Sn Mössbauer and ^{119}Sn n.m.r. data are presented for a series of sterically hindered tetraorganotin derivatives. For adamant-1-yl (ad) derivatives two quadrupole splittings (q.s.) are observed and the values of the tin chemical shifts, $\delta(^{119}Sn)$, are significantly more negative (resonances at higher field) than expected. Thus Sn(ad)$_4$ shows the presence of q.s. with values of 2.70 and 0.76 mm s^{-1} at 80 K. These tin sites are discussed. The $\delta(^{119}Sn)$ value of −73.5 p.p.m. (relative to SnMe$_4$) indicates increased electron density at the tin atom probably resulting from charge separation of the type $ad_3\overset{\Delta-}{Sn}\cdots\overset{\Delta+}{ad}$. Other sterically hindered derivatives show similar features, although less dramatically. The additivity effect of tin substituents in this series is also discussed. Long relaxation times were recorded for the more sterically hindered derivatives. The Mössbauer spectrum at 80 K for quench-frozen SnPh$_4$ is also presented. The spectrum shows a singlet with a large linewidth, which narrows on annealing at 193 K to give a very narrow line. The wide line is easily explained in terms of the known crystal structure.

Alkyl and aryl derivatives of the types SnR$_4$ and SnR$_3$R′ were amongst the first compounds to be studied by Mössbauer spectroscopy. Several reviews[1-3] and many papers have covered these in the last twenty years. The tetra-alkyl and tetra-aryl tin derivatives have all previously been assumed to have tetrahedral geometry and have shown no significant quadrupole splitting (q.s.). Differences in chemical isomer shift have been found to be small, and the total range is between 1.0 and 1.43 mm s^{-1}.[2] There are now several known SnR$_4$ crystal structures all of which contain tetrahedrally co-ordinated tin atoms, but some show distorted tetrahedra.[4,5]

In less symmetric compounds of the type SnR$_3$R′, quadrupole splitting is only found if R′ is a strong electron-withdrawing group such as C_6F_5[6,7] or CH$_2$C(O)Me.[8] From the relative insensitivity of the spectrum to the nature of X in compounds of the type SnR$_3$(CH$_2$X) it can be seen that such groups influence the tin environment by their electron donating or withdrawing power. Obviously the possibility of higher co-ordination using donor groups in the ligand must be considered. Such considerations for SnR$_3$(CH$_2$OMe) would involve inter- or intra-molecular bonding to tin *via* oxygen which could generate an electric-field gradient. The known structures[9] of unsymmetrical tetraorganotin compounds all show fairly regular tetrahedral geometries around the tin atoms except for C$_5$H$_4$(SnMe$_3$)$_2$-1,1′[4] which contains distorted tetrahedral tin environments.

There are few reports of room-temperature Mössbauer spectra for an SnR$_4$ or SnR$_3$R′ compound. One spectrum reported was that of tetrakis(2-thiophenolato)tin.[1,10] The reasons for such a lack of Mössbauer spectra at ambient temperatures are worth considering. Examples of tin compounds with a high recoil-free fraction, *f*, include SnO$_2$, SnO, SnR$_2$O, SnF$_4$, *etc.* The spectra of these compounds can be recorded at room temperature. The coefficient, *f*, is related in the lattice dynamics of the solid to the displacement of the absorber tin atom from its equilibrium position. The value of *f* should then be a function of the binding force constants holding the absorber atom in the lattice, and so being larger the more rigid the binding in the lattice.

Organotin compounds usually form molecular solids, *i.e.*, crystals consisting of molecules which retain their identity when assembled in the solid, in which two kinds of forces are important: (*a*) the binding of the tin atom in the molecule, and (*b*) the binding of the molecule in the crystal. The lattice force which affects the magnitude of *f* will in general depend on contributions from both intra- and inter-molecular forces.

The tin compounds which give Mössbauer spectra easily at room temperature have one feature in common; the tin atom is held in a polymeric lattice.[11] Although this dependence of the magnitude of *f* on the presence of a polymeric lattice seems to be established, it is dangerous to use the presence of a resonance at ambient temperatures as a test of polymeric binding. The absence of a resonance at room temperature gives no information, although its presence may be significant.[10]

All the known structures of SnR$_4$ and SnR$_3$R′ compounds show that they are molecular crystals.[9]

We report in this paper Mössbauer studies on compounds where the tin atom is bound to large organic groups, and discuss the effect these groups have on the geometry of the tin environments.

Results and Discussion

The Mössbauer data obtained in this work appear in Table 1. The most unusual data are those reported for tetra-adamant-1-yltin, Sn(ad)$_4$.† At 80 K, two sites are observed, both showing q.s., one very large (2.7 mm s^{-1}) (Figure 1) whilst the other is 0.76 mm s^{-1}. Both sites remain at all temperatures studied. These must be the result of distorted tetrahedral geometries or due to a tin environment where the co-ordination number of tin is greater than four. Slightly distorted SnR$_4$ tetrahedra [*e.g.* Sn(C$_6$F$_5$)$_4$[5]] do not appear to generate observable quadrupole splittings.[6,12] This may mean that the electronic environment is symmetric even though the crystallographic one is not, or that the Mössbauer spectrum does contain a small unresolved q.s. The point-charge models of Parish and Platt[13] and Fitzsimmons and co-workers[14] show that the only way a tetrahedral environment can generate a q.s. is when one ligand is very different to the others, and even then q.s. values of only *ca.* 1.66 mm s^{-1} are expected. In Sn(ad)$_4$[15] all the ligands are the same but one must be further from the Sn atom than the others. Molecular models show that four ad groups around a tin atom with normal Sn–C distances results in an extremely

---

† Adamant-1-yl = tricyclo[3.3.1.1^{3,7}]dec-1-yl.

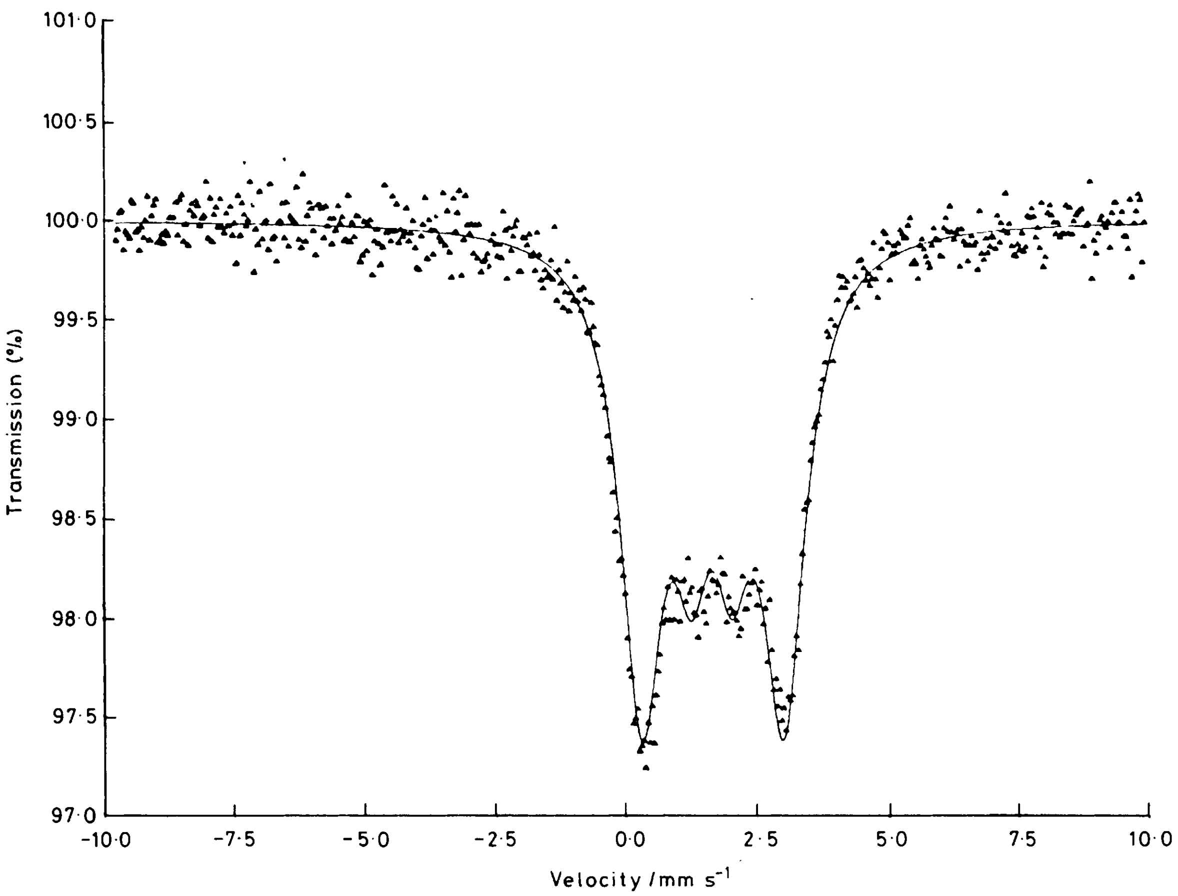


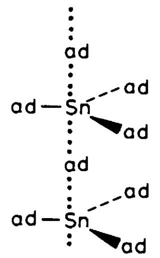
Figure 1. ^{119}Sn Mössbauer spectrum of Sn(ad)$_4$ at 80 K

Table 1. Tin-119 Mössbauer parameters (with standard deviations in parentheses) for SnR_4, SnR_3R', and $SnR_2R'R''$ derivatives together with ^{119}Sn n.m.r. chemical shifts (T = 80 K unless otherwise stated)

Compound		δ^a/ mm s^{-1}	ΔE/ mm s^{-1}	Γ^b/ mm s^{-1}	$\delta(^{119}Sn)^c$/ p.p.m.
$SnPh_4$		1.20(2)^d		0.88(2)^d	
	first fit	1.24(3)		0.82(14)	
		1.18(3)	0.52	0.79(14)	
	second fit	1.22(2)		1.60(2)	
Sn(ad)$_4$		1.60(5)	2.70(2)	0.97(4)	−73.4
		1.60(2)	0.76(2)	0.84(3)	−73.5^e
$SnMe_3$(ad)		1.26(2)		1.65(2)	−6.64
$SnMe_3$(tr)		1.25(2)		1.96(2)	−27.2
$SnPh_3$(ad)		1.33(2)		1.36(2)	−136.7
$SnPh_3$(tr)		1.24(2)		1.05(2)	−130.5^e
$SnPh_3(CH_2CH{=}CH_2)$		1.30(3)		1.09(2)	−121.6
$SnMe_2$(tr)$(CH_2CH{=}CH_2)$		1.40(2)		1.37(2)	−29.6
$SnPh_2$(tr)Me		1.26(2)		1.16(2)	−95.99
$SnPh_2$(ad)Me		1.34(2)		1.39(2)	−92.14
$Sn(CH_2CH{=}CH_2)_2$(tr)Me		1.30(2)		1.06(2)	−57.0
$Sn(CH_2CH{=}CH_2)_3$(tr)		1.37(2)		1.01(2)	−57.5

[a] Values relating to SnO_2. [b] Linewidths: full width at half height. [c] All values relating to $SnMe_4$ (negative values indicate resonances upfield from $SnMe_4$). [d] At 193 K. [e] [Cr(acac)$_3$] added.

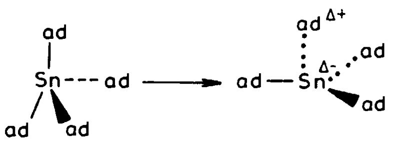
sterically hindered structure. The most likely result is that at least one Sn–C bond would be longer than the others. Lengthening one Sn–C bond would have the same effect on point-charge calculations as replacing it with a different ligand but, as stated, the larger observed q.s. is greater than might be expected from such a structure. The alternative is that the Sn atom has a larger co-ordination number, such as could be generated by a five-co-ordinate trigonal bipyramidal tin atom containing two longer Sn–C bonds to ad units which bridge Sn atoms in a polymeric fashion (see below). An Sn environment of this nature would be in keeping with such a q.s. value, however for such a structure it is difficult to envisage which bonding orbitals on the ad group are involved.* An alternative that would generate the same end result would be a distortion of a tetrahedron in which the Sn atom moves directly down a three-fold axis and results in an environment which has a geometry which is effectively a three-fold co-ordination with the other ad ligand balancing the charge in the lattice. This three-fold



---

* For the adamantyl cations $\overset{\Delta+}{(\text{ad})}$ to behave as bridging groups, the positive charge must be delocalised around the structure. A possible mechanism for this would involve overlaps of the empty carbon *p* orbital with the sp^3 lobes of electron density on the γ-carbon atoms (see later).

environment would allow the Sn to fit more easily between three ad ligands (see below).



The second site in Sn(ad)$_4$ has a much smaller q.s. of 0.76 mm s^{-1}. Such a site is what may be expected for a distorted tetrahedral environment (being less than 1.66 mm s^{-1})[13,14] where one Sn–C bond is much longer than the others. Such a tetrahedral tin geometry would be expected if some of the Sn atoms still had enough energy to move closer to the tetrahedral holes.

From the ratio of the two sites at 80 K, the large q.s. of 2.7 mm s^{-1} accounts for about two-thirds of the tin present. We have taken several spectra on different samples of the same material, frozen by both quench cooling and slow cooling, and yet always found a 2:1 Sn ratio in the sites in the spectra. From semi-logarithmic plots of relative Mössbauer peak area against temperature (Figure 2), both sites give Mössbauer temperatures, θ_m, of *ca.* 102 K. This can be interpreted in two ways. Either there is a phase change on cooling and some of the material passes through this change and the rest does not, or there are two distinct Sn sites in the material. From the temperature behaviour of the data and the fact that the Mössbauer temperatures of both sites are identical within experimental error, the latter explanation is the more likely. Such a material with two different Sn environments could be caused by the packing of the ad groups. This material would contain the two types of environment we have described. From the work of Herber and co-workers[11] and Harrison *et al.*[16] it would appear that the Mössbauer temperature and the relative recoil-free fraction of our work is in the region expected for a molecular material. Unfortunately it proved impossible to produce crystals of Sn(ad)$_4$ from any of the preparations. Even on very slow cooling, only amorphous powder was obtained, thus frustrating any hopes of a crystal structure investigation.

We can rule out the simple explanation to account for these observations, which is that as Sn(ad)$_4$ is cooled, its 'tetrahedral' geometry distorts so that it eventually undergoes a low-temperature phase change to the three-co-ordinate structure. Although this would explain the generation of the second Mössbauer site, on raising the temperature, data do not show sufficient progressive variations for such a phase change.

Having made these observations on Sn(ad)$_4$, we studied tetraphenyltin. On quench cooling commercially obtained material, we observed the spectrum as shown in Table 1 and Figure 3. This shows a very wide linewidth and this spectrum can be fitted either to a singlet, or to a singlet and doublet (q.s.). On slowly cooling to 193 K, we obtained a very narrow singlet from the same material. These results show that the material, when quench-cooled, contains either distorted tetrahedral Sn atoms, or other packing distortions generated by the quench cooling. If the two-site fit is correct, then some of the material has a q.s. caused by a distorted tetrahedral tin environment.

It is interesting that when examining the known crystal structure of SnPh$_4$[17,18] and the isostructural CPh$_4$[19] it can be seen that there is present 'much void space'. Chieh[20] shows that, from potential energy considerations, as the central atom becomes larger, the possible ranges of rotation of the phenyl groups increase.

The 'voids' which explain both the many low-density measurements for CPh$_4$ and also the fact that inclusion compounds, such as those with crystal violet and malachite green can be prepared, must also be present in SnPh$_4$. Indeed the increase in cell size for the Sn compound is surprisingly large (U = 933.8 for SnPh$_4$, 854.3 Å^3 for CPh$_4$) and also demonstrates the free space in the SnPh$_4$ structure. It is also well established that SnPh$_4$ crystals crack easily and are very sensitive to thermal shock.[21,22]

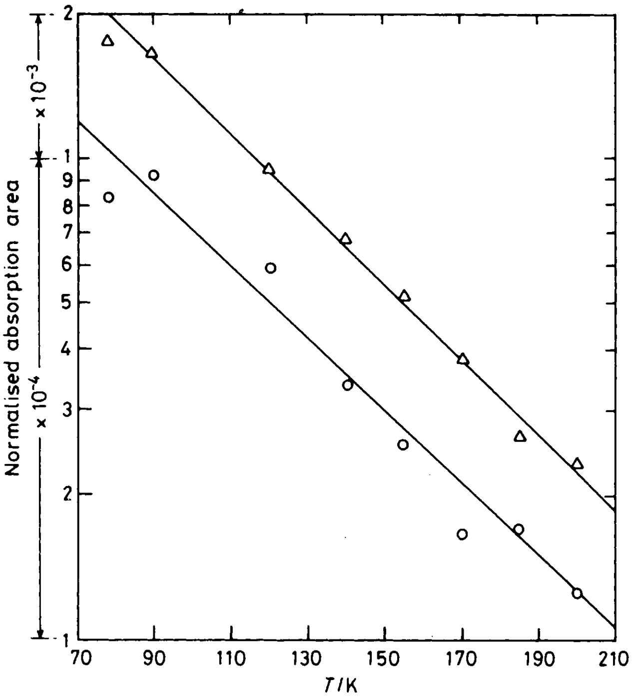


Figure 2. Variation of normalised absorption area with temperature (K) for Sn(ad)$_4$: △ = site 1, ○ = site 2

Quench cooling small crystals of SnPh$_4$ could therefore cause one of two possible effects. Either the SnPh$_4$ molecules could be 'frozen' in non-ideal crystallographic symmetry spreading into the voids, and the resulting distorted Sn environments generate the observed wide Mössbauer line, or defects could be caused in the structure due to cracking, and the internal stress thus caused might generate an increase in the linewidth. We consider the former mechanism more likely as very small crystals (powder) were used, and slow cooling of such materials (allowing slow relaxation) gives very narrow Mössbauer signals.

Many of the other compounds of the types SnR$_3$R$'$ and SnR$_2$R$'$R$''$ (see Table 1) gave broad singlets in their Mössbauer spectra. Many of these could obviously be fitted to more than one Sn site, and the results explained as for SnPh$_4$ above.

Only small differences in chemical isomer shifts have been observed in SnR$_4$ and SnR$_3$R$'$ compounds[2] and these have not been interpreted in meaningful terms. These differences have often been less than the order of the reproducibility between laboratories.[2]

The isomer shifts for both sites in Sn(ad)$_4$ are the same and are the highest yet recorded for an SnR$_4$ material. These high isomer shifts must be due to the electron donating properties of the ad groups allowing more '*s*' electron density to remain on the tin atoms (see later ^{119}Sn n.m.r. discussion). There is little change in the isomer shift (i.s.) on raising the temperature. On examining the i.s. data for other compounds containing ad groups, it is clear that exalted isomer shifts occur whenever ad is present.

^{119}Sn *Chemical Shifts.*—Although, with the advent of Fourier-transform n.m.r. spectrometers, measurement of ^{119}Sn

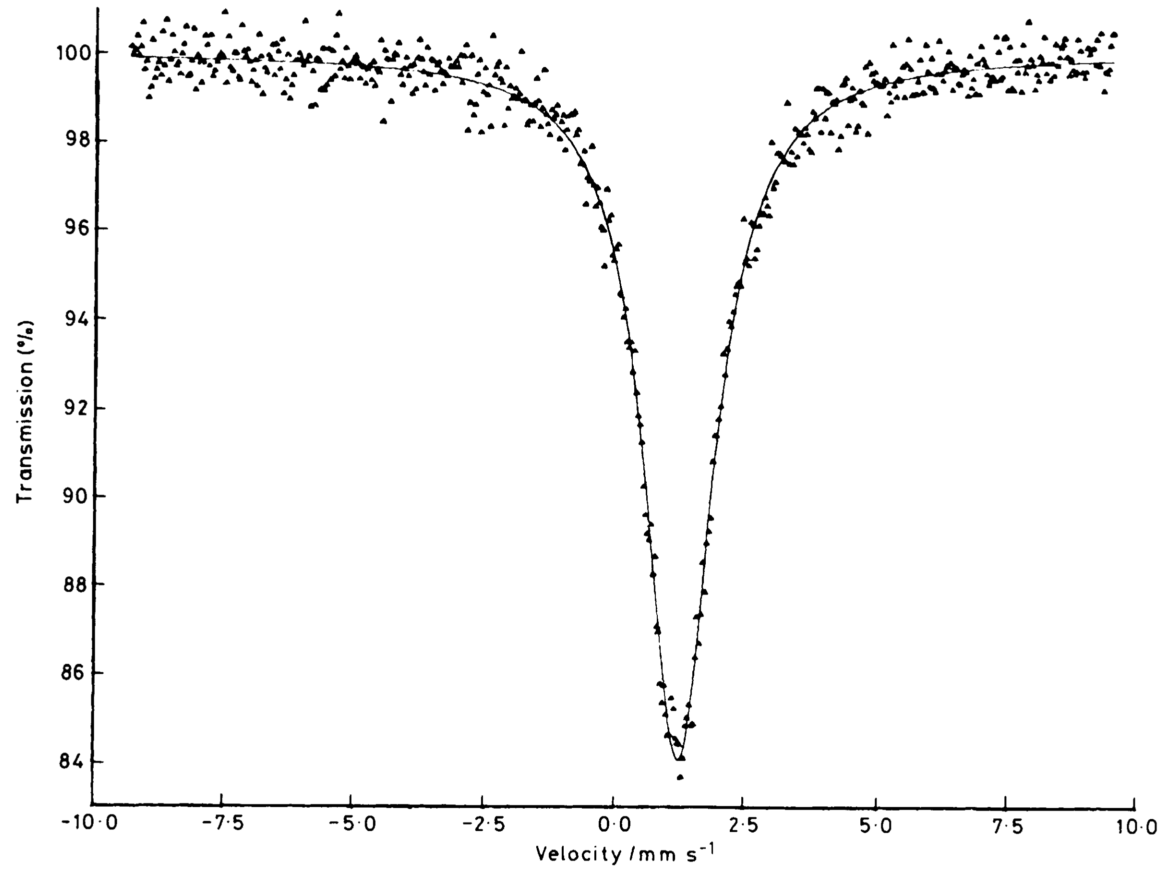
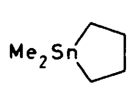
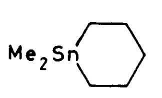


Figure 3. ^{119}Sn Mössbauer spectrum of quenched-cooled $SnPh_4$ at 80 K

resonances has become commonplace, there is as yet no unifying theory to account for the observed wide range of substituent effects. The current state of the subject has been admirably summarised by Kennedy and McFarlane,[23] and a number of important recent reviews report ^{119}Sn chemical shift data.[23-26] It is generally accepted that δ(^{119}Sn) is governed by paramagnetic rather than diamagnetic shielding in keeping with other heavy-element nuclei. It is also apparent that distortion of the normal tetrahedral geometry of the tin atom in SnR_4 derivatives markedly alters values of δ. For example, the Sn resonance of (**1**) lies some 90 p.p.m. downfield from that of (**2**)[27] for which the hybridisation of the tin atom is approximately tetrahedral. These large shift differences have been explained in terms of strain imposed on the tin–carbon bonds by the five-membered ring. Qualitatively similar results were obtained for cyclic stannadithia-alkanes. The effect of introducing saturated carbon atoms in aliphatic derivatives α, β, and γ to the tin atom is qualitatively very similar to that occurring in ^{13}C n.m.r.: α and β substitution produce downfield shifts whereas γ substitution causes shielding. Thus a β-methyl substituent causes, on average, a downfield shift of *ca.* 5 p.p.m. and a γ-methyl an upfield shift of *ca.* 6 p.p.m.[28] The effect appears to be approximately additive. It is therefore possible to calculate the δ(^{119}Sn) shifts for $SnMe_3$(ad) (where ad = adamant-1-yl or adamant-2-yl) and $Sn(ad)_4$. Table 2 shows the calculated and experimental values. For the adamant-1-yl derivative, $SnMe_3$(ad), 3 β-methylene substituents should produce a downfield shift of *ca.* 17 p.p.m. [*cf.* δ(^{119}Sn) for $SnMe_3(CMe_3)$ of + 17.5 p.p.m.]. The 3 γ-methine substituents would produce an upfield shift of 18 p.p.m. resulting in a calculated shift of *ca.* − 1.0 p.p.m. compared with the observed value of − 6.9 p.p.m.[28] The analogous calculated value for the adamant-2-yl derivative is − 15 compared with the experimental value of − 14 p.p.m. The agreement between calculated and experimental values for these relatively strain-free derivatives is reasonably good. However, very marked deviations occur for $Sn(ad)_4$. Mössbauer data described above are commensurate with an electronically unsymmetrical environment at the central



(**1**)



(**2**)

Table 2. Calculated[a] and observed tin chemical shifts[b] [δ(^{119}Sn)] for some tetraorganotin derivatives

Compound	Calculated	Experimental
$SnMe_3$(ad)	−0.5	−6.9
$Sn(ad)_4$	−28	−73.5
$SnPh_3(CH_2CH{=}CH_2)$	−109	−122
$SnPh_3$(tr)	−126	−130
$SnPh_3$(ad)	−106	−137
$SnPh_2$(tr)Me	−93	−96
$SnPh_2$(ad)Me	−73	−92
$Sn(CH_2CH{=}CH)_2$(tr)Me	−47	−57
$SnMe_2(tr)(CH_2CH{=}CH_2)$	−37	−30

[a] Using additivity factors of the substituents. [b] High-field resonances negative with respect to $SnMe_4$.

tin atom. Under the usual conditions for the observation of ^{119}Sn resonances, the signals for Sn(ad)$_4$ were very weak necessitating accumulation over a period of 24 h. The addition of the relaxing agent [Cr(acac)$_3$] (acac = acetylacetonate) markedly increased the intensities such that the accumulation time was cut to less than 2 h. The tin atom in this sterically hindered environment therefore has a long relaxation time, indicating that spin rotation and intramolecular dipole–dipole relaxation is slow (*cf.* CMe$_4$, ref. 29).

In large molecules, dipole–dipole relaxation dominates over spin rotation and is dependent on the distance of the CH dipole from the tin nucleus; β protons are less than half as effective in this mode of relaxation as α protons.[30] The absence of α protons in Sn(ad)$_4$ would thus automatically lead to longer relaxation times.

The pronounced upfield shift observed for Sn(ad)$_4$ of −73.5 p.p.m. supports the formation of a distorted structure in solution similar to that previously outlined for the low-temperature solid.

Stretching the Sn–ad bond could result in charge separation of the type $\mathrm{ad_3}\overset{\Delta-}{\mathrm{Sn}}\cdots\overset{\Delta+}{\mathrm{ad}}$. Such species would of course be in dynamic equilibrium with equivalent structures such that only one resonance would be observable. As commented on by one referee, the lack of any other tin resonance strongly indicates that only one species is present and that organotin halides are absent. The latter would have a resonance far removed from that observed (−73.5 p.p.m.) at *ca.* +140 p.p.m.

The adamant-1-yl cation itself (ad$^+$) is surprisingly stable. Recent ion-cyclotron resonance studies show it to be *ca.* 11 kcal mol^{-1} (*ca.* 46 kJ mol^{-1}) more stable than the t-butyl cation.[31] One reason advanced for the enhanced stability is that the empty *p* orbital could overlap with the rear lobe of the *sp*^{3} hybrids of the three bridgehead carbon atoms. Additionally, distortion to *sp*^{2} hybridisation does not involve any trans-annular compression present in the norborn-1-yl analogues.

The δ(^{119}Sn) value for Sn(ad)$_4$ is thus consistent with a structure where the tin atom assumes an almost *sp*^{2} hybridisation with resultant increased electron density on the tin.

Table 2 lists a range of tetraorganotin compounds including both adamant-1-yl and triptyc-9-yl (tr)* substituents. SnMe$_3$(tr) has a δ(^{119}Sn) of −27.2 p.p.m. The tin chemical shifts of the benzyl series, SnEt$_{4-n}$(CH$_2$Ph)$_n$ are additive,[32] each benzyl group contributing an upfield shift of *ca.* 8 p.p.m. The triptycyl group is therefore comparable to three benzyl substituents and indicates that each phenyl ring contributes to the shielding of the tin nucleus.

It is interesting to probe the range of applicability of the additivity principle for the more sterically hindered derivatives. SnPh$_3$(tr) should give a δ(^{119}Sn) value of −126 p.p.m. [3 × −33 + (−27)]. The observed value is reasonably close at −130 p.p.m. In view of the additivity of benzyl groups, allyl (–CH$_2$CH=CH$_2$) substituents should behave similarly. Sn(CH$_2$CH=CH$_2$)$_3$(tr) absorbs at −57.5 p.p.m. of which −27 p.p.m. is due to the tr group giving a ΔSn(CH$_2$CH=CH$_2$) of −10 p.p.m.

Using the increments calculated above, the shifts of a number of other tin derivatives may be calculated as shown in Table 2. For the most part, agreement between calculated and experimental shifts is reasonably good. The exceptions are found in the adamantyl-containing compounds where the observed shifts lie at significantly higher fields than those calculated. This again suggests a distortion of the tetrahedral geometry as described above. Interestingly, the triptycyl substituents do not show this effect and this probably reflects the known instability of carbenium ions and carbanions at bridgeheads of this type. The closely related tetrahydrodiethanonaphth-1-yl derivatives[33] also show only small upfield shifts relative to SnMe$_4$. All attempts to prepare Sn(tr)$_4$ failed, which again probably reflects the difficulty of the triptycyl group to sustain charges in the distortions which would have to occur [*cf.* Sn(ad)$_4$].

Experimental

Preparation of Tetraorganotin Derivatives.—Triphenyl(triptyc-9-yl)tin [SnPh$_3$(tr)],[34] (adamant-1-yl)triphenyltin [SnPh$_3$(ad)],[15] Sn(ad)$_4$,[15] and (adamant-1-yl)trimethyltin[15] were prepared by standard methods. All preparations were carried out in an argon atmosphere with exclusion of moisture. Analyses were performed by the Analytical Department at Manchester University, and the Alfred Bernhardt Analytical Laboratories, the results appearing in Table 3. In view of the novel structure of Sn(ad)$_4$, we feel it necessary to include the full analytical data for this compound in Table 4.

SnBr$_2$(ad)Ph. SnPh$_3$(ad) (12 g, 0.024 mol) was dissolved in a minimum volume of CCl$_4$ (AnalaR). This was then treated with a solution of bromine in the same solvent (48 cm^3 of 1 mol dm^{-3} solution). Reaction occurred almost immediately. The solvent was removed, leaving an oily liquid. On standing overnight at 0 °C white crystals were obtained. These were triturated with methanol and the crystals filtered off and recrystallised from methanol, m.p. 100 °C, yield 9 g (75%). ^{1}H N.m.r. (CCl$_4$ solution): δ, 7.5 (5 H, m), 1.4—2.7 p.p.m. (15 H, m).

SnPh$_2$(ad)Br. SnPh$_3$(ad) (2.45 g, 5 mmol) was dissolved in acetone (100 cm^3, AnalaR) and treated with HgBr$_2$ (1.80 g, 5 mmol), and the mixture refluxed for 4 h. On cooling to room temperature a white solid appeared which was filtered off. This was shown by n.m.r. and its melting point to be HgPhBr (m.p. 276 °C). The filtrate was evaporated *in vacuo* to give a white oily material. This was triturated with MeOH and allowed to stand overnight at −15 °C, whereupon crystallisation occurred. The crystals were filtered off. Crude yield, 2.1 g (86%). The crude

Table 3. Analyses[a] (%) of tetraorganotin derivatives

Compound	C	H	Br
SnBr$_2$(ad)Ph	38.9	4.0	32.2
	(39.2)	(4.1)	(32.6)
SnPh$_2$(ad)Br	54.5	5.2	16.2
	(54.2)	(5.2)	(16.4)
SnPh$_2$(ad)Me	64.5	6.4	—
	(65.2)	(6.6)	—
SnPh$_2$(tr)Br	64.2	3.9	12.6
	(63.4)	(3.8)	(13.2)
SnPh$_2$(tr)Me	72.3	4.9	—
	(73.2)	(4.8)	—
SnBr$_2$(tr)Me	47.2	3.1	28.2
	(47.1)	(3.0)	(29.0)
Sn(CH$_2$CH=CH$_2$)$_3$(tr)	69.8	5.7	—
	(70.3)	(5.7)	—
Sn(CH$_2$CH=CH$_2$)$_2$(tr)Br	57.6	4.2	15.9
	(58.4)	(4.3)	(15.0)
Sn(CH$_2$CH=CH$_2$)$_2$(tr)Me	68.7	5.6	—
	(69.1)	(5.6)	—

[a] Calculated values in parentheses.

Table 4. Analytical data for tetra-adamant-1-yltin (m.p. 238—240 °C)

Analyst	C(%)	H(%)	Sn(%)	*M*
A. Bernhardt Laboratory	73.05	9.25	—	673
Manchester University Analytical Laboratory	72.2	9.2	17.6	—
Calculated values	73.0	9.1	17.9	659

---

* Triptyc-9-yl = 9,10-dihydro-9,10-*o*-benzenoanthracen-9-yl.

material was extracted with CCl_4 and some insoluble material filtered off. The solvent was removed and an oily material was again obtained and treated as above to induce crystallisation. This yielded white crystals, m.p. 93—95 °C. ^1H N.m.r. (CCl_4 solution): δ, 7—8 (10 H, m), 1.5—2.65 p.p.m. (15 H, m).

$SnPh_2$(ad)Me. $SnPh_2$(ad)Br (1 g, 2.0 mmol) was dissolved in dry ether and added to a three-fold excess of MgMeI in dry ether under argon with stirring. The mixture was refluxed for 40 h, allowed to cool, and poured carefully into a solution of ammonium chloride. The ether layer was removed and then evaporated to give an oily material, which crystallised slowly on triturating with MeOH and cooling. The crystals were filtered off and washed with methanol and recrystallised from ether–ethanol, m.p. 108 °C (yield 60%). ^1H N.m.r.: δ, 7—7.9 (10 H, m), 2.5—1.7 (15 H, m), 0.4 p.p.m. [3 H, s, $J(^{117,119}Sn\text{–}H)$ 48 Hz].

$SnPh_2$(tr)Br. $SnPh_3$(tr) (2 g, 3.3 mmol) was dissolved in chloroform (40 cm^3, AnalaR) and placed in an ice-bath. A solution of bromine in chloroform (13.5 cm^3, 0.25 mol dm^{-3}, 0.5 g) was added dropwise over 2 h at 0 °C with very rapid stirring. The bromine colour disappeared completely after 3 h. The solvent was then removed *in vacuo* to give a slightly off-white solid. This was stirred with a little methanol, filtered, washed again, and dried. It was then recrystallised from benzene, m.p. 311—312 °C. ^1H N.m.r. ($CDCl_3$ solution): δ, 8.3—6.5 (22 H, m), 5.5 p.p.m. (1 H, s).

$SnPh_2$(tr)Me. $SnPh_2$(tr)Br (1 g, 1.64 mmol) was added to an excess of MgMeI in sodium-dried diethyl ether under dry argon. After a few minutes refluxing, the solid dissolved and the mixture became clear. The mixture was then refluxed for 40 h, allowed to cool, and poured carefully into an aqueous solution of ammonium chloride. The ethereal layer was then separated, dried over $MgSO_4$ (anhydrous), filtered, and evaporated. The resulting white solid was recrystallised from acetone, yield 72%, m.p. 246—247 °C. ^1H N.m.r. ($CDCl_3$ solution): δ, 8.2—6.3 (22 H, m), 5.48 (1 H, s), 0.98 p.p.m. [3 H, s, $J(^{117,119}Sn\text{–}H)$ 52 Hz].

$Sn(CH_2CH{=}CH_2)_3Cl$. Tetra-allytin[35] (42.6 g, 0.151 mol) was mixed with $SnCl_4$ (5.88 cm^3, 0.05 mol) under dry argon. The mixture was stirred for *ca.* 1 h, and then the contents were distilled *in vacuo*. A fraction was collected at 103 °C (*ca.* 354 Pa), n_D = 1.5541, yield 70%. ^1H N.m.r. (CCl_4 solution): δ, 5.86 (1 H, m), 4.98 (2 H, t), 2.5 p.p.m. [2 H, d, $J(^{117,119}Sn\text{–}H)$ 64 Hz].

$Sn(CH_2CH{=}CH_2)_3$(tr). n-Butyl-lithium (37.3 cm^3 of a 1.6 mol dm^{-3} solution in hexane, 0.06 mol) was added dropwise to a fine suspension of 9-bromotriptycene (10 g, 0.03 mol) in sodium-dried ether (150 cm^3) with vigorous stirring under dry argon. The mixture was stirred overnight. The supernatant liquid was removed by pipette and triallyltin chloride (7.8 g, 0.03 mol) was added with more dry ether. The mixture was stirred for *ca.* 40 h. Distilled water (100 cm^3) was added cautiously followed by benzene (300 cm^3) and the mixture stirred for 1 h. The organic phase was then separated, washed with water, and dried over magnesium sulphate. Conventional work-up yielded a white solid, which was recrystallised from ether to give plate-like crystals, yield 90%, m.p. 172—174 °C. ^1H N.m.r. (CCl_4 solution): δ, 7.43—7.08 (12 H, m), 6.12 (1 H, m), 5.45 (1 H, s), 5.4 (2 H, t), 2.4 [2 H, d, $J(^{117,119}Sn\text{–}H)$ 64 Hz].

$Sn(CH_2CH{=}CH_2)_2$(tr)Br. $Sn(CH_2CH{=}CH_2)_3$(tr) (4 g, 8.0 mmol) was dissolved in acetone (100 cm^3, AnalaR) under dry argon. Solid $HgBr_2$ (3.67 g, 8.0 mmol) was added and the mixture refluxed gently overnight. A solid suspension appeared which was cooled down and filtered off. The m.p. of the solid was 125—126 °C [$Hg(CH_2CH{=}CH_2)Br$]. The solvent was removed from the filtrate leaving a white solid which was stirred in CCl_4 and filtered to remove $Hg(CH_2CH{=}CH_2)Br$. The CCl_4 was then removed and the residue recrystallised from methanol, yield 65%, m.p. 188—189 °C. ^1H N.m.r.: δ, 7.8—6.8 (12 H, m), 6.1 (2 H, m), 5.3 (1 H, s), 5.2—4.65 (4 H, t), 2.88 p.p.m. [4 H, d, $J(^{117,119}Sn\text{–}H)$ 64 Hz].

$SnBr_2$(tr)Me. $SnPh_2$(tr)Me (5 g, 9.24 mmol) was dissolved in CCl_4. A solution of bromine in CCl_4 (119 cm^3 of a 0.155 mol dm^{-3} solution) was added to this dropwise over a period of *ca.* 30 min. The mixture was then gently refluxed for *ca.* 4 h until the colour due to bromine had disappeared. The solvent was removed to give a slightly oily solid which was treated with a small volume of boiling CCl_4, allowed to cool, filtered, and dried, m.p. 282—284 °C, yield, 75%. ^1H N.m.r. ($CDCl_3$ solution): δ, 8—7 (12 H, m), 5.62 (1 H, s), 2.0 p.p.m. [3 H, s, $J(^{117,119}Sn\text{–}H)$ 52 Hz].

$Sn(CH_2CH{=}CH_2)_2$(tr)Me. $SnBr_2$(tr)Me (3.5 g, 6.4 mmol) was added to an excess of freshly made $Mg(CH_2CH{=}CH_2)Br$ in sodium-dried diethyl ether and stirred under dry argon. The mixture was refluxed for *ca.* 40 h. After cooling, distilled water was added carefully dropwise with stirring to remove the excess of Grignard. The organic phase was separated, and washed with distilled water. The solvent was removed and a white solid was obtained which was recrystallised from methanol, m.p. 159—161 °C, yield 60%. ^1H N.m.r. (CCl_4 solution): δ, 7.6—6.7 (12 H, m), 6.04 (2 H, m), 5.2 (1 H, s), 4.97 (4 H, t), 2.33 [4 H, d, $J(^{117,119}Sn\text{–}H)$ 64 Hz], 0.6 [3 H, s, $J(^{117,119}Sn\text{–}H)$ 52 Hz].

Mössbauer Spectroscopy.—Mössbauer spectra were obtained at 80 K and 193 K, using a combined Harwell (waveform generator MWG200, servo amplifier MSA200, vibrator MV200, scintillation counter 1662B) and a Canberra spectrometer (multichannel analyser series 30, MV power supply 3102, amplifier 816, scintillation pre-amplifier 2005). The source was ^{119m}Sn (5 mCi) in a calcium stannate matrix (Radiochemical Centre, Amersham). The spectrometer was operated in a 'saw-tooth' mode and the spectra computer-fitted. The spectrometer was calibrated with a tin(IV) oxide–β-tin sandwich absorber. The peak separation in the spectrum of this absorber was measured against the spectrum of natural iron and was found to be 2.56 mm s^{-1}. All chemical shifts are referred to tin(IV) oxide as zero shift.

^{119}Sn *N.M.R. Spectroscopy.*—Spectra were obtained using a Bruker WP80SY spectrometer with broad-band decoupling. The following parameters were used: spectral width 20 000 Hz, relaxation delay 2 s, pulse width 16 μs. For the more sterically hindered tin derivatives *ca.* 5% [$Cr(acac)_3$] was added to the solutions. The relaxation agent caused no significant change in chemical shift. Spectra were run using 10% w/v solutions in CS_2. Occasionally $CDCl_3$ was used which gave changes in δ values of not more than 0.3 p.p.m. compared with those in CS_2.

References

1 J. J. Zuckeman, *Adv. Organomet. Chem.*, 1971, **9**, 22.

2 N. N. Greenwood and T. C. Gibb, in 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

3 P. J. Smith, *Organomet. Chem. Rev., Sect. A*, 1970, **5**, 373.

4 V. I. Kulishov, N. G. Bokii, A. F. Prikhot'ko, and Yu-T. Struchkov, *J. Strukt. Chem.*, 1975, **16**, 227, 231.

5 A. Karipedos, C. Forman, R. H. P. Thomas, and A. T. Reed, *Inorg. Chem.*, 1971, **10**, 529.

6 H. A. Stöckler and H. Sano, *Trans. Faraday Soc.*, 1968, **64**, 577.

7 M. Cordey-Hayes, R. D. W. Kemmitt, R. D. Peacock, and G. D. Rimmer, *J. Inorg. Nucl. Chem.*, 1969, **31**, 1515.

8 V. V. Khrapov, V. I. Goldanskii, A. K. Prokof'ev, and R. G Kostyanovskii, *J. Gen. Chem. USSR*, (*Engl. Transl.*), 1967, **37**, 1.

9 P. A. Cusack, P. J. Smith, J. D. Donaldson, and S. M. Grimes, 'A Bibliography of *X*-Ray Crystal Structures of Tin Compounds,' International Tin Research Institute, Brunel University, Publication no. 588, 1981.

10 G. M. Bancroft, K. D. Butler, and T. K. Sham, *J. Chem. Soc., Dalton Trans.*, 1975, 1483.

11 H. A. Stöckler, H. Sano, and R. H. Herber, *J. Chem. Phys.*, 1967, **47**, 1567.

12 M. Cordey-Hayes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 915, 2306.

13 R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 1969, 2145.

14 J. Ensling, P. Gutlich, K. M. Hasselbach, and B. W. Fitzsimmons, *J. Chem. Soc. A*, 1971, 1940.

15 R. M. G. Roberts, *J. Organomet. Chem.*, 1973, **63**, 159.

16 P. G. Harrison, R. C. Phillips, and E. W. Thornton, *J. Chem. Soc., Chem. Commun.*, 1977, 603.

17 P. C. Chieh and J. Trotter, *J. Chem. Soc. A*, 1970, 911.

18 N. A. Akhmad and G. G. Aleksandrov, *J. Struct. Chem.*, 1970, **11**, 824.

19 H. T. Sumsion and D. McLachlan, jun., *Acta Crystallogr.*, 1950, **3**, 217.

20 P. C. Chieh, *J. Chem. Soc., Dalton Trans.*, 1972, 1207.

21 H. W. Newkirk, *J. Chem. Soc., Dalton Trans.*, 1973, 12.

22 H. W. Newkirk, *J. Organomet. Chem.*, 1972, **44**, 263.

23 J. D. Kennedy and W. McFarlane, in 'NMR and the Periodic Table,' eds. R. K. Harris and B. E. Mann, Academic Press, London, 1978, pp. 342—366.

24 V. S. Petrosyan, *Prog. Nucl. Mag. Reson. Spectrosc.*, 1977, **11**, 115.

25 C. R. Lassigne and E. J. Wells, *Can. J. Chem.*, 1977, **55**, 927.

26 P. J. Smith and A. P. Tupcianskas, *Annu. Rep. NMR Spectrosc.*, 1978, **8**, 291.

27 J. D. Kennedy, W. McFarlane, and G. S. Pyne, *Bull. Soc. Chim. Belg.*, 1975, **84**, 289.

28 H-J. Kroth, H. Schumann, H. G. Kuivila, C. D. Schaeffer, jun., and J.-J. Zuckerman, *J. Am. Chem. Soc.*, 1975, **97**, 1754.

29 'NMR and the Periodic Table,' eds. G. A. Webb, R. K. Harris, and B. E. Mann, Academic Press, London, 1978, pp. 49—85.

30 S. J. Blunden, A. Frangon, and D. G. Gillies, *Org. Magn. Reson.*, 1982, **20**, 170.

31 R. H. Staley, R. D. Wieting, and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1977, **99**, 5964.

32 W. McFarlane, J. C. Maire, and M. Delmas, *J. Chem. Soc., Dalton Trans.*, 1972, 1862.

33 W. Kitching, G. Drew, W. Adcock, and A. N. Abeywickrema, *J. Org. Chem.*, 1981, **46**, 2252.

34 R. J. Ranson and R. M. G. Roberts, *J. Organomet. Chem.*, 1976, **107**, 295.

35 K. V. Vijayaraghavan, *J. Indian Chem. Soc.*, 1945, **22**, 135.

Received 2nd April 1984; *Paper* 4/524