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# The structure and dynamics of Cl-substituted tetraphenyl- and tetrabenzyl-tin(IV)

Markus Schürmann [a], Arturo Silvestri [b], Giuseppe Ruisi [b], Maria Assunta Girasolo [b], Adriana Barbieri Paulsen [c], Friedo Huber [a],*, Renato Barbieri [b,1]

[a] *Fachbereich Chemie, Universität Dortmund, Otto Hahn Straße 6, D-44221 Dortmund, Germany*
[b] *Dipartimento di Chimica Inorganica, Università di Palermo, Viale delle Scienze, I-90128 Palermo, Italy*
[c] *Institut für Physik, Medizinische Universität Lübeck, Ratzeburger Allee 160, D-23538 Lübeck, Germany*

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## Abstract

The crystal and molecular structure of ($o$-$ClC_6H_4CH_2)_4Sn$ has been determined by X-ray crystallography. Tin is in a slightly distorted environment. The molecular dynamics of ($p$-$ClC_6H_4)_4Sn$, ($o$-$ClC_6H_4)_4Sn$ and ($o$-$ClC_6H_4CH_2)_4Sn$ have been investigated by variable temperature $^{119}Sn$ Mössbauer spectroscopy (VTMS). A Debye-solid behaviour has been detected for ($p$-$ClC_6H_4)_4Sn$, where, on the other hand, no influence by hydrogen–chlorine interaction on the magnitude of the dynamics data and functions seems to occur. For the $o$-Cl-substituted derivatives, a non-Debye-solid character could be advanced. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Tin; Crystal structure; Molecular dynamics; $^{119}Sn$-Mössbauer-spectroscopy

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## 1. Introduction

The structure of tetraorganotin(IV) compounds has found wide interest, since the early 1920s [1]. Essentially tetrahedral tin environments ($\bar{4}$, or $\bar{1}$ symmetry) have been reported, mainly determined by X-ray crystallography (and related calculations) in the last decades for $(C_6H_5)_4Sn$ [2–6], $(C_6H_5CH_2)_4Sn$ [7], ($p$-$ClC_6H_4)_4Sn$ [8,9], ($p$-$CH_3C_6H_4)_4Sn$ [10,11], ($m$-$CH_3C_6H_4)_4Sn$ [12], ($o$-$CH_3C_6H_4)_4Sn$ [6], $(C_6F_5)_4Sn$ [13], $(2\text{-}C_4H_3S)_4Sn$ [14]; in the $(CH_3OC_6H_4)_4Sn$ derivatives, $p$- and $o$- substituted species are nearly of $\bar{4}$ symmetry [as ($p$-$CH_3S$–$C_6H_4)_4Sn$], while the $m$-substituted species is severely distorted [15,16]. For $(CH_3)_4Sn$ in the gaseous phase, electron diffraction measurements are consistent with a tetrahedral tin environment [17]; the same has been detected by X-ray diffractometry on crystals at 135 K [18].

The dynamics of tin nuclei in tetraorganotin(IV) compounds have been investigated by variable temperature $^{119}Sn$ Mössbauer spectroscopy (VTMS) in a series of $R_4Sn$ derivatives, R being Me [19,20], Ph [19–22], Benzyl [20], Cyclohexyl [23]; moreover, phenyl substituted species $(C_6F_5)_4Sn$ [23,24], $(C_6H_5)_3Sn(C_6F_5)$ [23,24], $(C_6H_5)_2Sn(C_6F_5)_2$ [23,24], ($m$-$CF_3C_6H_4)_4Sn$ [22], ($p$-$CF_3C_6H_4)_4Sn$ [22], $[(3,5\text{-}CF_3)_2C_6H_3]_4Sn$ [22] have been investigated by VTMS. Tetra-$p$-styryl tin, ($p$-$CH_2{=}CHC_6H_4)_4Sn$, and di-$p$-tolyl-di-$p$-styryl tin, [($p$-$CH_3C_6H_4)_2$($p$-$CH_2{=}CHC_6H_4)_2]Sn$, have been studied both in monomeric and polymeric forms with respect to the styryl radical, obtaining information on the dependence of the dynamic functions from the polymeric character of the carbon skeletons [25]; VTMS of the polymers $[R_3SnC_6H_4\text{–}p(CHCH_2)]_n$ ($R = CH_3$, $C_6H_5$), $[–(C_6H_5)_2Sn(CH_2)_2C_6H_4(CH_2)_2–]_n$ and $[–({}^nC_4H_9)_2Sn\text{-}OCH(CCl_3)O–]_n$ has been reported and commented

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* Corresponding author. Tel.: + 49-231-7553801; fax: + 49-231-7553797.

[1] Also corresponding author.

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Table 1
Analytical data of tetraorganotin(IV) derivatives

| Compound | Yield (%) | Analytical data (Found (calc.) (%)) | | M.p. (°C) | Molecular weight (Found in $CHCl_3$ (calc.)) |
|---|---|---|---|---|---|
| | | C | H | | |
| $(p\text{-}ClC_6H_4)_4Sn$ | 46 | 50.9 (51.0) | 2.9 (2.9) | 214 | 543 (564.9) |
| $(o\text{-}ClC_6H_4)_4Sn$ | 29 | 50.7 (51.0) | 2.8 (2.9) | 205 | 578 (564.9) |
| $(o\text{-}ClC_6H_4CH_2)_4Sn$ | 45 | 54.4 (54.2) | 4.0 (3.9) | 99 | 613 (621.0) |

[26]. Among the investigated species, a pronounced motional anharmonicity has been detected [20] for $(CH_3)_4Sn$ and $(C_6H_5CH_2)_4Sn$, the latter being discussed in terms of structural features [20].

In the context described above, as a part of our research program on the structure and dynamics of tin compounds, the dynamic properties of tin in $(p\text{-}ClC_6H_4)_4Sn$ and $(o\text{-}ClC_6H_4)_4Sn$, as well as in $(o\text{-}ClC_6H_4CH_2)_4Sn$, have been investigated, in order to possibly establish the influence of chlorine atoms as substituents in the aryl radicals. To this purpose, the crystal and molecular structure of $(o\text{-}ClC_6H_4CH_2)_4Sn$ has been determined by X-ray crystallography, and hydrogen bonding between Cl and aryl H atoms has been established for $(p\text{-}ClC_6H_4)_4Sn$ on the basis of a previously determined X-ray diffractometric structure [8], the latter in order to eventually correlate structure and dynamics of Sn atoms, in these compounds.

The results obtained are reported and discussed in the present paper. Neither crystal and molecular structures, nor Mössbauer studies, have been apparently reported until the present time for the *o*-Cl-substituted derivatives.

## 2. Experimental

Reagents and solvents were commercial products, which were purified and dried by standard procedures [27].

The derivatives $(p\text{-}ClC_6H_4)_4Sn$ and $(o\text{-}ClC_6H_4)_4Sn$ were synthesized by the Grignard reaction, according to standard procedures [28]. The compound $(o\text{-}ClC_6H_4CH_2)_4Sn$ was obtained by a one-step reaction, according to the procedure by Smith and Kipping [29] for the synthesis of $(C_6H_5CH_2)_4Sn$:

$$4(o\text{-}ClC_6H_4CH_2)Cl + 4Mg + SnCl_4$$
$$\rightarrow (o\text{-}ClC_6H_4CH_2)_4Sn + 4MgCl_2$$

A solution of 800 mmol $o\text{-}ClC_6H_4CH_2Cl$ in 200 ml of dry $Et_2O$ was slowly added under intensive stirring and under cooling with ice to a mixture of 200 mmol $SnCl_4$, 800 mmol Mg and 100 ml $Et_2O$. After heating for 3 h under reflux, further stirring at room temperature for 24 h and hydrolysis with water, the product was purified by vapour distillation. The aqueous phase was extracted with $CHCl_3$. The organic phases were united, and volatiles were evaporated. The residue was recrystallized from $Et_2O$/petroleum ether (b.p. 30–60°C) at 30°C. The colourless solid compound is air and water stable (for analytical data, see Table 1).

Analyses were effected with an Elemental Analyzer 1106, Carlo Erba (Milan). Melting points were measured with an instrument Büchi SMp 20 (Flawil, Switzerland), and molecular weights by a vapour pressure osmometer from Knauer (Berlin). NMR spectra were measured at 37°C by spectrometers Bruker AM 300 and AC 200 (Karlsruhe). X-ray crystallographic data were determined at 170 K by a Nicolet R3m/V diffractometer with graphite-monochromated Mo–$K_\alpha$ radiation (Madison, Wisconsin). The Mössbauer (nuclear $\gamma$ resonance) spectrometers and the related instrumentation (cryostats, sample holders, and apparatus for VTMS) were as previously described [30].

X-ray diffractometric intensity values for the colourless $(o\text{-}ClC_6H_4CH_2)_4Sn$ crystals were collected with

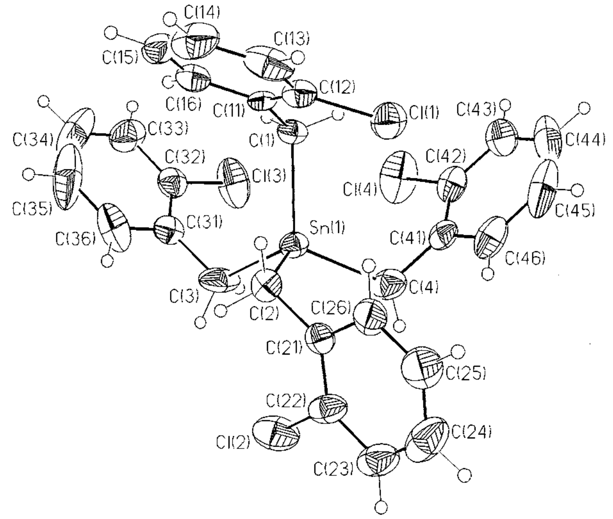


Fig. 1. General view (SHELXTL-PLUS) of $(o\text{-}ClC_6H_4CH_2)_4Sn$ showing 50% probability displacement ellipsoids and the atom numbering scheme.

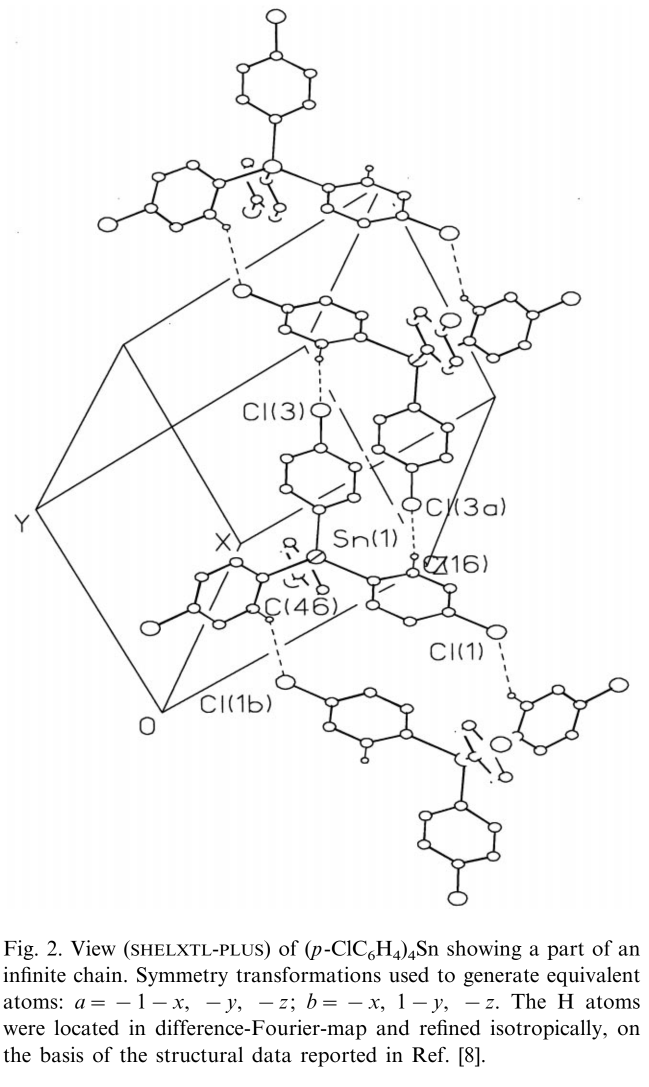


Fig. 2. View (SHELXTL-PLUS) of $(p\text{-}ClC_6H_4)_4Sn$ showing a part of an infinite chain. Symmetry transformations used to generate equivalent atoms: $a = -1-x,\ -y,\ -z$; $b = -x,\ 1-y,\ -z$. The H atoms were located in difference-Fourier-map and refined isotropically, on the basis of the structural data reported in Ref. [8].

$\omega - 2\vartheta$ scans. The lattice parameters were determined from a symmetry-constrained least-squares fit of the angular settings for 47 reflections with $2\vartheta_{max} = 30.0°$. Six standard reflections were recorded every 300 reflections and an anisotropic intensity loss up to 3.0% as detected during X-ray exposure. The data were corrected for Lorentz-polarization, for decay, and for absorption effects. Systematic absences for $(0k0)$ $k = 2n + 1$ and $(00l)$ $l = 2n + 1$ were detected. The structure was solved by direct methods SHELXS86 [31] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL93 [32].

The H atoms were placed in geometrically calculated positions and refined with a common isotropic temperature factor for different C–H types [$H_{methylene}$:C–H = 0.99 Å, $U_{iso} = 0.041(6)$ Å$^2$; $H_{aryl}$: C–H = 0.95 Å, $U_{iso} = 0.069(5)$ Å$^2$]. Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from International Tables for X-ray Crystallography [33]. Figs. 1 and 2 were created by SHELXTL-PLUS [34].

The $^{119}$Sn Mössbauer data reduction procedures were as previously detailed [35]. The VTMS spectra were determined on finely ground absorber samples and refined according to earlier reports [26,30,36,37]. A comprehensive treatment of the field has been recently published [38].

## 3. Results and discussion

The quality of the tetraorganotin(IV) compounds, synthesized in the present work, is shown by the data reported in Table 1, as well as by the $^1$H-, $^{13}$C- and $^{119}$Sn-NMR spectra in Table 2.

Tetraorganotin(IV) derivatives have been investigated in detail by $^1$H-, $^{13}$C- and $^{119}$Sn-NMR spectroscopy [28,39], and the related parameters have been discussed comprehensively [39]. As far as the compounds here investigated are concerned, the main features merging from the spectral data in Table 2 are as follows:

1. parameters $\delta(^1H)$ for $(p\text{-}ClC_6H_4)_4Sn$ and $(o\text{-}ClC_6H_4)_4Sn$ essentially agree with the corresponding data for $(C_6H_5)_4Sn$ [28]; besides, in $(o\text{-}ClC_6H_4CH_2)_4Sn$ the values $\delta(^1H)$ [H(6) and H(7)], as well as the coupling constant $^2J(^{119}Sn-^1H)$, are analogous to those for $(C_6H_5CH_2)_4Sn$ [40,41];
2. parameters $\delta(^{13}C)$, $\delta(^{119}Sn)$, and $^1J(^{119}Sn-^{13}C)$, inherent to $(p\text{-}ClC_6H_4)_4Sn$, correspond to literature values [42]; data $\delta(^{13}C)$ and $^1J(^{119}Sn-^{13}C)$ for $(o\text{-}ClC_6H_4CH_2)_4Sn$ are related to reports for $(C_6H_5CH_2)_4Sn$ [43,44].
3. $\delta(^{119}Sn)$ for $(o\text{-}ClC_6H_4)_4Sn$ is shifted upfield, possibly due to the increase of electron charge on Sn due to the Cl atom through the phenyl ring; coordination Cl → Sn is in fact excluded by the $^{119}$Sn Mössbauer parameters and functions (vide infra).

The molecular structure of $(o\text{-}ClC_6H_4CH_2)_4Sn$, determined in the present work, is reported in Fig. 1; the related crystallographic data are in Table 3, and selected bond distances and angles in Table 4.

From the data in Table 4, and the structure in Fig. 1, it clearly appears that the tin environment in $(o\text{-}ClC_6H_4CH_2)_4Sn$ is quasi-regular tetrahedral, in line with a series of $R_4Sn$ derivatives [1–16,18] (see Section 1). The crystal structure data in Table 3, as well as the bond distances and angles at tin (Table 4) essentially correspond to values reported for $(C_6H_5CH_2)_4Sn$ [7].

An interesting feature of the structure of $(p\text{-}ClC_6H_4)_4Sn$ is the chainlike arrangement of the molecules, the closest intermolecular contacts existing between Cl and H of neighbouring molecules as indicated in Fig. 2. Close van der Waals contacts may be assumed, but further studies should clarify whether positive lattice energy contributions might also come from hydrogen bonding interaction. In this respect it is interesting to remark that $(p\text{-ClC}_6H_4)_4Sn$ crystallises triclinic [8,9], while in contrast the other tetraaryltins studied crystallise in the tetragonal system [2–6,10–13].

The Mössbauer parameters, and the dynamics data and functions, concerning $(p\text{-ClC}_6H_4)_4Sn$, $(o\text{-ClC}_6H_4)_4Sn$ and $(o\text{-ClC}_6H_4CH_2)_4Sn$, reported in Table 5 and Figs. 4 and 5, are essentially in line with expectations for monomeric species showing quasi-regular Sn–$C_4$ tetrahedral type environments. The isomer shift, $\delta$, parameters (Table 5) essentially correspond to values reported for a number of $R_4Sn$ derivatives [38,45–47]. In particular, $\delta$s are invariant with the temperature, which would exclude the occurrence of phase transitions in the $T$ range investigated [48]. The magnitude of $\delta$s for $(o\text{-ClC}_6H_4)_4Sn$ and $(p\text{-ClC}_6H_4)_4Sn$ fully agree with data for $(C_6H_5)_4Sn$ [19,20], and $\delta$ for $(o\text{-ClC}_6H_4CH_2)_4Sn$ with the value for $(C_6H_5CH_2)_4Sn$ [20]. The narrowness of line widths, $\Gamma_{av}$ in Table 5, indicates the occurrence of one-line resonant absorptions, as shown in Fig. 3, parameters nuclear quadrupole splitting $\Delta E = 0.00$ mm s$^{-1}$. The latter is typical for symmetrical $R_4Sn$ compounds (as well as for a number of unsymmetrical derivatives) [19,22,25,45–47], according to the structure of the tin environment, with the consequent null values of the diagonal components of the electric field gradient tensor [49,50].

The treatment of the VTMS experimental data (the quality of the measured spectra being shown in Fig. 3) has been effected according to commonly employed principles and procedures (see Ref. [38]) outlined as follows.

From the slope of the function total area under the resonant peaks ($A$) versus temperature ($T$), 'relative' values of the Lamb–Mössbauer factor ($f_a^{rel}$) are obtained by Eq. (1):

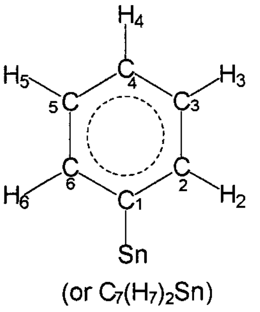
$$\frac{d\ln A}{dT} = \frac{d\ln f_a}{dT} = \frac{-3E_\gamma^2}{Mc^2K\vartheta_D^2} \qquad (1)$$

where $E_\gamma$ is the energy of the Mössbauer transition, $M$ the mass of the vibrating atom (e.g. Sn) or the molecular unit (e.g. $R_4Sn$ in the present context), $c$ is the velocity of light, $K$ the Boltzmann constant, and $\vartheta_D$ the Debye temperature [38]. Eq. (1) holds for Debye solids in the high-temperature limit ($T \geq \vartheta_D/2$). 'Relative'

Table 2
NMR spectral data for tetraorganotin(IV) derivatives[a]

| No. | Compound | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *(I) $^1$H-NMR* | | H(2) | H(3) | H(4) | H(5) | H(6) | H(7) | |
| 1 | $(p\text{-ClC}_6H_4)_4Sn$ | 7.46 d | 7.41 d | – | 7.41 d | 7.46 d | – | |
| 2 | $(o\text{-ClC}_6H_4)_4Sn$ | – | | 7.24–7.42 m[b] | | 7.65 d | – | |
| 3 | $(o\text{-ClC}_6H_4CH_2)_4Sn$ | – | 7.31–7.22 m | | 7.07–6.92 m[c] | 6.65–6.61 m | 2.32 s[d] | |
| *(II) $^{13}$C-NMR* | | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) |
| 1 | $(p\text{-ClC}_6H_4)_4Sn$ | 134.62 | 138.08 | 129.18 | 136.22 | 129.18 | 138.08 | – |
| 2 | $(o\text{-ClC}_6H_4)_4Sn$ | 141.78 | 140.20 | 128.71 | 130.95 | 126.72 | 138.95 | – |
| 3 | $(o\text{-ClC}_6H_4CH_2)_4Sn$ | 139.98 | 132.01 | 128.98 | 125.22 | 126.61 | 129.28 | 19.89[e] |
| *(III) $^{119}$Sn-NMR* | | | | | | | | |
| 1 | $(p\text{-ClC}_6H_4)_4Sn$ | −118 [8], −119 [42] | | | | | | |
| 2 | $(o\text{-ClC}_6H_4)_4Sn$ | −144 | | | | | | |
| 3 | $(o\text{-ClC}_6H_4CH_2)_4Sn$ | −25 | | | | | | |

[a] $\delta$ (ppm) in $CDCl_3$ solutions, 37°C; (I) and (II), $\delta$(TMS) = 0.0; (III), $\delta$(TMT) = 0.0. s, singlet; d, doublet; m, multiplet. Numbering of atoms:



[b] $\delta$ data for H(3), H(4), H(5).

[c] $\delta$ data for H(4) and H(5).

[d] $^2J(^{119}Sn–^1H) = 61$ Hz.

[e] $^1J(^{119}Sn–^{13}C) = 257$ Hz.

Table 3
Crystallographic data for ($o$-ClC$_6$H$_4$)$_4$Sn

| | |
|---|---|
| Empirical formula | $C_{28}H_{24}Cl_4Sn$ |
| Formula weight | 621.0 |
| Crystal system | Monoclinic |
| Crystal size (mm) | 0.22 × 0.20 × 0.15 |
| Space group | $P2_1/c$ |
| $a$ (Å) | 11.026(3) |
| $b$ (Å) | 21.967(8) |
| $c$ (Å) | 11.683(3) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 110.33(2) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 2653.4(14) |
| $Z$ | 4 |
| $D_{\text{calc.}}$ (Mg m$^{-3}$) | 1.554 |
| $\mu$ (mm$^{-1}$) | 1.381 |
| $F$(000) | 1240 |
| Absorption corr. (type) | Empirical (Ψ scan) |
| Max./min. transmission | 0.905, 0.736 |
| $\theta$ Range (°) | 1.97 to 25.05 |
| Index ranges | $-13 \leq h \leq 0$, $-1 \leq k \leq 26$, $-13 \leq l \leq 13$ |
| Reflections collected | 5224 |
| Independent reflected | 4695 [$R_{\text{int.}} = 0.0352$] |
| Refinement parameters | 300 |
| Reflections observed [$I > 2\sigma(I)$] | 2775 |
| Goodness-of-fit on $F^2$ | 0.831 |
| $R$ [$I = 2\sigma(I)$] | $R_1$ ($F$) = 0.0420 |
| $R$ indices (all data) | $wR_2$ ($F^2$) = 0.0912 |
| $(\Delta/\sigma)_{\text{max}}$ | 0.001 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.504 and −0.523 |

values of $\vartheta_D$ may be obtained for assumed $M$, and then the related Debye cut-off frequencies $\tilde{\nu}_D$:

$$\tilde{\nu}_D = \frac{K\vartheta_D}{h} \tag{2}$$

$K$ being the Boltzmann constant and $h$ the Planck constant [38]. Mean square displacements of the $^{119}$Sn nucleus, $<x^2>(T)$, are then calculated from the Lamb–Mössbauer factor:

$$f_a = \exp(-K^2 <x^2>) \tag{3}$$

$K$ being the wave vector of γ-rays [38].

In the case functions $\ln A(T)$ are not linear, 'absolute' Lamb–Mössbauer factors, $f_a^{\text{abs}}$, are calculated from the recoil-free fraction of the source (Ca$^{119}$SnO$_3$ in the present context), the latter being obtained from Mössbauer spectra of β-tin absorbers at 77.3 K; absorber thickness corrections are effected using Lang's approach, and Eq. (4) is employed for one-line Mössbauer spectra:

$$f_a^{\text{abs}} = \frac{t}{(\pi/2)\Gamma_{\text{nat}}\sigma_0 N} \tag{4}$$

where $t$ is the effective absorber thickness related to the area of the peak in the spectrum, $\Gamma_{\text{nat}}$ is the natural

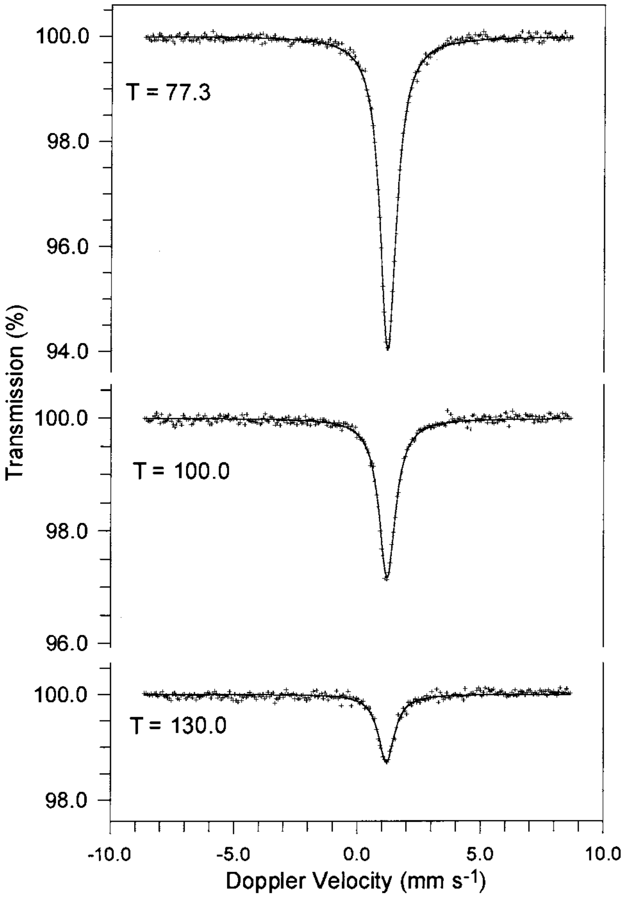


Fig. 3. The quality of variable temperature $^{119}$Sn Mössbauer spectra: data for ($p$-ClC$_6$H$_4$)$_4$Sn.

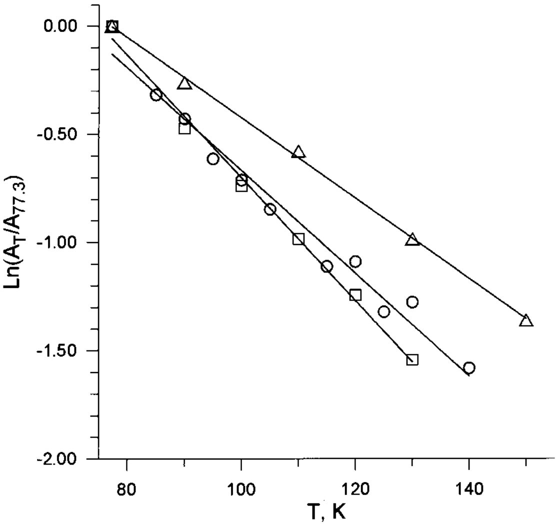


Fig. 4. Temperature dependence of the normalized Lorentzian areas, $A$, under the $^{119}$Sn Mössbauer peaks, for: △ ($o$-ClC$_6$H$_4$)$_4$Sn; □ ($p$-ClC$_6$H$_4$)$_4$Sn; ○: ($o$-ClC$_6$H$_4$CH$_2$)$_4$Sn. Full lines are the least-squares fits of the linear functions to the experimental data points, the related equations being: △: $\ln(A_T/A_{77.3}) = -0.0186T + 1.435$; □: $\ln(A_T/A_{77.3}) = -0.0284T + 2.134$; ○: $\ln(A_T/A_{77.3}) = -0.0238T + 1.708$.

linewidth of $^{119}$Sn, $\sigma_0$ is the resonant absorption cross-section of $^{119}$Sn, and $N$ is the number of resonant absorber atoms per cm$^2$. From $f_a^{abs}$ data, 'absolute' values of $\vartheta_{D,}$ $\tilde{\nu}_D$ and $<x^2>(T)$ are extracted by Eqs. (1)–(3) [38]. The effective vibrating mass $M$ (Eq. (1)) has been taken as the molecular mass.

Data and functions in Table 5 and Figs. 4 and 5 are essentially corresponding to values reported for $Ar_4Sn$ compounds [19–24], including $C_4Sn$ units embedded into polymeric materials [25,26]. In particular, values for $\vartheta_D$ and $M\vartheta_D^2$ are typical for monomeric species [23], and functions $<x^2>(T)$ lie in the zone for monomers

Table 4
Selected bond distances (Å) and bond angles (°) in ($o$-$ClC_6H_4CH_2)_4Sn$

| | | | | | |
|---|---|---|---|---|---|
| *Bond distances* | | | | | |
| Sn(1)–C(11) | 2.143(4) | C(14)–Cl(1) | 1.749(4) | C(32)–C(33) | 1.374(6) |
| Sn(1)–C(21) | 2.124(4) | C(24)–Cl(2) | 1.747(4) | C(33)–C(34) | 1.362(6) |
| Sn(1)–C(31) | 2.111(4) | C(34)–Cl(3) | 1.737(5) | C(34)–C(35) | 1.376(6) |
| Sn(1)–C(41) | 2.131(4) | C(44)–Cl(4) | 1.750(5) | C(35)–C(36) | 1.375(6) |
| C(11)–C(12) | 1.347(6) | C(21)–C(22) | 1.382(6) | C(41)–C(46) | 1.371(6) |
| C(11)–C(16) | 1.366(6) | C(22)–C(23) | 1.389(6) | C(41)–C(42) | 1.384(6) |
| C(12)–C(13) | 1.380(8) | C(23)–C(24) | 1.346(6) | C(42)–C(43) | 1.385(7) |
| C(13)–C(14) | 1.349(8) | C(24)–C(25) | 1.380(6) | C(43)–C(44) | 1.356(7) |
| C(14)–C(15) | 1.338(6) | C(25)–C(26) | 1.387(6) | C(44)–C(45) | 1.363(6) |
| C(15)–C(16) | 1.379(6) | C(31)–C(32) | 1.396(5) | C(45)–C(46) | 1.399(6) |
| C(21)–C(26) | 1.379(6) | C(31)–C(36) | 1.401(5) | | |
| *Bond angles* | | | | | |
| C(31)–Sn(1)–C(21) | 113.5(2) | | | C(13)–C(14)–Cl(1) | 119.9(5) |
| C(31)–Sn(1)–C(41) | 107.8(2) | | | C(23)–C(24)–Cl(2) | 119.9(5) |
| C(21)–Sn(1)–C(41) | 109.2(2) | | | C(25)–C(24)–Cl(2) | 119.9(4) |
| C(31)–Sn(1)–C(11) | 110.5(2) | | | C(33)–C(34)–Cl(3) | 119.3(5) |
| C(21)–Sn(1)–C(11) | 107.8(2) | | | C(35)–C(34)–Cl(3) | 119.7(5) |
| C(41)–Sn(1)–C(11) | 107.8(2) | | | C(43)–C(44)–Cl(4) | 120.1(5) |
| C(15)–C(14)–Cl(1) | 120.4(5) | | | C(45)–C(44)–Cl(4) | 119.5(5) |

Table 5
$^{119}$Sn Mössbauer parameters, and molecular dynamics data

| Compound | $\delta_{av}$[a] (mm s$^{-1}$) | $\Gamma_{av}$[b] (mm s$^{-1}$) | $10^2 \times [d(\ln A)/dT]$[c] (K$^{-1}$) | $\vartheta_D$[d] (K) | $\tilde{\nu}_D$[e] (cm$^{-1}$) | $10^{-6} \times M\vartheta_D^2$[f] (amu × deg$^2$) |
|---|---|---|---|---|---|---|
| ($p$-$ClC_6H_4)_4Sn$ | $1.203 \pm 0.004$ | $0.795 \pm 0.006$ | −2.836 (0.997) | $37.8 \pm 0.2$ (36.5)[g] | $26.3 \pm 0.2$ (25.3)[g] | 0.81 (0.75)[g] |
| ($o$-$ClC_6H_4)_4Sn$ | $1.213 \pm 0.008$ | $0.973 \pm 0.023$ | −1.859 (0.999) | $50.5 \pm 1.2$ (45.0)[g] | $35.0 \pm 0.8$ (31.3)[g] | 1.44 (1.15)[g] |
| ($o$-$ClC_6H_4CH_2)_4Sn$ | $1.437 \pm 0.008$ | $0.886 \pm 0.023$ | −2.376[h] (0.989) | $41.9 \pm 0.6$ (38.0)[g] | $29.1 \pm 0.4$ (26.4)[g] | 1.09 (0.90)[g] |

[a] Isomer shift with respect to $CaSnO_3$ at RT (data averaged over the whole temperature range (see Figs. 4 and 5), with standard error).

[b] Full width at half height of the resonant peak (data averaged over the whole temperature range (see Figs. 4 and 5), with standard error).

[c] Slopes of functions: areas under the resonant peak (Lorentzian, $A = (\pi/2)\varepsilon\Gamma$, $\varepsilon$ being the percentage resonant effect) versus $T$; correlation coefficients in parentheses (see Fig. 4).

[d] Debye temperature, derived from $f_a^{abs}$ values, with standard error.

[e] Debye cut-off frequency; see (d).

[f] Parameter of intermolecular force constant; $M$ = molecular mass.

[g] 'Relative' values extracted from $d(\ln A)/dT$. See text.

[h] Value determined by assuming the occurrence of a linear $\ln A(T)$ function in the $T$ range investigated (see Fig. 4).

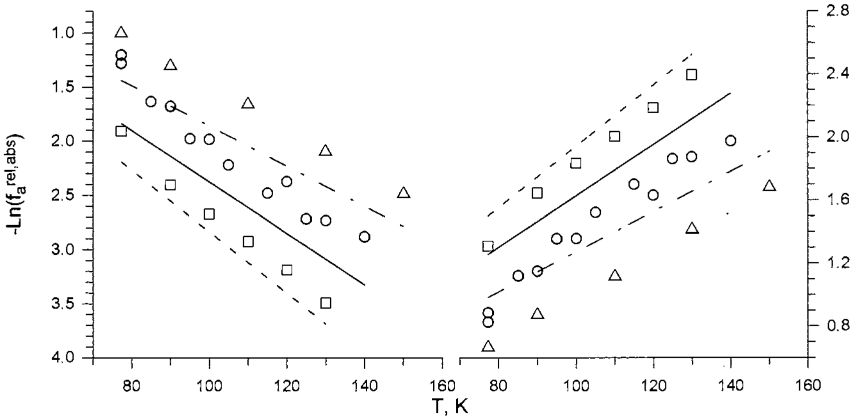


Fig. 5. Recoil-free fractions of $^{119}$Sn nuclei, $f_a$, and mean square displacements of $^{119}$Sn, $<x^2>$, as function of temperature for: △ (dash–dot line): $(o\text{-ClC}_6\text{H}_4)_4\text{Sn}$; ☐ (– – –): $(p\text{-ClC}_6\text{H}_4)_4\text{Sn}$; ○ (solid line): $(o\text{-ClC}_6\text{H}_4\text{CH}_2)_4\text{Sn}$. Lines are $f_a^{rel}(T)$ and $<x^2>(T)$ functions obtained from slopes d(ln $A$)/d$T$; data points are $f_a^{abs}$ and related $<x>^2$ values. See text and Table 5.

and monodimensional polymers [24]. The effect of $p$-Cl substitution in the phenyl ring, with respect to $o$-Cl, appears to consist in a larger slope ln $A(T)$ and $<x^2>(T)$ values, and in lesser values for $\vartheta_D$, $\tilde{\nu}_D$, $M\vartheta_D^2$ (Table 5 and Figs. 4 and 5), i.e. a better agreement with data for monomers [19–26]. Data for the $(o\text{-ClC}_6\text{H}_4\text{CH}_2)_4\text{Sn}$ slope d(ln $A$)/d$T$, Table 5 and Fig. 4, essentially correspond to the value concerning $(\text{C}_6\text{H}_5\text{CH}_2)_4\text{Sn}$ in the $T$ range 115–175 K, where the function appears to be linear [20].

Lastly, 'absolute' and 'relative' values $\vartheta_D$, $\tilde{\nu}_D$, $M\vartheta_D^2$, $f_a(T)$ and $<x^2>(T)$ for $(p\text{-ClC}_6\text{H}_4)_4\text{Sn}$ appear to mutually correspond (Table 5 and Fig. 5), while substantially larger differences occur for $(o\text{-ClC}_6\text{H}_4)_4\text{Sn}$ and $(o\text{-ClC}_6\text{H}_4\text{CH}_2)_4\text{Sn}$, where 'relative' values are about 10% less with respect to the 'absolute' data. Moreover, for $(o\text{-ClC}_6\text{H}_4\text{CH}_2)_4\text{Sn}$, functions $\ln(A_T/A_{77.3})$ versus $T$ (Fig. 4), and in a special way the data points $\ln f_a^{abs}$ and related $<x^2>$ versus $T$ (Fig. 5), are significantly scattered. These trends could be interpreted in terms of the occurrence of a transition around 110 K; two linear zones would be then assumed to occur in the $T$ ranges 77.3–ca. 110 K and ca. 110–140 K, respectively, in line with the trend reported for $[(\text{CH}_3)_3\text{SnC}_6\text{H}_4\text{-}p(\text{CHCH}_2)]_n$ [26]. The latter would be tentatively attributed to a 'non-Debye' character of the $o$-Cl substituted species, which would cause the lack of applicability of Eq. (1).

Finally, if in fact intermolecular Cl–H interactions exist according to Fig. 2, this would provoke no effect in the dynamics of the tin nuclei in $(p\text{-ClC}_6\text{H}_4)_4\text{Sn}$. This would be in line with findings concerning $(\text{C}_6\text{H}_5)_4\text{Sn}$ polymeric species [25,26].

## 4. Conclusions

The occurrence of linear functions $A(T)$, $f_a^{rel,\,abs}(T)$, $<x^2>(T)$, as well as the correspondence between relative and absolute values for $\vartheta_D$, $\tilde{\nu}_D$, $M\vartheta_D^2$, suggest that $(p\text{-ClC}_6\text{H}_4)_4\text{Sn}$ behaves as a Debye solid, in line with its molecular structure. No influence by possible Cl–H interactions is detected in the molecular dynamics functions, as shown by the large slopes of $A(T)$ and $f_a^{rel,\,abs}(T)$ functions, as well as by the consistent increase of $<x^2>$ parameters with increasing temperature. In the $T$ range investigated, molecular dynamics functions are still linear for $(o\text{-ClC}_6\text{H}_4)_4\text{Sn}$, although absolute and relative values for $\vartheta_D$, $\tilde{\nu}_D$ and $M\vartheta_D^2$ are consistently differing; as far as $(o\text{-ClC}_6\text{H}_4\text{CH}_2)_4\text{Sn}$ is concerned, functions $\ln(A_T/A_{77.3})$, $f_a^{abs}$ and the corresponding $<x^2>$, versus $T$, could be assumed as non-linear with a transition in the neighbourhood of 110 K; moreover, data for relative and absolute parameters also differ as in $(o\text{-ClC}_6\text{H}_4)_4\text{Sn}$. The two $o$-Cl substituted species would then not behave as Debye solids.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 115540 for $(o\text{-ClC}_6\text{H}_4\text{CH}_2)_4\text{Sn}$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www.http://www.ccdc.cam.ac.uk).

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