Structure, Bonding and Lattice Dynamics of Tri- and Tetraphenyltin Derivatives as Studied by Mössbauer and Multinuclear NMR Spectroscopy

BALDWIN KING
Department of Chemistry, Drew University, Madison, N.J. 07904, U.S.A.

HELLMUT ECKERT*, DOROTHY Z. DENNEY and ROLFE H. HERBER
Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, N.J. 08903, U.S.A.

(Received June 7, 1986)

Abstract

The structure and bonding properties of a number of closely related tetraphenyltin- and triphenyltin chloride compounds have been studied by the ^{119}Sn Mössbauer effect and multinuclear NMR spectroscopy. The comparison of liquid and solid state ^{13}C and ^{119}Sn NMR spectra and of glassy solution matrix and neat solid state Mössbauer spectra provides information about the extent of intermolecular association effects in these compounds. The results indicate that all materials with the exception of $(p\text{-CF}_3\text{Ph})_3\text{SnCl}$ are adequately described as monomeric solids with tetrahedral geometry around the metal atom. For the latter compound spectroscopic evidence for the presence of a five-coordinated tin species is presented.

Introduction

The structure of aryltin chlorides $R_{4-x}SnCl_x$ in the solid state has been the subject of numerous studies and extensive discussion [1–8]. It is generally accepted that in tetraarylstannanes ($x = 0$) such as Ph_4Sn the tetrahedral geometry of the isolated molecules is preserved in the solid state [1]. Likewise, X-ray [2] and vibrational spectroscopic data [3] indicate that solid Ph_3SnCl at room temperature is composed of discrete tetrahedral units, but the possibility of dimerization at low temperatures has been discussed [4–6]. For Ph_2SnCl_2, the original interpretation of the X-ray data in terms of a monomeric structure [7] has been questioned [8]. Since dimerization raises the coordination number of tin from 4 to 5, both the ^{119m}Sn Mössbauer effect as well as ^{119}Sn and (to a lesser extent) ^{13}C solid state NMR should serve as suitable probes for such changes in the environment of the metal atom. In the present study, such results for a series of closely related tri- and tetraphenyltin derivatives are presented. The approach utilizes the comparison of spectra obtained on the compounds in their monomeric states, *i.e.* by multinuclear NMR in solution and Mössbauer spectroscopy in a frozen glassy matrix, with those obtained for the neat solids.

While in the past both NMR and Mössbauer spectroscopy have served to characterize the detailed effect of subtle electronic modifications caused by changes in the ligand electronegativity [9–11], correlated studies using both techniques have been rare [12], and restricted to the comparison of liquid state NMR with solid state Mössbauer data. In the present study, this comparison has been extended to include solid state NMR data and Mössbauer spectra obtained in frozen solutions. With respect to the above questions, an attempt is made to evaluate the potential of both spectroscopic methods to provide relevant information about the bonding properties of these compounds.

Experimental

Syntheses

The tetraaryl derivatives were prepared from the respective bromobenzenes by a Grignard reaction with tin(IV) halide [13, 14], while the triaryltin chlorides were prepared by a redistribution reaction between the tetraaryl compound and tin(IV) chloride [13]. All starting materials, except the 3,5-bis(trifluoromethyl)bromobenzene (Alfa Inorganics) were obtained from Aldrich Chemicals and used without further purification. SnI_4, enriched with ^{119}Sn was synthesized from SnO_2 (84% ^{119}Sn, ORNL) by reaction with NH_4I at elevated temperatures. Magnesium turnings suitable for Grignard reactions and anhyd-

---

*Present address: Department of Chemistry, California Institute of Technology, Mailcode 164-30, Pasadena, Calif. 91125, U.S.A.

0020-1693/86/$3.50

rous diethyl ether were obtained from Fisher Chemicals.

All syntheses were carried out under dry nitrogen in an apparatus fitted with a calcium chloride drying tube. Elemental analyses were carried out by Robertson Laboratory, Florham Park, N.J.. Melting points were recorded on a Hoover capillary melting point apparatus, and are uncorrected. Melting points and analytical percentages (literature data and calculated values in parentheses) were:

Tetrakis(3-trifluoromethylphenyl)tin, (**III**): 140–141 °C (143–144); C, 48.02 (48.08); H, 2.35 (2.30).

Tetrakis(4-trifluoromethylphenyl)tin, (**IV**): 150–151 °C (150); C, 48.20 (48.08); H 2.39 (2.30).

Tetrakis(3,5-bis(trifluoromethyl)phenyl)tin, (**V**): 162–163 °C (not available); C, 39.48 (39.6); H, 1.51 (1.25).

Tris(2-trifluoromethylphenyl)tin chloride, (**VII**): 83.5–84 °C (not available); C, 42.43 (42.76); H, 2.13 (2.05); Cl, 6.76 (6.79).

Tris(4-trifluoromethylphenyl)tin chloride, (**IX**): 82–83 °C; C, 42.67 (42.76); H, 2.35 (2.05); Cl, 6.02 (6.79); F, 28.28 (29.02).

The remaining organotin compounds examined in the present study were obtained commercially (Alfa Inorganics) and suitably purified by recrystallization or sublimation before spectroscopic examination.

Nuclear Magnetic Resonance Spectroscopy

The liquid state ^{13}C NMR data were obtained in $CDCl_3$ solution using a Bruker WM 500 high resolution spectrometer at the Southern California Regional NMR Facility. A 45° flip angle, power-gated broadband decoupling and a 6 s pulse delay were used. ^{19}F spectra were obtained undecoupled on a Varian FT-80 spectrometer using 45° pulses. The ^{119}Sn data were obtained on the same spectrometer using 90° pulses and gating the proton decoupler off during a 60 s relaxation delay. Some additional single-pulse experiments were carried out using the WM 500 spectrometer. All the data reported in Tables I–III were found independent of concentration within the range of solubility of the materials under study. Chemical shifts are reported relative to TMS (^{13}C), $CFCl_3$ (^{19}F), and $(CH_3)_4Sn$ (^{119}Sn).

TABLE I. Comparison of the Solution and Solid State ^{13}C Chemical Shifts of the Compounds under Study with Values Calculated from the Additivity Rule

Compound	Chemical shift (ppm)			
	C atom	Solution[a,b]	Solid state[c]	Calculated
I $(C_6H_5)_6Sn_2$[d]	1	138.48	138.0	
	2, 6	137.38	137.4	
	3, 5	128.63	128.9	
	4	128.76	128.9	
II $(C_6H_5)_4Sn$[e]	1	137.96	137.7	
	2, 6	137.21	137.7	
	3, 5	128.60	128.4	
	4	129.09	129.4	
III $(m\text{-}CF_3C_6H_4)_4Sn$	1	136.68	136.6	138.2
	2	133.10	n.a.[f]	133.9
	3	131.36	130.2	130.7
	4	126.86	127.5	125.8
	5	129.39	130.2	128.8
	6	140.23	141.1	140.4
	7	123.98	124[j]	
IV $(p\text{-}CF_3C_6H_4)_4Sn$	1	140.72	139.9	141.1
	2, 6	137.24	137.3	137.4
	3, 5	125.50	124.3	125.5
	4	132.11	133.1	131.2
	7	123.88	124[j]	
V $((3,5\text{-}CF_3)_2C_6H_3)_4Sn$	1	136.33		138.3
	2, 6	136.33		137.1
	3, 5	132.85		130.9
	4	125.06		122.5
	7	122.94		

(continued)

TABLE I. *(continued)*

Compound	Chemical shift (ppm)			
	C atom	Solution[a,b]	Solid state[c]	Calculated
VI $(C_6H_5)_3SnCl$[g]	1	137.20	137.0	
	2, 6	136.07	136.3	
	3, 5	129.10	130.1	
	4	130.44	131.3	
VII $(o\text{-}CF_3C_6H_4)_3SnCl$	1	135.84	135.2	134.1
	2	135.45	136.3	138.2
	3	127.10	127.1	125.9
	4	130.54	131.4	130.7
	5	131.84	131.4	132.4
	6	137.18	135.5	136.4
	7	124.46	125[j]	
VIII $(m\text{-}CF_3C_6H_4)_3SnCl$[h]	1	137.1		137.6
	2	132.3		132.9
	3	131.4		131.3
	4	127.8		127.2
	5	129.7		129.4
	6	139.2		139.4
	7	123.8		
IX $(p\text{-}CF_3C_6H_4)_3SnCl$	1	140.58	145.1	140.6
	2, 6	136.3	136.5	136.4
	3, 5	125.88	125.0	125.9
	4	133.06	131.9	132.6
	7	123.64	n.a.[f]	
X $(C_6H_5)_2SnCl_2$[i]	1	137.0		
	2, 6	134.9		
	3, 5	129.7		
	4	131.8		

[a] ±0.02 ppm; *vs.* TMS. [b] Saturated solution in $CDCl_3$. [c] ±0.2 ppm; *vs.* TMS. [d] Additional data in ref. 20. [e] ^{119}Sn isotopically enriched material. [f] Not assignable. [g] Additional data in refs. 20 and 25. [h] From ref. 27. [i] From ref. 25. [j] Broadened by dipolar and scalar coupling to ^{19}F.

TABLE II. $^nJ(^{13}C-^{117/119}Sn)$ Coupling Constants

Compound	^nJ (C–Sn) coupling constant (Hz)			
	^1J[a]	^2J[b]	^3J[b]	^4J[c]
I $(C_6H_5)_6Sn_2$[d]	413 (395)	40.5	47.6	n a.[f]
II $(C_6H_5)_4Sn$[e]	531	37.0	51.2	12.0
III $(m\text{-}CF_3C_6H_4)_4Sn$	544 (520)	43.6 (C2)	51.0 (C5)	12.5
		36.5 (C6)	53.8 (C3)	
IV $(p\text{-}CF_3C_6H_4)_4Sn$	535 (511)	39.4	53.7	n.a.
V $((3,5\text{-}CF_3)_2C_6H_3)_4Sn$	546 (521)	43.0	n.a.	n.a.
VI $(C_6H_5)_3SnCl$[g]	613 (587)	48.5	62.8	12.6
VII $(o\text{-}CF_3C_6H_4)_3SnCl$	679 (652)	42.0 (C6)	51.0 (C3)	12.6
		35.9 (C2)	64.6 (C5)	
VIII $(m\text{-}CF_3C_6H_4)_3SnCl$[h]	n.a.	33.0 (C2)	62 (C5)	n.a.
		48.0 (C6)		
IX $(p\text{-}CF_3C_6H_4)_3SnCl$	623 (596)	52.0	65.2	n.a.
X $(C_6H_5)_2SnCl_2$[i]	785	63	90	n.a.

[a] $^1J(^{119}Sn-^{13}C)$ is listed; $^1J(^{117}Sn-^{13}C)$ given in parenthesis. Experimental error: ±1 Hz. [b] ±0.2 Hz; average $^{117,119}Sn-^{13}C$ coupling constant. [c] ±0.5 Hz; average $^{117,119}Sn-^{13}C$ coupling constant. [d] Additional data in ref. 20. [e] ^{119}Sn isotopically enriched material. [f] Not assigned. [g] Additional data in refs. 20 and 25. [h] From ref. 27. [i] From ref. 25.

TABLE III. ^{119}Sn and ^{19}F Chemical Shifts in Solution and ^{19}F–^{119}Sn Coupling Constants

Compound		$-\delta$ (^{119}Sn) (ppm)^a	$-\delta$ (^{19}F) (ppm)^b	$^nJ(^{19}F-^{119}Sn)$ (Hz)^c
I	$(C_6H_5)_6Sn_2$	145.8		
II	$(C_6H_5)_4Sn$	130.6		
III	$(m\text{-}CF_3C_6H_4)_4Sn$	128.6	63.14	4.1
IV	$(p\text{-}CF_3C_6H_4)_4Sn$	132.3	63.52	5.2
V	$((3,5\text{-}CF_3)_2C_6H_3)_4Sn$	128.1^d	63.38	
VI	$(C_6H_5)_3SnCl$	47.0		
VII	$(o\text{-}CF_3C_6H_4)_3SnCl$	65.5		
IX	$(p\text{-}CF_3C_6H_4)_3SnCl$	55.7		
X	$(C_6H_5)_2SnCl_2$^{e}	32.0		

[a] Upfield from Me_4Sn; ±0.2 ppm. [b] Upfield from $CFCl_3$; ±0.05 ppm. [c] ±0.2 Hz. [d] ±0.5 ppm; Signal/noise too low to extract coupling constant. [e] From ref. 11.

Solid state ^{13}C and ^{119}Sn NMR data were obtained on a homebuilt 200 MHz spectrometer at the Southern California Regional NMR Facility. The tin spectra were acquired at 74.5 MHz in a high-power broadband probe, by single 90° pulses of 3 μs length, using delays between 2 and 10 min. The solid state ^{13}C NMR data were obtained at 50.4 MHz in a CP-MAS probe from Doty Scientific at spinning speeds between 3.5 and 5 kHz. The ^{1}H 90° pulse length was 5 μs, corresponding to 50 kHz decoupling power. Crosspolarization contact times were 5 ms, and the Hartmann–Hahn condition was set using an adamantane standard, whose methylene peak provided a secondary chemical shift reference at 38.56 ppm from TMS [15]. The cross-polarization pulse program incorporated spin-temperature inversion [16] to suppress artifacts, and 'flipback' of the ^{1}H magnetization to decrease the rather long recycle delay needed for the protons to relax. Further experiments were carried out by adding a delay time after crosspolarization during which the decoupler was turned off, resulting in the disappearance of signals arising from directly protonated carbon atoms ('dipolar dephasing' [17]). This method allows the selective observation of non-protonated C-atoms and thus aids in the assignments.

Variable temperature Mössbauer Spectroscopy

Variable temperature ^{119}Sn Mössbauer data were obtained on samples of known thickness using the techniques and spectrometer system described earlier [18]. All isomer shifts are reported with respect to a $CaSnO_3$ absorber spectrum at 295 K. Spectrometer calibration was achieved using NBS SRM metallic iron at room temperature, before and after each series of temperature dependence measurements, as described previously [19]. All Mössbauer data were fitted using a matrix inversion least squares fitting routine on the Rutgers University NS 9000 computer, in which effect magnitude, line position, and line width at half maximum were allowed to vary as free parameters. The optical (Mössbauer) thickness of all samples was less than 1.5, and thus no saturation corrections were applied to the data. For obtaining glassy solution spectra, the sample compound was dissolved in n-butylbenzene, the resultant solution injected into a Mylar or thin glass window fitted copper sample holder, and quickly frozen in liquid nitrogen, prior to the start of the spectral data accumulation, which was carried out in transmission geometry as usual.

Results and Discussion

Bonding Properties of the Molecular Compounds

Tables I–III give a complete overview of the NMR parameters obtained for the present materials. The ^{13}C chemical shifts for tetraphenyltin show only moderate agreement with data published previously for this compound [20a]. In accordance with the characteristic substituent effects observed in other organometallics [21], the C-1 as well as the C-2, C-6 positions of the aromatic ring are found to be highly deshielded, while the influence of the tin moiety upon *meta* and *para* carbon atoms seems to be negligible. Thus, as far as tetraaryltin derivatives and other compounds in which tin is entirely coordinated to carbon, are concerned, there seems to be no indication of carbon–tin π-backbonding, a conclusion, which has also been reached by previous proton NMR studies [22]. If, however, aryl substituents are successively replaced by chlorine atoms, deshielding effects become increasingly noticeable in the *para* position. At the same time the downfield shift of the *ortho* carbons gradually diminishes, hence indicating the possible involvement of carbon–tin π-backbonding effects for these materials.

Table I contrasts the experimental ^{13}C chemical shifts with the values predicted from the respective

TABLE IV. ^{119m}Sn Mössbauer Data and Lattice Parameters of the Tri- and Tetraphenyltin Compounds under Study

Compound		*IS*[a,b] (mm s^{-1})	*QS*[a,c,d] (mm s^{-1})	d ln *A*/d*T*[e] (10^{-2} K^{-1})	ω[f] (cm^{-1})
I	$(C_6H_5)_6Sn_2$	1.41	0	1.95	28.5
II	$(C_6H_5)_4Sn$	1.30	0	1.63	39
III	$(m\text{-}CF_3C_6H_4)_4Sn$	1.28	0	2.12	23.4
IV	$(p\text{-}CF_3C_6H_4)_4Sn$	1.29	0	2.20	23.4
V	$((3,5\text{-}CF_3)_2C_6H_3)_4Sn$	1.256 ± 0.007	0	1.60	n.d.
VI	$(C_6H_5)_3SnCl$	1.35	2.56	2.16	33.7
	in n-Bubz[g]	1.33	2.45	n.d.	n.d.
VII	$(o\text{-}CF_3C_6H_4)_3SnCl$	1.275 ± 0.008	1.99 ± 0.016	1.95	n.d.
	in n-Bubz	1.30	2.12	n.d.	n.d.
IX	$(p\text{-}CF_3C_6H_4)_3SnCl$	1.405 ± 0.004	3.43 ± 0.026	2.13	n.d.
	in n-Bubz	1.30	2.43	n.d.	n.d.
X	$(C_6H_5)_2SnCl_2$[e]	1.39	2.81	2.21	41
	in n-Bubz	1.33	2.63	n.d.	n.d.

[a] At 78 K. [b] With respect to $CaSnO_3$ at 295 K; ±0.01 mm s^{-1} unless specified. [c] ±0.020 mm s^{-1} unless specified. [d] The linewidths for all compounds varied unsystematically between 0.84 and 0.96 mm s^{-1}. [e] The temperature range over which ln *A* was determined was 78–300 K for I, II, X; 78–160 K for II and III; 78–130 K for V; 78–125 K for VII; 78–115 K for IX, and 90–170 K for VI. [f] Raman active lattice mode frequency associated with intermolecular vibrations; see ref. 31 for discussion. [g] n-Bubz = n-butyl benzene, a glass-forming solvent.

data sets for benzotrifluoride [23], tetraphenyltin (this work), and triphenyltin chloride [20, 25], assuming additivity of the respective substituent contributions. For all the disubstituted compounds of the present study, excellent agreement is found when making this assumption. In addition, a re-inspection of the data reported previously [24] for a series of substituted monoaryl–trimethyltin compounds reveals similar agreement, showing, that, in general, tin moieties obey the additivity rule quite well. An exception occurs for the chemical shifts of the C-1 and C-2 carbon atoms of compound **VII**, indicating the possibility of intramolecular interaction between the two *ortho* substituents. This interaction must be relatively weak, however, since the solid state and frozen solution Mössbauer data give no indication of tin–fluorine bonding interactions in this compound (*vide infra*).

Magnitudes and general trends reported in previous studies of related compounds [11, 20, 25–28] also hold true for the ^{13}C–^{119}Sn coupling constants determined for the compounds examined in the present study. Replacement of one aromatic substituent by chlorine increases the coupling constants, hence reflecting either increased s-character of the C–Sn bond due to rehybridization of the Sn atoms [25], or the presence of carbon–tin π-backbonding. The latter explanation is favored, however, since earlier work [25] of alkyltin chlorides, R_{4-x}·$SnCl_x$, has shown, that the effect of tin rehybridization is an order of magnitude smaller than the effects encountered in the present study. In contrast, the observed enhancement of ^1J(C–Sn) by the presence of CF_3 substituents is most likely due to rehybridization, since the magnitude of this effect shows a distinct correlation with the distance of the CF_3 group to the C-atom under consideration. (The effect upon the long range C–Sn coupling constans appears less systematic.)

The ^{119}Sn chemical shifts are typical for aromatic stannanes [11]. Owing to the low solubility of tetraphenyltin in all common non-complexing organic solvents, the literature data concerning the ^{119}Sn chemical shift [29] suffer from low accuracy. Using isotopically enriched material in the present study, $\delta(^{119}Sn)$ was re-determined to be −130.6 ± 0.2 ppm. In a recent investigation of substituted trimethylarylstannanes, a regular dependence of the ^{119}Sn chemical shift on the substituent electronegativity was found [30]; in particular, the electron donating groups giving rise to the most upfield chemical shift values. The present study shows a more complicated picture. As can be seen from Table III, the chemical shift of tetraphenyltin is unexpectedly found to be intermediate between those of the *meta* and *para* trifluoromethyl derivatives, whereas the triphenyltin chlorides yield an order opposite to that predicted in ref. 30. These results indicate that the numerical values arise from a more complex interplay of the parameters governing the paramagnetic contributions to the shielding constants.

The parameters extracted from the ^{119m}Sn Mössbauer studies are summarized in Table IV. The isomer shifts observed at 78 K are unexceptional and are in acceptable agreement (where appropriate) with values reported earlier. As noted previously [31], the temperature dependence of tin isomer shifts is relatively small, and cannot be used to extract meaningful data concerning the effective vibrating mass of the Mössbauer reporter atom. In contrast to the trends observed in solution NMR data, the Mössbauer isomer shift differences among compounds **II**–**V** as well as those among **VI**, **VII** and **IX** (in the glassy matrix state) are close to the experimental error limits, and these data indicate the small influence of even severely perturbing substituents such as the trifluoromethyl group on the s-electron density at the tin atom. Comparison with literature data [32] shows that this insensitivity of Mössbauer isomer shifts is a quite general feature in ring-substituted systems. In view of these results the significantly increased isomer shift in bulk (p-CF_3-$Ph)_3SnCl$ and the unusually large quadrupole splitting of this compound are especially noteworthy. As will be discussed below, this behavior is consistent with a different coordination of the tin atom indicating a dimeric or polymeric structure of this compound.

Coordination of Tin in the Solid State

The solid state ^{13}C NMR spectra of compounds **II**, **VI**, **VII**, and **IX** are shown in Fig. 1. The chemical shifts agree within ±1 ppm with the respective solution data for all the compounds under discussion, with the noticeable exception of (p-$CF_3C_6H_4)_3SnCl$, for which, in the solid state, a substantial downfield shift of 4.5 ppm is found for C-1 (see arrow in Fig. 2). A recent solution ^{13}C NMR study has shown that the complexation of triphenyltin chloride by electron donor species (DMSO, pyridine) which increases the tin coordination number from four to five is associated with a downfield shift of *ca.* 6 ppm for the C-1 atom [33]. The observation of a similar effect for compound **IX** in going from solution to the solid state thus provides strong support for a change in coordination number from four to five.

Figure 3 shows the solid state ^{119}Sn NMR spectra of compounds **II**, **VI**, **VII** and **IX**. While the rather large asymmetric broadening (arising from both static dipolar coupling to the quadrupolar Cl nuclei and chemical shift anisotropy) and low signal to noise ratios (owing to long spin-lattice relaxation times) do not permit an accurate analysis, it is worth noting that in the spectrum of (p-$CF_3C_6H_4)_3SnCl$ the center of gravity is strongly displaced upfield as compared to the corresponding unsubstituted and *ortho*-substituted triphenyltin chlorides. Again, the comparison with ^{119}Sn solution NMR data reported for Ph_3SnCl complexes with DMSO and pyridine [33] reveals that this effect is in accordance with a five-coordinated tin species.

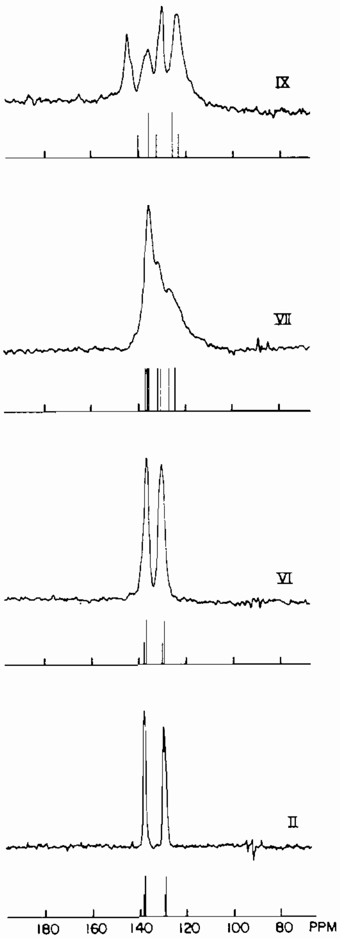

Fig. 1. Solid state ^{13}C CP-MAS spectra at 50.36 MHz of compounds **II**, **VI**, **VII** and **IX**. The vertical lines indicate the respective chemical shifts observed in the solution spectra.

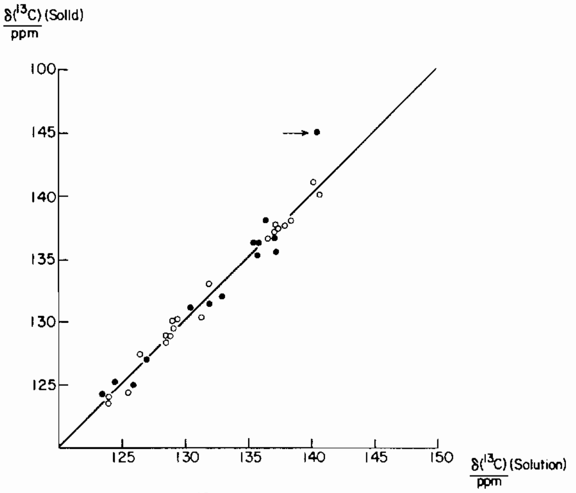

Fig. 2. Plot of the ^{13}C chemical shifts in the solid state *vs.* the respective data in the solution state for the compounds under study. Open circles: tetraaryltin compounds. Filled circles: triaryltin chlorides.

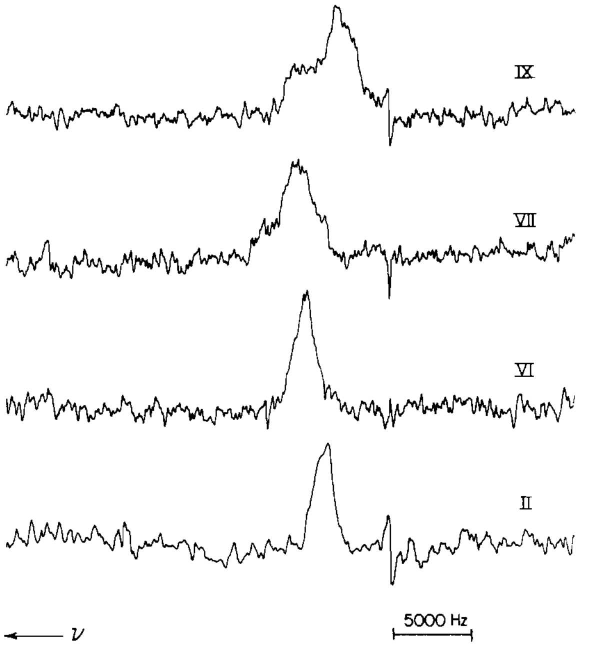

Fig. 3. Solid state ^{119}Sn NMR spectra at 74.5 MHz of compounds **II**, **VI**, **VII** and **IX**.

Both the NMR and Mössbauer data are consistent with the expected discrete monomeric nature of all tetraphenyltin derivatives in the solid state. The same conclusion holds for triphenyltin chloride(VI) at room temperature as indicated by the observation that the ^{13}C NMR chemical shifts are almost identical in solution and the solid, consistent with earlier detailed investigations by room temperature vibrational spectroscopy [2] and X-ray diffraction [3]. For this compound, however, pentacoordination of the metal atom by chlorine bridging at lower temperatures has been discussed by Zuckerman [4] with reference to an earlier ^{35}Cl NQR study [5]. In an extensive review of structural data [6] the possibility is raised that coordination about the metal atom – which is tetrahedral at room temperature – may transform to trigonal bipyramidal on cooling to liquid nitrogen temperature. To examine this point further, in the present study, earlier Mössbauer results obtained on this compound [34] were re-investigated in the temperature range $5.5 < T < 170$ K. The temperature dependence of the recoil-free fraction is shown in Fig. 4. The data in the interval $90 < T < 170$ K are well fitted by a linear regression, with a correlation coefficient of 0.997 for the 8 data points, and the slope in this interval has been used to evaluate the lattice dynamical parameters [35] listed in Table IV. The departure from linearity in the temperature region below 90 K is expected, since in the low temperature limit the latter parameter becomes temperature independent, and then reflects primarily the effect of zero point motion. The quadrupole splitting is temperature independent below 90 K, while at higher temperatures this parameter shows the expected effects due to thermal expansion, reaching a value of 2.52 ± 0.02 mm s^{-1} at 170 K . The temperature dependence of the isomer shift is $-2.23\ 10^{-4}$ mm s^{-1} K^{-1} over the whole temperature range, a value typical of organometallic tin(IV) compounds, and the data are reasonably well fitted by a linear regression with a correlation coefficient of 0.95. None of these data indicate any change in the coordination about the metal atom within the temperature range $5.5 < T < 170$ K, and it is therefore inferred that it is appropriate to consider solid triphenyltin chloride at all temperatures as composed of non-interacting monomeric entities. Finally, the close resemblance of the liquid nitrogen temperature ^{119m}Sn Mössbauer spectra of Ph_3SnCl and a 0.2 M frozen solution of this material in n-butyl benzene support the treatment of Ph_3SnCl as a monomeric compound under the conditions of the Mössbauer studies herein reported. The same conclusion is valid for $(o\text{-}CF_3C_6H_4)_3SnCl$ (**VII**) for which the neat solid and frozen solution spectra are again very similar (Fig. 5a).

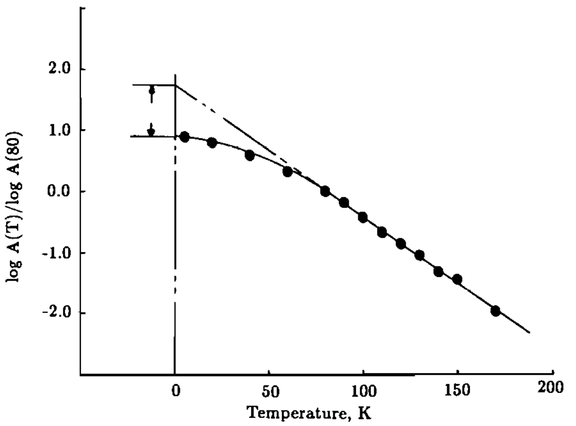

Fig. 4. Temperature dependence of the normalized area under the Mössbauer resonance curve for triphenyltin chloride (**VI**). The effect of zero point motion (zpm) is indicated on the ordinate of the plot.

In marked contrast, Fig. 5b illustrates a striking difference between the bulk solid and frozen solution state Mössbauer spectra of $(p\text{-}CF_3C_6H_4)_3SnCl$ (**IX**). The quadrupole hyperfine interaction in the neat solid is 3.43 mm s^{-1} while that extracted from the frozen solution spectra is smaller by 1 mm s^{-1}. Similarly, the difference in the isomer shift is about four times larger than for the unsubstituted and *ortho*-CF_3 substituted triaryltin chlorides. The ratio of the quadrupole splitting to isomer shift parameter [34] is equal to 2.44 in the neat solid, consistent with the general qualitative observation that values of this ratio larger than *ca.* 2.1 reflect

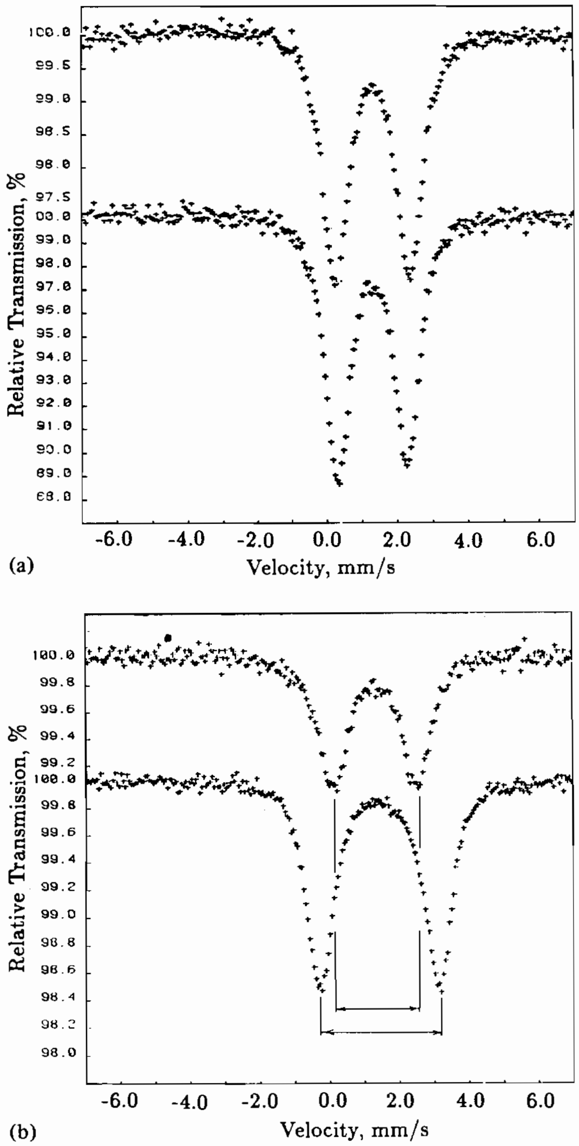

Fig. 5. Comparison of the liquid nitrogen temperature spectrum of (a) (o-$CF_3C_6H_4)_3SnCl$ (**VII**) and (b) (p-$CF_3C_6H_4)_3SnCl$ (**IX**), in a frozen solution in n-butylbenzene (top trace), and as a neat solid (bottom trace). The vertical lines are guides to the eye indicating the large difference in the quadrupole splitting between the two spectra.

a coordination number exceeding four. This result correlates very well with the conclusions drawn for this compound from the solid state ^{13}C and ^{119}Sn NMR spectra. Altogether, the data provides strong support for the hypothesis that the coordination about the metal atom in the *para*-substituted homologue is five-coordinate. This type of coordination, which is presumed to involve bridging chlorine atoms, is expected to give rise to either a dimeric or a two-dimensional polymeric structure with the three aryl groups in equatorial positions around a trigonal bipyramidally coordinated metal center. In this context, it might be expected that the different tin coordination number for compound **IX** should manifest itself in a different temperature dependence of the recoil-free fraction (as monitored by the temperature dependence of the relative area under the resonance curve, $-d\ln A/(dT)$). In contrast, however, Table IV indicates that this parameter is almost the same in **VI**, **VII** and **IX**. This may simply mean that the formation of a dimer or a linear chain polymer does not play a dominant role in determining the vibrational amplitude of the metal atom in these compounds [36]. It appears that the motional amplitude of the tin atom – which is the parameter pertinent to the Mössbauer lattice dynamical data – is governed to a large extent by the low frequency librational motions of the aryl groups and thus does not depend much on the intermolecular association. To restate a previously articulated generalization [35, 37] the temperature dependence of the recoil-free fraction in organotin compounds cannot be used as the sole criterion for inferring the coordination around the metal atom, but rather must be considered in the context of both the nature of the ligands bonded to the metal atom, as well as the relative strengths of the inter- and intramolecular vibrations which govern the motion of the Mössbauer probe atom.

In conclusion, a coordination change in (p-CF_3-$C_6H_4)_3SnCl$ has been detected by correlated solution/solid state studies of ^{13}C and ^{119}Sn NMR and ^{119m}Sn Mössbauer spectroscopy. The NMR chemical shifts as well as the ^{119m}Sn quadrupole splittings are the parameters most sensitive to this effect, while the temperature dependence of the recoil-free fraction cannot be used to infer the coordination number of tin in tri- and tetraaryl stannanes.

Acknowledgements

This research has been supported by grant DMR 81-02940 from the U.S. National Science Foundation and by a grant from the Center for Computer and Information Services of Rutgers University, and in part by a Sloan Foundation grant to one of us (B.K.). This support is herewith gratefully acknowledged. The solid state and some of the solution NMR spectra were obtained with the equipment available at the NSF-funded Southern California Regional NMR Facility at Caltech (grant CHE 84-40137). We thank Dr. J. P. Yesinowski for making the solid state NMR facilities available and for valuable discussions. The authors are also indebted to Prof. F. B. Bramwell for valuable suggestions related to the synthesis of some of the organotin compounds herein reported.

References

1 P. C. Chieh and J. Trotter, *J. Chem. Soc.*, 911 (1970).

2 N. G. Bokii, G. N. Zakarova and Yu. T. Struckov, *Zh. Strukt. Khim. USSR, 11*, 895 (1970); J. J. Zuckerman, private communication.

3 H. Kriegsmann and H. Geissler, *Z. Anorg. Allg. Chem., 323*, 170 (1963).

4 J. J. Zuckerman, *Adv. Organomet. Chem., 9*, 21 (1970).

5 T. S. Srivastava, *J. Organomet. Chem., 10*, 373 (1967).

6 B. Y. K. Ho and J. J. Zuckerman, *J. Organomet. Chem., 49*, 1 (1973).

7 P. T. Greene and R. F. Bryan, *J. Chem. Soc. A, 2549* (1971); D. W. Allen, D. J. Derbyshire, J. S. Brooks, S. J. Blunden and J. Smith, *J. Chem. Soc., Dalton Trans.*, 1889 (1984).

8 N. G. Bokii, Yu. T. Struckkov and A. K. Prokof'ev, *Zh. Strukt. Khim., 13*, 665 (1972).

9 H. Schumann and I. Schumann, Zinnorganische Verbindungen', 'Gmelin Handbuch der Anorganischen Chemie', Part I, Vol. 26, 8th edn., Springer, Berlin, 1975; J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem., 24*, 251 (1978); P. J. Smith, *J. Organomet. Chem. Lib., 12*, 7 (1981).

10 N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy', Chapman Hall, London, 1971; T. C. Gibb, 'Principles of Mössbauer Spectroscopy', Chapman Hall, London, 1976; V. I. Goldanskii and R. H. Herber, 'Chemical Applications of Mössbauer Spectroscopy', Academic Press, New York, 1968, and refs. therein.

11 R. K. Harris and B. E. Mann, 'NMR and the Periodic Table', Academic Press, New York, 1978 and refs. therein, V. S. Petrosyan, *Prog. NMR Spectrosc., 11*, 115 (1977).

12 F. W. B. Einstein, C. H. W. Jones, T. Jones and R. D. Sharma, *Can. J. Chem., 61*, 2611 (1983).

13 A. Stern and E. L. Becker, *J. Org. Chem., 29*, 3221 (1964).

14 G. Eng and C. R. Dillard, *Inorg. Chim. Acta, 28*, 99 (1978).

15 W. L. Earl and D. L. VanderHart, *J. Magn. Reson., 48*, 35 (1982).

16 E. O. Stejskal and J. Schaefer, *J. Magn. Reson., 18*, 560 (1975).

17 M. Alla and E. Lippmaa, *Chem. Phys. Lett., 37*, 260 (1976).

18 R. H. Herber, *Phys. Rev. B, 27*, 4013 (1983); R. H. Herber, A. Shanzer and J. Libman, *Organometallics, 3*, 586 (1984) and refs. therein.

19 R. H. Herber and Y. Hazony, in A. Weissberger and B. W. Rossiter (eds.), 'Physical Methods of Chemistry', Wiley Interscience, New York, 1972; J. J. Spijkerman, J. DeVoe and J. C. Travis, *Natl. Bur. Stand. U.S., Spec. Publ.*, 260 (1970).

20 (a) M. J. Vaickus and D. G. Anderson, *Org. Magn. Reson., 14*, 278 (1980); (b) B. Mathiasch, *Org. Magn. Reson., 17*, 296 (1981).

21 J. Stothers, 'Carbon-13 NMR Spectroscopy', Academic Press, New York, 1972, p. 212 and refs. therein.

22 G. Barbieri and F. Taddei, *J. Chem. Soc., Perkin Trans., 2*, 1323 (1972).

23 D. Doddrell, M. Barfield, W. Adcock, M. Aurangzeb and D. Jordan, *J. Chem. Soc., Perkin Trans., 2*, 402 (1976).

24 D. Doddrell, M. Bullpitt, C. J. Moore, C. W. Fong, W. Kitching, W. Adcock and B. D. Gupta, *Tetrahedron Lett., 9*, 665 (1973).

25 T. N. Mitchell, *J. Organomet. Chem., 59*, 189 (1973).

26 J. D. Kennedy, W. McFarlane, G. S. Pyre, P. L. Clarke and J. D. Wardell, *J. Chem. Soc., Perkin Trans., 2*, 1234 (1975).

27 T. Butters, K. Schefter, H. B. Stegmann, U. Weber and W. Winter, *J. Organomet. Chem., 272*, 351 (1984).

28 C. D. Schaeffer, Jr. and J. J. Zuckerman, *J. Organomet. Chem., 78*, 373 (1974); *J. Organomet. Chem., 99*, 407 (1975).

29 W. McFarlane, J. C. Maire and M. Delmas, *J. Chem. Soc., Dalton Trans.*, 1862 (1972); M. Barnard, P. J. Smith and R. F. M. White, *J. Organomet. Chem., 77*, 189 (1974).

30 H. J. Kroth, H. Schumann, H. G. Kuivila, C. D. Schaeffer, Jr. and J. J. Zuckerman, *J. Am. Chem. Soc., 97*, 1754 (1975).

31 A. J. Rein and R. H. Herber, *J. Chem. Phys., 63*, 1021 (1975); R. H. Herber and A. E. Smelkinson, *Inorg. Chem., 16*, 953 (1977).

32 D. W. Allen, J. S. Brooks and R. Formstone, *J. Organomet. Chem., 172*, 299 (1979).

33 J. Holecek, M. Nadvornik, K. Handlir and A. Lycka, *J. Organomet. Chem., 241*, 177 (1983).

34 R. H. Herber, H. A. Stöckler and W. T. Reichle, *J. Chem. Phys., 42*, 2447 (1965).

35 R. H. Herber, in R. H. Herber (ed.), 'Chemical Mössbauer Spectroscopy', Plenum, New York, 1984, Chap. VIII.

36 K. C. Molloy, M. P. Bigwood, R. H. Herber and J. J. Zuckerman, *Inorg. Chem., 21*, 3709 (1982).

37 J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, J. Haiduc, M. Curtui, C. Guta and D. Ruse, *Inorg. Chem., 19*, 2861 (1980) and refs. therein.