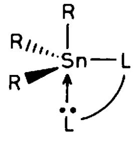
Organotin Biocides. Part 2.[1] Variable-temperature ^{119}Sn Mössbauer Study of Phenyl- and Cyclohexyl-tin Compounds

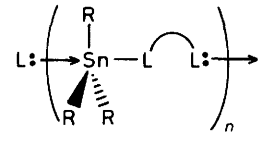
Kieran C. Molloy * **and Kieran Quill**
National Institute for Higher Education, Glasnevin, Dublin 9, Ireland

The temperature dependence of the recoil-free fraction ($a = -\mathrm{d}\ln f/\mathrm{d}T$) for 13 phenyl- and 11 cyclohexyl-tin compounds has been investigated, and the results interpreted in terms of the lattice structures of the compounds. This interpretation is aided by a classification of organotin polymers based upon the stereochemical disposition of tin and the bridging groups. Lattices based upon non-interacting units, or polymers which are helical (Class 4) or 'S'-shaped (Class 3), show the highest *a* values. The value of this parameter is generally reduced for zigzag (Class 2) polymers, while the most rigid lattices (lowest *a*) are based upon a rod-like (Class 1) architecture.

The current depth of understanding of solid-state organotin chemistry owes much to the availability of a battery of physical techniques which can be brought to bear on the structural problem. In the absence of definitive *X*-ray crystallographic data, indirect spectroscopic probes must suffice, and amongst the available techniques Mössbauer spectroscopy has assumed a particular prominence. From the single-temperature (78 K) experiment, conventional isomer shift (i.s.) and quadrupole splitting (q.s.) data can yield both the oxidation state and co-ordination number at tin, and under favourable circumstances distinguish between alternative geometric isomers.[2] Less clear cut under these experimental conditions are situations in which potential association within the solid can generate either monomeric or polymeric compositions, as exemplified by compounds (**1**) and (**2**) for a triorganotin (SnR_3) derivative of a bidentate ligand (L–L). Q.s. data for the two geometries can often be too close to permit unambiguous resolution, and the situation is exacerbated by distortions from ideal geometry. Furthermore, no distinction can be made on the basis of q.s. data alone between short chain, cyclic oligomers (**2**; *n* up to *ca.* 10) and true polymers (**2**; *n* up to ∞).



(**1**)



(**2**)

Such situations can potentially be resolved by variable-temperature Mössbauer spectroscopy (v.t.M.s.), in which the mean-square amplitude of vibration of the tin, $\langle x(T)^2\rangle$, is related to the recoil-free fraction of the absorber, $f(T)$ [equation (1)], where $\bar{\lambda}$ is the wavelength of the Mössbauer transition

$$f(T) = \exp[-\langle x(T)^2\rangle/\bar{\lambda}^2] \qquad (1)$$

divided by 2π. In the high-temperature limit ($T \geqslant \theta_D/2$), the Debye model for solids is applicable and hence we obtain equation (2), where E_R is the Mössbauer recoil energy, k the

$$\frac{\mathrm{d}f(T)}{\mathrm{d}T} = \frac{\mathrm{d}\exp(-6E_RT/k\theta_D^2)}{\mathrm{d}T} \qquad (2)$$

Boltzmann constant, and θ_D the Debye temperature for the lattice. For 'thin absorbers' ($N\sigma_0 < 1$, where N = number of absorber atoms per cm^2, and σ_0 = resonant absorption cross-section for ^{119}Sn), $A(T)$, the area under the spectral envelope, and $f(T)$ are linearly related and plots of ln $[A(T)/A(78)]$ *vs.* T are linear. Normalisation of data to 78 K is merely to facilitate inter-sample comparison. The temperature coefficient of f derived from these plots, $a = -\mathrm{d}\ln A(T)/\mathrm{d}T$, characterises the tightness with which the tin atom is bound into the lattice, and hence the degree of molecular association.

Most previous work in this area[3] has broadly elucidated *a*/structure systematics for methyltin derivatives. These systematics are not necessarily applicable to phenyl- and cyclohexyl-tin compounds where both steric bulk and a structured nature to the hydrocarbon can lead to different lattice dynamics. Understanding the v.t.M.s. behaviour of these two classes of organotins is a prerequisite to application of the methodology to structure determination of novel compounds of interest for their high biocidal activity, which is exploited commercially in a number of tin-based agrochemicals.[4a] We herein report our findings in this area.

Experimental

Organotin reagents and ligands were purchased from normal commercial sources (usually Aldrich or Merck) and were used in syntheses without further purification. Samples of tetraphenyltin (Aldrich) and triphenyltin chloride (Merck) used for Mössbauer spectra were recrystallised from toluene or diethyl ether. Triphenyltin hydroxide, tricyclohexyltin hydroxide, and diphenyltin oxide were gifts from the International Tin Research Institute (Greenford); the two $SnR_3(OH)$ compounds were recrystallised from cold acetone and toluene, respectively. Diphenyltin dichloride (BDH) was recrystallised from toluene. Tetracyclohexyltin was prepared from cyclohexylmagnesium chloride and tin(IV) chloride in diethyl ether[5] and recrystallised from toluene. Dicyclohexyltin dichloride was obtained by a redistribution reaction between tetracyclohexyltin and tin(IV) chloride (1:1) under established conditions[6] and purified by recrystallisation from diethyl ether.

The remaining organotin compounds used in this study were largely prepared by standard metathesis reactions, involving either an organotin hydroxide and a protonated form of the ligand, with the water formed in the reaction removed azeotropically in a Dean and Stark apparatus (route 1), or from an organotin halide and an alkali-metal (Na or K) salt of the ligand (route 2). Route 1 was employed to prepare the

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* *Present address*: School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY.

Table 1. Analytical data[a] for phenyl- and cyclohexyl-tin compounds

Compound	Analysis (%)			M.p. (°C)[b]	i.s.[c]	q.s.[c]
	C	H	N			
$SnPh_4$				224—226 (224—225)	1.27 (1.27)	0.00
$SnPh_3F$	58.70 (58.60)	4.00 (4.10)		320 (decomp.) (357, decomp.)	1.30 (1.25)	3.62 (3.53)
$SnPh_3Cl$				104—106 (105.5—107)	1.35 (1.37)	2.53 (2.45)
$SnPh_3(NCS)$	56.10 (55.90)	3.70 (3.70)	3.20 (3.45)	162—164	1.40 (1.35)	3.44 (3.54)
$SnPh_3(OH)$				119—120 (119—120)	1.18 (1.24)	2.82 (2.98)
$(Ph_3Sn)_2O$				123—124 (124)	1.16 (1.07)	1.37 (1.63)
$SnPh_3(O_2CMe)$	58.35 (58.70)	4.40 (4.45)		120—121 (121—122)	1.28 (1.28)	3.35 (3.36)
$SnPh_3(O_2CH)$	57.60 (57.75)	4.00 (4.10)		206—207 (201)[d]	1.48 (1.37)	3.48 (3.58)
$SnPh_3(O_2PPh_2)$	63.15 (63.55)	4.70 (4.45)		280 (decomp.)	1.23	3.33
$SnPh_3$(triaz)	56.50 (57.45)	3.75 (4.10)	9.90 (10.05)	306—308	1.25 (1.29)	2.89 (2.76)
$SnPh_2O$					0.89 (0.95)	1.90 (1.87)
$SnPh_2Cl_2$				42—44 (42—44)	1.41 (1.40)	2.85 (2.80)
$SnPh_2Cl_2$·0.75 pyz	44.40 (44.60)	3.25 (3.25)	5.15 (5.20)	114—115	1.37 (1.32)	3.08 (3.00)
$Sn(C_6H_{11})_4$	63.50 (63.85)	10.0 (9.30)		263—264 (263—264)	1.46 (1.57)	0.00
$Sn(C_6H_{11})_3F$	55.55 (55.85)	8.65 (8.60)		310 (decomp.) (305, decomp.)	1.47 (1.56)	3.71 (3.96)
$Sn(C_6H_{11})_3Cl$	53.75 (53.55)	8.20 (8.25)		127—129 (129—130)	1.68 (1.64)	3.52 (3.49)
$Sn(C_6H_{11})_3(OH)$	56.35 (56.10)	9.05 (8.90)		198—202 (220—222)[e]	1.41 (1.40)	2.99 (2.99)
$Sn(C_6H_{11})_3(O_2CMe)$	56.45 (56.25)	8.45 (8.50)		61—63 (61—63)	1.59 (1.57)	3.35 (3.27)
$Sn(C_6H_{11})_3(O_2CH)$	55.25 (55.25)	8.65 (8.30)		152—153	1.59	3.79
$Sn(C_6H_{11})_3$(iaa)	62.20 (62.00)	7.75 (7.65)	2.50 (2.60)	150—152	1.54	3.00
$Sn(C_6H_{11})_3(O_2PPh_2)$	61.50 (61.55)	7.45 (7.40)		300 (decomp.)	1.56	3.93
$Sn(C_6H_{11})_3$(triaz)	55.00 (55.10)	8.20 (8.10)	9.45 (9.65)	202—205 (218)[f]	1.51	3.26
$Sn(C_6H_{11})_2Cl_2$	40.35 (40.50)	6.55 (6.25)		88—89 (88—89)	1.78 (1.76)	3.40 (3.47)
$Sn(C_6H_{11})_2F_2$	43.60 (44.60)	7.30 (6.85)		275 (278)	1.37	3.31

[a] Required values given in parentheses. [b] Literature values (in parentheses) are taken from R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, 1960, 60, unless stated otherwise. [c] Literature values (mm s^{-1}) in parentheses are taken from ref. 2 and J. N. R. Ruddick, *Rev. Silicon, Germanium, Tin, Lead Comp.*, 1976, **2**, 115. [d] B. F. E. Ford, B. V. Liengme, and J. R. Sams, *J. Organomet. Chem.*, 1969, **19**, 53. [e] C. A. Kraus and R. H. Bullard, *J. Am. Chem. Soc.*, 1929, **51**, 3605. [f] Ref. 41.

triphenyltin derivatives of 1,2,4-triazole, diphenylphosphinic, formic, and acetic acids, and the tricyclohexyltin derivatives of 1,2,4-triazole, diphenylphosphinic, formic, acetic, hydrochloric, and indol-3-ylacetic[7] acids. Triphenyltin fluoride and isothiocyanate, tricyclohexyltin fluoride, and dicyclohexyltin difluoride were all prepared by route 2. Bis(triphenyltin) oxide was obtained by dehydration of $SnPh_3(OH)$ in boiling toluene under the conditions used in route 1. The pyrazine (pyz) adduct of diphenyltin dichloride precipitated from a 1:1 mixture of the reagents in light petroleum b.p. 40—60 °C, and was recrystallised from the same solvent.[8]

All the compounds subjected to v.t.M.s. analysis were confirmed by i.r., m.p., and (in most cases) C, H, and N microanalyses (microanalytical service, University College, Dublin). Mössbauer i.s. and q.s. data (Table 1) are in good agreement with published values.

Details of our Mössbauer spectrometer, method of data collection and manipulation have been described elsewhere.[1] Samples were utilised as finely ground powders (to minimise orientation effects), with up to 2 mg ^{119}Sn per cm^2 to comply as fully as possible with the criteria for a 'thin sample' while maintaining the viability of the experimental method, *i.e.* good-quality spectra accumulated in *ca.* 12 h. In certain instances, quantities of absorber in excess of 2 mg were used (up to a maximum of 4 mg), usually at elevated temperatures for species with relatively non-rigid lattices, leading to a curvature in the ln A *vs.* T plots. In such cases it was found that a range of equally valid 'best straight lines' was possible (as judged by the correlation coefficient, r) depending on the temperature range over which the linear relationship was assumed to hold. In reporting these results, we quote a single value for the slope for the complete data set, followed in parentheses by maximum and minimum slopes for segments of the data which could be considered to obey a linear relationship, and which do not show any significant reduction in correlation coefficient. Data for which only a single fit are given show no appreciable deviation from a linear relationship, from which it may be concluded that vibrational anharmonicity within the lattice is also absent. The quoted correlation coefficients are related to the complete data set for a given compound.

Discussion

Variable-temperature Mössbauer spectroscopic data for phenyl- and cyclohexyl-tin compounds are given in Tables 2 and 3 respectively. For both series we have concentrated our efforts on a study of compounds of known (X-ray crystallographic) lattice structure, or whose structure can be reliably assumed from their formulation and ancillary spectroscopic data. This has posed some restrictions on the range of compounds available, since relatively few crystallographic studies have been made on these two classes of organotins, particularly for polymeric arrangements.[9] Tables 2 and 3 also contain compounds of uncertain crystal structure, and v.t.M.s. data from other laboratories for comparison.

It is worth prefacing our analysis of these data with a note of caution. The temperature dependence of f is only a theoretically linear function for a 'thin sample,' in the high-temperature limit ($T \geqslant \theta_D/2$) for the Debye model of solids upon which the systematics are based. Deviations from a linear function are not uncommon in both our own experience (Figure 1) and that of others,[10] and even in cases where a 'thin absorber' is rigorously employed, non-linearity of plots of ln A *vs.* T can arise from lattice vibrational anharmonicity.[11] Where relatively minor curvature occurs, linear fits remain acceptable as judged by r, the correlation coefficient, but do not represent a totally reliable value for d ln f/dT. Correlation of data from a number of sources, which inevitably introduces variations in sample

Table 2. Variable-temperature ^{119}Sn Mössbauer data for phenyltin compounds

Compound[a]	$10^2\ a/K^{-1}$	$-r$ (T range/K, points)	Structure
(3) $(Ph_2Sn)_6$	2.80[b]		Monomer[c]
(4) $\{Ph_2Sn[(CH_2)C_6H_4(CH_2)_2]\}_n$	2.72[d]		Polymer (3 or 4)[d,e]
(5) $(Ph_3Sn)_4Sn$	2.42[b]		Monomer
(6) $SnPh_2(C_6F_5)_2$	2.37[b]		Monomer
(7) $[Ph_3Sn(C_6H_4CHCH_2)]_n$	2.30[d]	0.991 (77—130, 14)	Polymer[d,f]
(8) $SnPh_2[S_2P(OPr^n)_2]_2$	2.19[g]	(78—110, 5)	Monomer[h]
(9) $SnPh_2H_2$	2.19[b]		Monomer
(10) $SnPh_3(C_6F_5)$	2.17[b]		Monomer
(11) $Ph_3SnO_2C(CH_2)_2C(O)Me$	2.17[b]		Polymer (3 or 4)[e,h]
(12) $Ph_3SnO_2CC(Me)CH_2$	2.13[b,i]		Monomer[h]
(13) $SnPh_3(O_2PPh_2)$	2.09 (2.09—1.43)[j]	0.985 (78—150, 12)	Polymer (3)
(14) $Ph_3SnSnPh_3$	2.09[b]		Monomer[c]
(15) $(Ph_3Sn)_2NCN$	2.08[k]		Polymer (4)[e,h]
(16) $SnPh_3H$	2.01[b]		Monomer
(17) $SnPhCl_3$	1.97[b]		Monomer[h]
(18) $SnPhCl_3{\cdot}H_2salen$	1.94[l]	0.995 (78—115, 4)	Polymer (3)[e,h]
(19) $SnPh_2[S_2P(OEt)_2]_2$	1.92[g]	(78—145, 8)	Monomer[c]
(20) $SnPh_3(O_2CMe)$	1.91[m]	0.998 (78—145, 8)	Polymer (3)[e,m]
(21) $Ph_3SnON(Ph)C(O)Ph$	1.85[n]		Monomer[c]
(22) $SnPh_3(NCS)$	1.84[j]	0.997 (78—110, 7)	Polymer (3)[c,e]
(23) $SnPh_3(ONC_6H_{10})$	1.82[n]		Monomer[h]
(24) $SnPh_2Cl_2{\cdot}0.75pyz$	1.79[j]	0.998 (78—205, 13)	Monomer, polymer (2)[c,e]
(25) $\{SnPh_2[OP(S)(OPh)_2]OH\}_2$	1.76[o]	0.995 (77—160, 6)	Dimer[c]
(26) $SnPh_3(CN)$	1.73[k]		Monomer[h]
(27) $Ph_2SnOC_6H_4O$	1.73[b]		Polymer (3 or 4)[e,h]
(28) $Ph_3SnO_2CC_6H_4(o\text{-}N_2R^1)$	1.71[p]		Monomer[h]
(29) $Ph_3SnO_2CC_6H_4(o\text{-}N_2R^2)$	1.60[p]		Monomer[h]
(30) $Ph_3SnO_2CC_6H_4(o\text{-}N_2R^3)$	1.59[p]		Monomer[h]
(31) $SnPh_3Cl$	1.56 (1.56—1.43)[j,q]	0.998 (78—145, 6)	Monomer[c]
(32) $(Ph_3Sn)_2O$	1.56 (1.56—1.38)[j]	0.996 (78—145, 7)	Monomer[c]
(33) $SnPh_2Cl_2$	1.54 (1.54—1.39)[j,r]	0.998 (78—145, 7)	Monomer[c]
(34) $Ph_3SnO_2CC_6H_4(o\text{-}N_2R^4)$	1.53[p]		Monomer[p]
(35) $SnPh_3F$	1.49[j,s]	0.999 (78—160, 13)	Polymer (2)[e,h]
(36) $SnPh_3[S_2P(OEt)_2]$	1.43[t]	0.999 (77—150, 7)	Monomer[c]
(37) $SnPh_3[S_2P(OPr^i)_2]$	1.40[t]	0.998 (77—155, 9)	Monomer[h]
(38) $SnPh_4$	1.37[j]	1.000 (78—140, 6)	Monomer[c]
(39) $\{SnPh_3[O_2P(OPh)_2]\}_6$	1.37[o]	0.984 (77—170, 6)	Cyclic hexamer[c]
(40) $SnPh_2Cl_2{\cdot}H_2salen$	1.27[l]	0.995 (78—140, 7)	Polymer (2)[e,h]
(41) $SnPh_2(trop)_2$	1.20[u]		Monomer[h]
(42) $SnPh_3(O_2CH)$	1.15 (1.15—1.03)[j]	0.997 (78—145, 7)	Polymer[h]
(43) $SnPh_2O$	1.15 (1.15—0.94)[j,v]	0.996 (78—200, 8)	Polymer (2)[e,h]
(44) $SnPh_3(OH)$	1.10 (1.10—1.08)[j]	0.998 (78—145, 6)	Polymer (2)[c,e]
(45) $SnPh_2[S_2P(OPr^i)_2]_2$	1.06[g]	(78—160, 9)	Monomer[c]
(46) $SnPh_3(triaz)$	1.04[j]	1.000 (78—145, 6)	Polymer (2)[e,h]
(47) $SnPh_2Cl_2{\cdot}dppoe$	1.04[w]	(77—110, 6)	Polymer (1)[e,h]
(48) $SnPh_2[OP(S)(OMe)_2]_2$	0.97[o]	0.972 (77—170, 6)	Monomer[h]
(49) $SnPhCl_3{\cdot}pyz$	0.90[x]	0.999 (79—150, 5)	Polymer (1)[e,h]

[a] Abbreviations: H_2salen = *N,N'*-ethylenebis(salicylideneimine); pyz = pyrazine; R^1 = 4-hydroxynaphthyl; R^2 = 2-hydroxynaphthyl; R^3 = 4-dimethylaminophenyl; R^4 = 2-hydroxy-5-methylphenyl; trop = tropolonate (2-hydroxycyclohepta-2,4,6-trien-1-onate); triaz = 1,2,4-triazol-1-yl; dppoe = 1,2-bis(diphenylphosphoryl)ethane; ONC_6H_{10} is cyclohexanone oximate. [b] Ref.43. [c] From *X*-ray crystallographic data (see ref. 9 and Discussion section). [d] Ref. 39*a*. [e] Figures in parentheses define the polymer class (see Figure 2 and Discussion section). [f] Ph_3Sn pendant to polymer chain. [g] J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, I. Haiduc, M. Curtui, C. Guta, and D. Ruse, *Inorg. Chem.*, 1980, **19**, 2861. [h] On the basis of v.t.M.s. and other spectroscopic data. [i] H. Sano and R. Kuroda, *Chem. Phys. Lett.*, 1971, **11**, 512. [j] This work. [k] A. J. Rein and R. H. Herber, Proceedings of the 5th International Conference of Raman Spectroscopy, eds. E. D. Schmid, J. Brandmeuller, and W. Kiefer; Hans Ferdinand Schultz Verlag, Freiburg (F.R.G.), 1976, p. 66; *Chem. Abstr.*, 1978, **88**, 14527. [l] Ref. 10. [m] Ref. 1; also quoted as 2.17 × $10^{-2}\ K^{-1}$.[b] [n] Ref. 24. [o] F. A. K. Nasser and J. J. Zuckerman, *J. Organomet. Chem.*, 1983, **244**, 17. [p] Ref. 19. [q] Also quoted as 1.53 × $10^{-2}\ K^{-1}$.[k] [r] Also quoted as 2.21 × $10^{-2}\ K^{-1}$.[k] [s] Also quoted as 1.33 × $10^{-2}\ K^{-1}$.[b] [t] J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, I. Haiduc, C. Guta, and D. Ruse, *Inorg. Chem.*, 1980, **19**, 1662. [u] A. J. Rein and R. H. Herber, *J. Chem., Phys.*, 1975, **63**, 1021. [v] Also quoted as 1.30 × $10^{-2}\ K^{-1}$.[b] [w] P. G. Harrison, N. W. Sharpe, C. Pelizzi, G. Pelizzi, and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1983, 921. [x] E. Rivarola, A. Silverstri, and R. Barbieri, *Inorg. Chim. Acta*, 1978, **28**, 223.

thickness and the subjectivity of what is an acceptable linear range for the data, is *potentially* unreliable, particularly if too much is read into minor variations in a. In this light, our discussion is restricted to trends within the body of data as a whole, although on the basis of our conclusions we do draw inferences on the structures of specific, structurally uncharacterised compounds.

Phenyltin Compounds.—Of the compounds studied, those which are known to have lattices made up of non-interacting units comprise the monomers **(3)**,[12] **(14)**,[13] **(19)**,[14] **(21)**,[15] **(31)**,[16] **(32)**,[17] **(33)**,[18] **(34)**,[19] **(36)**,[20] **(38)**,[21] the dimer **(25)**,[22] and the cyclic hexamer **(39)**[23] and on the basis of spectroscopic evidence also include **(5)**, **(6)**, **(8)**, **(10)**, **(16)**, **(29)**, **(30)**, and **(37)**; all show a large value of a, (1.37—2.80) × $10^{-2}\ K^{-1}$, reflecting

Table 3. Variable-temperature ^{119}Sn Mössbauer data for cyclohexyltin compounds

Compound[a]	$10^2\ a^b$/K^{-1}	$-r$ (T range/K, points)	Structure[c]
(50) $Sn(C_6H_{11})_3$(iaa)	1.75 (1.75—1.45)	0.996 (78—165, 6)	Polymer (3)[d]
(51) $Sn(C_6H_{11})_3Br$	1.64[e]	0.999 (77—175, 6)	Monomer[f]
(52) $Sn(C_6H_{11})_3I$	1.60[e]	1.000 (77—175, 5)	Monomer[f]
(53) $Sn(C_6H_{11})_3(O_2CMe)$	1.59	0.997 (78—145, 7)	Polymer (3)[e]
(54) $Sn(C_6H_{11})_3(O_2PPh_2)$	1.58 (1.96—0.82)	0.988 (78—200, 8)	Polymer (3)
(55) $Sn(C_6H_{11})_3Cl$	1.40 (1.40—1.28)[g]	0.998 (78—145, 7)	Polymer (1)[f]
(56) $Sn(C_6H_{11})_3$(triaz)	1.31 (1.31—1.10)	0.993 (78—145, 6)	Polymer (2)[f]
(57) $Sn(C_6H_{11})_3O_2CC_6H_4$(*o*-$N_2R$)	1.30	(78—175, 9)	Polymer (3)[h]
(58) $Sn(C_6H_{11})_2F_2$	1.23	0.999 (78—160, 11)	Polymer (2)[h]
(59) $Sn(C_6H_{11})_4$	1.14[i]	0.996 (78—165, 9)	Monomer[h]
(60) $Sn(C_6H_{11})_2Cl_2$	1.13 (1.13—0.94)	0.996 (78—160, 7)	Polymer (2)[h]
(61) $Sn(C_6H_{11})_3F$	0.91 (0.91—0.79)	0.996 (78—145, 6)	Polymer (1)[f]
(62) $Sn(C_6H_{11})_3(O_2CH)$	0.93	0.992 (78—150, 10)	Polymer[g]
(63) $Sn(C_6H_{11})_3(OH)$	0.66	0.999 (78—135, 6)	Polymer (1)[h]

[a] Abbreviations: iaa = indol-3-ylacetate; R = 2-hydroxy-5-methylphenyl. [b] This work unless specified otherwise. [c] Figures in parentheses (also in Table 2) define the polymer class (see Figure 2 and Discussion section). [d] Ref. 7. [e] Ref. 28. [f] *X*-ray crystallographic data (see ref. 9 and Discussion section). [g] Also quoted as 1.60×10^{-2} K^{-1}.[e] [h] On the basis of v.t.M.s. and other spectroscopic data. [i] Quoted as 1.78×10^{-2} K^{-1}.[43]

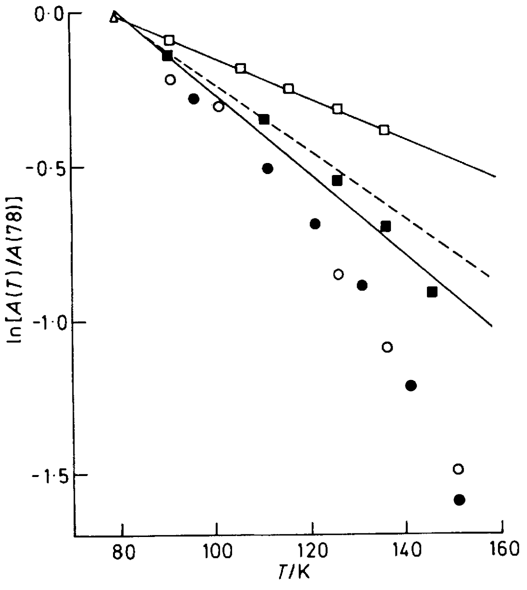

Figure 1. Representative variable-temperature Mössbauer data: (□), $Sn(C_6H_{11})_3(OH)$, linear over whole T range ($a = 0.66 \times 10^{-2}$ K^{-1}); (■), $Sn(C_6H_{11})_3$(triaz), showing mild curvature (78—145 K); the range of 'best straight lines' is given by —— (1.31×10^{-2} K^{-1}, all data) and - - - (1.10×10^{-2} K^{-1}, three points); (●,○), $SnPh_3(O_2PPh_2)$, showing a marked deviation from linearity over the whole T range. For the latter, data correspond to two separate data sets (●, 1 mg ^{119}Sn per cm^2; ○, 4 mg ^{119}Sn per cm^2) collected over a time interval of 4 months. The point △ (78,0.00) is common to all plots shown

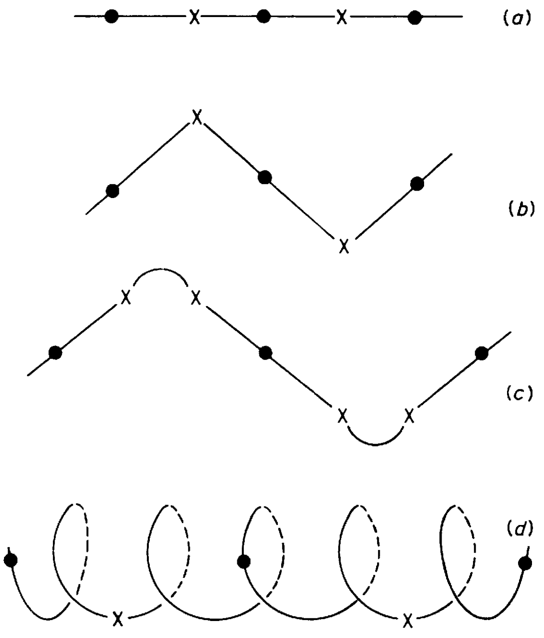

Figure 2. Schematic classification of organotin polymers: (*a*) Class 1 (rod), (*b*) Class 2 (zigzag), (*c*) Class 3 ('S'), and (*d*) Class 4 (helical)

the relative vibrational freedom of the tin atom in each case. This range of values of *a* embraces (in part) data for compounds whose lattices are strengthened by hydrogen bonding,[24] suggesting that with regular, well structured groups bonded to tin, *e.g.* C_6H_5, packing factors can play an important part in determining lattice dynamics.

Phenyltin compounds which are known to have polymeric structures fall into two groups: **(44)**[25] ($a = 1.10 \times 10^{-2}$ K^{-1}) and **(20)**,[1] **(22)**,[26] and **(24)**[8] (*a ca.* 1.80×10^{-2} K^{-1}). The lower value of *a* for **(44)** relative to the non-associated lattices discussed above is in consonance with the restrictions imposed on the vibrational motion of the tin when it is incorporated into a polymer chain. Such a simple rationale is clearly not applicable for the second group of polymers, whose *a* values are all in the 'non-polymeric' region of the systematics.

In order to understand the behaviour of organotin polymers under the conditions of the v.t.M.s. experiment, it is necessary to understand fully the architecture of the polymer, which we define as having three layers of complexity: the *primary structure*, which is related to the monomer from which the polymer is built, its co-ordination number, geometry, stereochemistry, *etc.*; the *secondary structure* we will use to describe the dimensionality of the polymer, one-, two-dimensional, chain, sheet, *etc.*; and the term *tertiary structure* which covers the three-dimensional disposition of secondary structure. While the primary and secondary structures play a major role in defining the characteristics of the polymer, they do not alone necessitate a restriction in the vibrational motion of the atoms incorporated into the polymer, as evidenced by the v.t.M.s. data for the second group of phenyltin polymers. The role of the polymer's tertiary structure must therefore be considered more fully, a pre-requisite for which is a classification of existing structures, which we present here for the first time in a collective form.

The tertiary structure of the polymer can be classified in terms of the relative spacial disposition of the R_nSn and bridging ligand (X) sub-units. We have identified four classes of tertiary structure which will serve as a framework for the analysis, and these are depicted schematically in Figure 2. For simplicity, we have excluded polymeric structures arising from hydrogen bonding due to the presence of lattice water, and confined ourselves to instances where X is covalently bound to R_nSn, as well as bridging to an adjacent tin moiety. Class 1 is a rod polymer, in which the Sn and X groups are collinear, *e.g.* $Sn(C_6H_{11})_3X$ (X = Cl[27] or F[28]), $SnMe_3(CN)$,[29] or $Me_3SnO_2CCH_2NH_2$[30] (where the bridging group straddles the Sn ••• Sn vector) all of which have a one-dimensional secondary structure, and $SnMe_2F_2$[31] which is two-dimensional. Class 2 is a zigzag arrangement, exemplified by $SnPh_3(OH)$,[25] $SnMe_3Cl$,[32] $SnMe_2Cl_2$,[33] and $Bu_2Sn\overline{O(CH_2)_3O}$,[34] all of which are one-dimensional, the first two with single and the latter two with double bridges. Where the group X contains several atoms, the structure expands and becomes more flexible (Class 3, 'S'-shaped). The compound $SnPh_3(NCS)$[26] is placed in Class 3, although the tin atoms remain collinear and together with the rigid NCS group the overall tertiary structure retains some Class 2 character. Where more flexible groups X are involved, and particularly where the tin atoms are no longer collinear along the chain, the 'S'-shape becomes more pronounced, *e.g.* $SnPh_3(O_2CMe)$,[1] $Sn(C_6H_{11})_3(O_2CMe)$ (one-dimensional),[19,35] and $SnMe_2(SO_3F)_2$ (two-dimensional).[36] As the extent of coiling of the polymer increases, a clearly helical structure is reached (Class 4), *e.g.* α-$SnMe_3[O_2P(Ph)OH]$,[37] and $SnMe_3(O_2SMe)$.[38] In such cases, the bridging group X may embody complete primary units, and the only tin atoms shown in Figure 2 are the starting points of the unique repeating coil section.

In terms of the v.t.M.s. experiment, the lattice rigidity decreases as (*a*) the strength of the bridging bond (X ••• Sn) decreases or (*b*) as the bridging mass is progressively displaced away from the Sn ••• Sn vector (Class 1 ———→ Class 4), or some combination of these factors. Class 2 polymers, *e.g.* (**44**), do reduce the vibrational motion of the tin relative to a non-interacting lattice. More flexible arrangements, as in the Class 3 polymers (**20**) and (**22**), on the other hand, afford a vibrational freedom to the tin akin to a non-polymeric structure. In the light of this assessment it must be concluded that the tertiary structure of compound (**4**) ($a = 2.72 \times 10^{-2}$ K^{-1}) must be severely coiled (Class 4, or an irregular variation thereof). Compound (**24**) must be reviewed independently to the other phenyltin polymers. The structure consists of both $2SnPh_2Cl_2\cdot pyz$ monomers and the $(SnPh_2Cl_2\cdot pyz)_n$ polymer.[8] The latter is of Class 2 type, accentuated by the large (but rigid) pyrazine bridge. It is plausible that this lengthy bridge would increase the value of *a* from *ca.* 1.1×10^{-2} K^{-1} [the value for compound (**44**)] in its own right, but in any case the experiment is measuring the average rigidity of the two types of tin site, which are indistinguishable in their Mössbauer q.s. values. On this basis the measured value of *a* (1.79×10^{-2} K^{-1}) is not anomalous.

Two other features of these phenyltin data have been noted previously, but are worth reiterating in the generality of this treatment. First, compound (**7**) in which a Ph_3Sn group is pendant to a polymer chain, has the vibrational characteristics of a monomer, irrespective of the tertiary structure of the polymer.[39] Secondly, monomeric (**45**) packs in the lattice very regularly in a pseudo-one-dimensional, doubly bridged, Class 3 polymer[40] (of which there are no genuine organotin examples[9]), reducing the *a* value to 1.06×10^{-2} K^{-1} and underlining the potential influence of packing forces on these experimental data.

Cyclohexyltin Compounds.—V.t.M.s. data for 11 cyclohexyltin compounds are given in Table 3, and can be interpreted in a similar fashion to those of the phenyltin compounds. The monomers (**51**) and (**52**) both show high values for *a* (*ca.* 1.60×10^{-2} K^{-1}), as does the weakly polymeric (Class 3) (**53**).[19,35] The tricyclohexyltin ester of indol-3-ylacetic acid (**50**) is also of Class 3 type, but in this case the polymer arises from hydrogen bonding between C=O ••• H–N units onto which an essentially four-co-ordinate tin is appended,[7] and this is reflected in a slight increase in *a* (1.75×10^{-2} K^{-1}) relative to the true Class 3 polymer (**53**). On the basis of these systematics, the value of *a* for $Sn(C_6H_{11})_4$ (**59**) is remarkably low, and can only arise from packing factors within the lattice, underlining the warnings outlined above.

The triazole (**56**) is a polymer of Class 2 type,[41] and this reflected in a reduction of the *a* value to 1.31×10^{-2} K^{-1}. Similarly, data for the two lightest tricyclohexyltin halides (**55**) and (**61**) reflect the onset of formation of the rigid Class 1 polymer lattice,[27,28] relative to the random orientation of molecules in the solid bromide (**51**) and iodide (**52**).[28] Other workers have[28] found a similar value for *a* for all four $Sn(C_6H_{11})_3X$ (X = halide) (*ca.* 1.60×10^{-2} K^{-1}), but in our work we observe a sequential stiffening of the lattice from the chloride (1.40×10^{-2} K^{-1}) to the fluoride (0.91×10^{-2} K^{-1}). No detailed assessment of intermolecular bond strengths can be made in terms of the available crystallographic data[28] which suffer from crystal decomposition in the *X*-ray beam, and result in *R* factors in excess of 0.1. However, our data are entirely consistent with the widely held belief that the strength of the intermolecular bond should increase in parallel with electronegativity of the bridging atom. Furthermore, the relatively low value of *a* for compound (**61**) suggests that Class 1 polymers do indeed produce more rigid lattices than similar Class 2 polymers, a phenomenon which has a direct bearing on our initial structural data for $Sn(C_6H_{11})_3(OH)$ (see below).

Compounds of Unconfirmed Structure.—Included in Tables 2 and 3 are structural assignments for lattices for which crystallographic evidence is lacking, based entirely on indirect, spectroscopic measurements, including v.t.M.s. These inferences are largely in accord with those of the original authors, but it is pertinent to comment here both on those compounds for which v.t.M.s. data are recorded for the first time, and where alternative structural possibilities to those offered previously suggest themselves in the light of the present work.

The compound $SnPh_3(CN)$ (**26**) ($a = 1.73 \times 10^{-2}$ K^{-1}) must be monomeric, given that any lattice association would be of Class 1 type. Of the organotin halides (**35**), (**58**), and (**60**), $SnPh_3F$ is presumed to be a polymer on the basis of q.s. data (3.53 mm s^{-1})[42] which specify a five-co-ordinated, *trans*-R_3SnX_2 geometry at tin. Since this polymer will be of Class 2 type, we conclude that the intermolecular bond is relatively weak (anisobidentate bridging), resulting in a comparatively high *a* value (1.49×10^{-2} K^{-1}) for this polymer class. In the case of the two dicyclohexyltin dihalides (**58**) and (**60**), v.t.M.s. data suggest polymeric formulations, which are probably doubly-bridged Class 2 (*cf.* $SnMe_2Cl_2$[33]) rather than Class 1 (*cf.* $SnMe_2F_2$[31]) in construction.* The two polymeric oxygen-

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* Despite the fair analytical data and a m.p. in agreement with the literature value, we are concerned about the authenticity of our $Sn(C_6H_{11})_2F_2$ sample. The q.s. (3.31 mm s^{-1}) seems unreasonably low, particularly when compared to the corresponding chloride (3.40 mm s^{-1}). Moreover, a lower value of *a* than observed would be anticipated on the basis of our results for the tricyclohexyltin halides.

bonded diphenyltin compounds $Ph_2SnOC_6H_4O$ (**27**) (presumably of *para* stereochemistry), and $SnPh_2O$ (**43**) both have higher *a* values (1.73×10^{-2},[43] 1.15×10^{-2} K^{-1}, respectively) than might have been expected. It seems reasonable then that the former polymer belongs to Class 3 or 4, facilitated by a tetrahedral geometry at tin, and the latter to Class 2, but with little or no cross-linking between chains. Bulky groups on tin are known to reduce the degree of association of diorganotin oxides,[4b] and in this respect the steric effect of the C_6H_5 groups seems to generate a polymer similar to $SnPr^i{}_2S$,[44] rather than a sheet polymer as proposed for $SnMe_2O$[4b] ($a = 0.87 \times 10^{-2}$ K^{-1}).[24] The compound $SnPh_3$(triaz) (**46**) can also be assigned a Class 2 polymer structure ($a = 1.04 \times 10^{-2}$ K^{-1}) corroborated by a *trans*-R_3SnN_2 primary structure as specified by the q.s. data (2.89 mm s^{-1}), and isostructural with $Sn(C_6H_{11})_3$(triaz).[41]

The situation is less clear cut for three pairs of compounds (**28**) and (**57**), (**42**) and (**62**), and (**13**) and (**54**). Of the two triorganotin arylazobenzoates, the triphenyltin derivative (**28**) has been assigned a monomeric, *mer*-R_3SnON geometry on the basis of q.s. (3.06 mms^{-1}) and v.t.M.s. ($a = 1.71 \times 10^{-2}$ K^{-1}) data.[19] That no precedent for this geometry in organotin chemistry exists,[9] and the acknowledged lack of rationale for the structure change in the light of the structure of the related compound (**34**),[19] prompts us to offer two alternative structural possibilities. First, a *trans*-R_3SnO_2 geometry with a Class 3 tertiary structure for the resulting polymer *is* consistent with both data (despite being previously discounted) and would follow the normal structure adopted by associated organotin carboxylates. This would, however, still fail to explain the reason for the change in structure from that of compound (**34**). Secondly, a highly distorted six-co-ordinate, *mer*-$R_3SnO_2(OH)$ geometry, in which the only intermolecular interaction is a long Sn $\cdots$ OH bond, which, in conjunction with a Class 2 or 3 type tertiary structure, would maintain the high *a* value. This latter type of bonding scheme would be plausible, in that the 4-hydroxynaphthyl group in compound (**28**) would, on steric grounds, be free from the intramolecular hydrogen-bonding role played by the 2-hydroxyphenyl moiety in (**34**). The general features of this second architecture, which we prefer of the two alternatives, have recently manifest themselves in the structure of $Ph_3SnO_2CC_6H_4(OH)$-*o*.[45] In the case of (**57**), the tricyclohexyl homologue of (**34**), the first of the above two alternatives was proposed in the original report to explain the Mössbauer data (q.s. = 3.35 mm s^{-1}, $a = 1.30 \times 10^{-2}$ K^{-1}).[19] The *a* value however, seems too low for this rationale [*cf.* $Sn(C_6H_{11})_3(O_2CMe)$, $a = 1.59 \times 10^{-2}$ K^{-1}], unless the lattice receives additional stabilisation, possibly *via* intermolecular hydrogen bonds.*

The two formates (**42**) and (**62**) both show distinctly more rigid lattices ($a = 1.15 \times 10^{-2}$ and 0.93×10^{-2} K^{-1} respectively) than their acetate counterparts (**20**) and (**53**) ($a = 1.91 \times 10^{-2}$ and 1.59×10^{-2} K^{-1} respectively), and enhanced q.s. values. We have no definitive explanation for these data at present, but speculate that the Class 3 polymer may receive stabilisation involving a more symmetrical six-co-ordinate, *mer*-R_3SnO_3 primary structure than seen in $SnPh_3(O_2CMe)$.[1] We hope to report a crystallographic rationale in the near future.

Still less can be inferred structurally from the v.t.M.s. data alone about the two diphenylphosphinates (**13**) and (**54**), which show ln *A vs. T* plots which are markedly curved over the whole temperature range (Figure 1), irrespective of the quantities of sample used in the experiments. Q.s. data for the compounds (3.33 and 3.93 mm s^{-1} respectively) specify a co-ordination number at tin greater than four, and the fact that both compounds decompose without melting at *ca.* 300 °C suggests lattice association. The *a* values when the majority of data points are included in the analysis are *ca.* 1.50×10^{-2} K^{-1} for both compounds (lower values of *a* arising from the effect of the data at 78—110 K) which would suggest polymeric Class 3 structures akin to that of $SnPh_3(O_2CMe)$[1] and isostructural with $SnMe_3[OP(S)Me_2]$ and $SnMe_3(O_2PMe_2)$.[46]

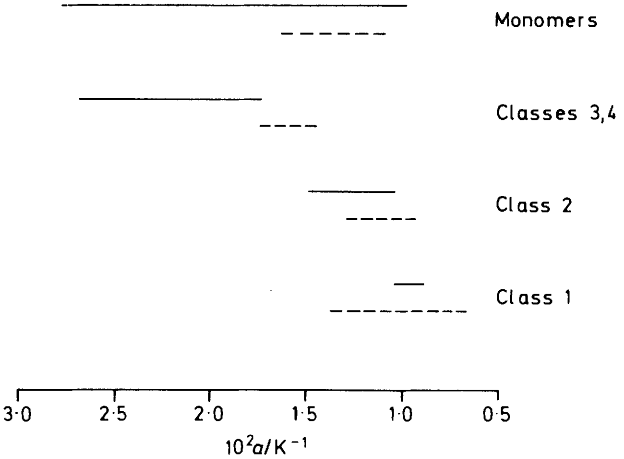

Figure 3. Classification of *a* values according to lattice type for phenyl- (——) and cyclohexyl-tin compounds (- - -)

Finally, we turn our attention to tricyclohexyltin hydroxide (**63**), one of the commercially marketed organotin agrochemical miticides,[4a] and which exhibits the lowest *a* value (0.66×10^{-2} K^{-1}) recorded in this study. The compound is unquestionably polymeric, with a *trans*-R_3SnO_2 primary structure (q.s. = 2.99 mm s^{-1}), and in comparison with the analogous Class 2 polymer (**44**) (Sn–O–Sn 137.8°)[25] the lattice is significantly more rigid. Extrapolation of the crystallographic and v.t.M.s. data for compounds (**55**) and (**61**) leads us to believe that $Sn(C_6H_{11})_3(OH)$ is a Class 1 polymer, in which Sn–O–Sn is *ca.* 180°. Such a structure is consistent with the steric demands of the hydrocarbon groups pendant to the polymer backbone, which must be greater for the chair C_6H_{11} group than the planar C_6H_5 ring, and suggests that Class 1 polymers are a common feature of tricyclohexyltin chemistry.

Conclusions

Despite the fact that v.t.M.s. *a* values for different lattice types do not fall into discrete, non-overlapping bands, the interpretation of such data can be aided by consideration of the nature of the (potentially) bridging group(s) and the tertiary structure of any viable polymeric arrangements. A guide to the application of v.t.M.s. data applied to phenyl- and cyclohexyl-tin compounds can be derived from Figure 3, which collates the available data into groups based upon the different classes of lattice type. The ranges in *a* values for each class will undoubtedly change as further crystallographic and v.t.M.s. data become available, and in any case only reflect the subjective opinion of the authors as to where the cross-over between an ordered array of non-interacting units and a weakly associated polymer can be drawn.

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* We have observed a parallel trend in the organotin derivatives of indol-3-ylacetic acid, where *a* for $SnMe_3$(iaa) is 1.35×10^{-2} K^{-1} (K. C. Molloy and T. G. Purcell, unpublished work).

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