Fourier Transform Nuclear Magnetic Resonance Investigations of Organotin Compounds. Part 6.[1] Tin-119 and Carbon-13 Nuclear Magnetic Resonance. Spectra of Hexaorganoditins and Octaorganotritins

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In a series of closely related hexa-alkylditins or octaorganotritins, the magnitude of $^1J(\text{Sn--Sn})$ varies greatly according to the nature of the alkyl groups; in the ditin series a linear relationship is found between $^1J(\text{Sn--Sn})$ and the sum of the Taft σ^* constants of the alkyl groups. Application of this relation to the tritins allows estimation of σ^* values for the trialkyltin groups: similar values for σ^* are obtained by considering the values of $^1J(\text{Sn--C})$ in di- or tri-tins. σ^* Values for Me_3Si and Me_3Ge have also been obtained. Replacement of alkyl groups in a hexa-alkylditin by electronegative acetoxy groups causes a large increase in $^1J(\text{Sn--Sn})$; replacement of alkyl groups by phenyl groups causes only small variations. The ^{119}Sn and ^{13}C chemical shifts and long-range coupling constants are discussed. The larger hexa-alkylditins and octa-alkyltritins exhibit relatively large negative nuclear Overhauser effects, which may be partially eliminated by adding chromium tris(acetylacetonate) to the solution under investigation.
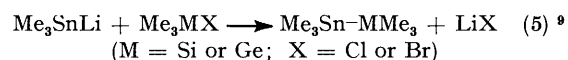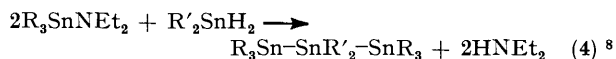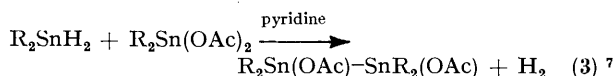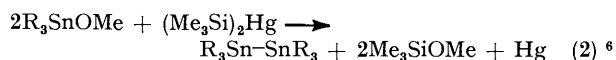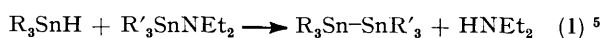
DURING the course of a preliminary investigation [2] of the ^{13}C spectra of organotin compounds, we observed that while $^1J(\text{Sn--C})$ in three hexaorganoditins was almost invariant, $^2J(\text{Sn--Sn--C})$ showed large variations. We then recorded the tin-119 spectra of a series of hexaorganoditins and observed large variations in $^1J(\text{Sn--Sn})$.[3] This paper presents tin-119 and carbon-13 n.m.r. data on a total of 21 ditins and 13 tritins.

Since tin-119 (and tin-117) have negative magnetogyric ratios, proton noise decoupled tin-119 n.m.r. signals may become negative if dipole–dipole (DD) relaxation plays an important part in the overall relaxation of the tin nuclei. Lippmaa et al.[4] have shown that spin–rotation (SR) relaxation is dominant for small organotin molecules; it appeared likely, however, that in larger molecules such as ditins the situation might well be different.

EXPERIMENTAL

Spectra were recorded in the pulse Fourier transform mode with proton noise decoupling, using a Bruker HFX-90 spectrometer operating at 22.628 (^{13}C) or 33.546 MHz (^{119}Sn) and coupled to a Nicolet series 1080 computer. Tin-119 spectra consisted (after transformation) of 4K or 8K data points (sweep width 12 500 Hz, digital resolution *ca.* 3 or 1.5 Hz), carbon-13 spectra of 8K data points (sweep width 6 024 Hz, digital resolution *ca.* 0.8 Hz). The normal operating temperature was *ca.* 45 °C; the samples [neat liquids or, for solids (unless otherwise stated) saturated solutions in CDCl_3] contained *ca.* 2% Me_4Si or Me_4Sn as internal standard and, for liquids, *ca.* 5% C_6D_6 as internal lock substance. For a number of measurements Cr(acac)_3 was added in order to partially suppress the nuclear Overhauser effect (NOE): this caused no change in the coupling constants, but led to some line broadening and to small variations in the chemical shifts. Shift values are therefore given for solutions to which no Cr(acac)_3 has been added. The substances investigated were prepared using

published procedures; equations (1)—(6) describe the methods of preparation used.

$$\text{R}_3\text{SnH} + \text{R}'_3\text{SnNEt}_2 \longrightarrow \text{R}_3\text{Sn--SnR}'_3 + \text{HNEt}_2 \quad (1)\ [5]$$

$$2\text{R}_3\text{SnOMe} + (\text{Me}_3\text{Si})_2\text{Hg} \longrightarrow$$
$$\text{R}_3\text{Sn--SnR}_3 + 2\text{Me}_3\text{SiOMe} + \text{Hg} \quad (2)\ [6]$$

$$\text{R}_2\text{SnH}_2 + \text{R}_2\text{Sn(OAc)}_2 \xrightarrow{\text{pyridine}}$$
$$\text{R}_2\text{Sn(OAc)--SnR}_2\text{(OAc)} + \text{H}_2 \quad (3)\ [7]$$

$$2\text{R}_3\text{SnNEt}_2 + \text{R}'_2\text{SnH}_2 \longrightarrow$$
$$\text{R}_3\text{Sn--SnR}'_2\text{--SnR}_3 + 2\text{HNEt}_2 \quad (4)\ [8]$$

$$\text{Me}_3\text{SnLi} + \text{Me}_3\text{MX} \longrightarrow \text{Me}_3\text{Sn--MMe}_3 + \text{LiX} \quad (5)\ [9]$$
$$(\text{M} = \text{Si or Ge}; \ \text{X} = \text{Cl or Br})$$

All ditins examined were pure compounds, except for tetraisopropyldi-t-butylditin, which could not be satisfactorily purified; new compounds had satisfactory elemental analyses. In the tritin series, compounds (24), (25), and (27)—(30) are new compounds. Compounds (29) and (30) could not be prepared in a pure state, since attempted vacuum distillation led to decomposition; large amounts of tetraisopropyltin, hexaisopropylditin, and polytins were formed as by-products. The remaining four compounds were obtained in a pure state as oils, as shown by elemental analysis, mass spectrometry and by the various n.m.r. spectra. B.p.s, yields, and analytical data were as follows: $\text{Me}_6\text{Pr}^i_2\text{Sn}_3$, b.p. 102° at 0.05 mmHg, 60% (Found: C, 27.55; H, 6.5. $\text{C}_{12}\text{H}_{32}\text{Sn}_3$ requires C, 27.05; H, 6.05%); $\text{Et}_6\text{Me}_2\text{Sn}_3$, b.p. 167° at 0.01 mmHg, 84% (Found: C, 30.45; H, 6.9. $\text{C}_{14}\text{H}_{36}\text{Sn}_3$ requires C, 30.0; H, 6.45%); $\text{Et}_6\text{Pr}^i_2\text{Sn}_3$, b.p. 162° at 0.005 mmHg, 40% (Found: C, 34.9; H, 7.3. $\text{C}_{18}\text{H}_{38}\text{Sn}_3$ requires C, 35.05; H, 7.2%); $\text{Pr}^i_6\text{Me}_2\text{Sn}_3$, b.p. 145° at 0.001 mmHg, 23% (Found: C, 37.6; H, 7.65. $\text{C}_{20}\text{H}_{48}\text{Sn}_3$ requires C, 37.25; H, 7.5%). In the ^1H n.m.r. spectra of these tritins, $\delta[(\text{CH}_3)_3\text{Sn}]$ is *ca.* 0.27, $^2J(^{119}\text{Sn--H})$ *ca.* 48, and $^3J(\text{Sn--Sn--H})$ 12—22 Hz; $\delta[(\text{CH}_3)_2\text{Sn}]$ is *ca.* 0.42, $^2J(\text{Sn--H})$ *ca.* 43, and $^3J(\text{Sn--Sn--H})$ *ca.* 15 Hz.

RESULTS AND DISCUSSION

The n.m.r. parameters of the compounds investigated are listed in Tables 1—7. No sign determinations for

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[3] T. N. Mitchell, *J. Organometallic Chem.*, 1974, **70**, C1.

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[5] W. P. Neumann, B. Schneider, and R. Sommer, *Annalen*, 1966, **692**, 1.

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TABLE 1

^{119}Sn Chemical shifts in hexaorganoditins $R_3Sn-SnR'_3$
[in p.p.m.; $\delta(Me_4Sn) = 0$] [a]

Compound	R	R'	$\delta(SnR_3)$	$\delta(SnR'_3)$
(1)	Me	Me	-108.7
(2)	Me	Et	-108.1	-61.8
(3)	Me	Pr	-108.9	-88.8
(4)	Me	Pr^i	-105.4	-32.4
(5)	Me	Bu	-108.6	-82.1
(6)	Me	Bu^s	-105.3	-45.3
(7)	Me	Cyclohexyl	-103.8	-78.3
(8)	Et	Et	-59.9
(9)	Et	Bu	-65.7	-79.7
(10)	Pr^i	Pr^i	-29.1
(11)	Bu	Bu	-83.2
(12)	Bu^i	Cyclohexyl	-93.2	-85.2
(13)	Pr$^i_2$Bu^t	Pr$^i_2$Bu^t	-21.5
(14)	Bu^t	Bu^t	-3.4
(15)	C$_8$H$_{17}$	C$_8$H$_{17}$	-83.5
(16)	Bu$_2$(OAc)	Bu$_2$(OAc)	-126.8
(17) [b]	Me	Ph	-91.5	-150.6
(18)	Et	Ph	-48.7	-140.4
(19)	Bu^i	Ph	-86.8	-146.9
(20)	Cyclohexyl	Ph	-64.7	-134.1
(21)	Ph	Ph	-143.6

[a] The sign convention used is that shifts to high field of Me$_4$Sn are negative. [b] Lit.,[21] $\delta(^{119}$Sn$)$ -91.5, -153 ± 2 p.p.m.

chemical shift range of *ca.* 100 p.p.m. The total chemical shift range for organotins is *ca.* 1 300 p.p.m.;

TABLE 2

^{119}Sn Chemical shifts in octaorganotritins $R_3Sn-SnR'_2-SnR_3$ [in p.p.m.; $\delta(Me_4Sn) = 0$] [a]

Compound	R	R'	$\delta(SnR_3)$	$\delta(SnR_2)$
(22) [b]	Me	Me	-99.5	-261.7
(23)	Me	Et	-99.1	-199.1
(24)	Me	Pr^i	-97.0	-139.5
(25)	Et	Me	-56.0	-272.8
(26)	Et	Et	-54.8	-205.9
(27)	Et	Pr^i	-57.3	-139.3
(28)	Pr^i	Me	-34.3	-272.1
(29)	Pr^i	Et	-31.0	-206.7
(30)	Pr^i	Pr^i	-35.0	-132.9
(31)	Et	Bu^i	-63.9	-214.4
(32)	Bu^i	Bu^i	-92.8	-236.2
(33)	Cyclohexyl	Bu^i	-84.3	-224.8
(34)	Ph	Bu^i	-138.2	-221.0

[a] The sign convention used is that shifts to high field of Me$_4$Sn are negative. [b] Lit.,[10] $\delta(SnMe_3)$ -100.8 ± 2, $\delta(SnMe_2)$ -263 ± 1.5 p.p.m.

the ditin series shows a shift range much larger than that generally observed in other groups of closely related compounds.

TABLE 3

^{13}C Chemical shifts in hexaorganoditins $R_3Sn-SnR'_3$ [in p.p.m.; $\delta(Me_4Si) = 0$]

Compound	$\delta(C_{1R})$	$\delta(C_{2R})$	$\delta(C_{3R})$	$\delta(C_{4R})$	$\delta(C_{1R'})$	$\delta(C_{2R'})$	$\delta(C_{3R'})$	$\delta(C_{4R'})$
(1)	-10.22				-10.22			
(2)	-9.44				1.21	12.47		
(3)	-9.40				13.00	22.32	19.33	
(4)	-8.66				15.64	23.57		
(5)	-9.41				9.98	30.88	27.55	13.79
(6)	-8.33				27.41	20.09—30.72	14.67	
(8)	0.02	11.09			0.02	11.09		
(9)	1.62	12.40			10.38	31.12	27.78	13.82
(10)	16.02	23.57			16.02	23.57		
(11)	10.25	31.02	27.78	13.82	10.25	31.02	27.78	13.82
(12)	24.41	27.61	27.24		28.76	34.32	30.00	28.56
(14) [a]	32.27	34.28			32.27	34.28		
(15)	10.90	26.52	34.12	29.41	10.90	26.52	34.12	29.41
(16)	18.11	29.10	27.04	13.76	18.11	29.10	27.04	13.76
(17) [b]	-9.00				140.16	137.36	128.49	c
(19)	24.02	28.29	26.83		141.08	137.53	128.12	128.00
(20)	28.80	33.82	29.47	27.01	141.69	137.54	128.06	127.84
(21)	140.39	137.60	128.50	c	140.39	137.60	128.50	c

Numbering of carbon atoms is as follows: C_1 is directly bound to tin, C_2, C_3, C_4 are further removed along the carbon chain or in the ring.

[a] In C$_6$D$_6$ (saturated solution). [b] Lit.,[20] $\delta(CH_3)$ -8.4 p.p.m. [c] Resonance hidden.

coupling constants were carried out; it is known from the literature that ^1J(Sn–Sn) is generally positive [10] and ^1J(Sn–C) generally negative.[11] Reduced coupling constants ^nK are not tabulated, but may be calculated from the relation $K_{XY} = 4\pi^2 J_{XY}/\gamma_X\gamma_Y h$.[12] The various features of the spectra will be discussed separately.

Tin-119 Chemical Shifts.—The theoretical basis of the chemical shifts exhibited by heavier nuclei has been discussed by several authors,[13,14] and a theoretical interpretation of ^{119}Sn chemical shifts in methyltin compounds has been published.[15]

For the hexa-alkylditins (1)—(15) (Table 1), we find a

It will be observed that each group R_3Sn absorbs over a relatively small chemical shift range, apparently *ca.* 6 p.p.m.; typical chemical shifts are as follows: Me_3Sn -105, Et_3Sn -60, Pr_3Sn -90, Bu_3Sn -80, Bu^i_3Sn -90, (cyclohexyl)$_3Sn$ -85, octyl$_3Sn$ -83, Pr^i_3Sn -30, Bu^s_3Sn -45, Bu^t_3Sn -4 p.p.m. Thus, considering the straight-chain alkyl groups, the shifts tend to oscillate about a value of *ca.* -83 p.p.m., the oscillation amplitude decreasing with increasing chain length. There is no linear relation between the tin chemical shift and the electronegativity of the alkyl groups R (as measured by the Taft σ^* constants); the general trend is that de-

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[12] J. A. Pople and D. P. Santry, *Mol. Phys.,* 1964, **8**, 1.

[13] J. D. Kennedy and W. McFarlane, *Rev. Silicon, Germanium, Tin and Lead Compounds,* 1974, **1**, 235.

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[15] R. Radeglia and G. Engelhardt, *Z. Chem.,* 1974, **14**, 319.

TABLE 4

^{13}C Chemical shifts in octaorganotritins $R_3Sn\text{–}SnR'_3\text{–}SnR_3$ [in p.p.m.; $\delta(Me_4Si) = 0$]

Compound	$\delta(C_{1R})$	$\delta(C_{2R})$	$\delta(C_{3R})$	$\delta(C_{4R})$	$\delta(C_{1R'})$	$\delta(C_{2R'})$	$\delta(C_{3R'})$
(22)	−9.23				−14.04		
(23)	−9.60				−0.90	13.60	
(24)	−8.26				15.36	25.05	
(25)	1.89	12.49			−13.40		
(26)	2.23	12.55			0.45	14.94	
(27)	2.40	12.36			15.40	25.42	
(28)	16.44	23.59			−11.50		
(29)	16.64	22.65			a	a	
(30)	17.03	23.79			16.05	25.74	
(32)	24.30	28.16	26.98		22.15	29.70	26.98
(33)	b	34.41	29.75	b	23.28	29.75	27.25
(34)	141.44	138.30	129.26	b	23.57	29.70	26.78

^{a} Not measured. ^{b} Not observed. Numbering of carbon atoms as in Table 3.

TABLE 5

Tin–tin and tin–carbon coupling constants in hexaorganoditins $R_3Sn\text{–}SnR'_3$ (in Hz)

Compound	$^1J(Sn\text{–}Sn)$ ^{a}	$^1J(Sn\text{–}C_{1R})$	$^2J(Sn\text{–}C_{1R})$ ^{b}	$^2J(Sn\text{–}C_{2R})$	$^1J(Sn\text{–}C_{2R'})$	$^2J(Sn\text{–}C_{1R'})$	$^2J(Sn\text{–}C_{2R})$
(1)	4.404	244.2	56.5		244.2	56.5	
(2)	3 496	234.0	42.0		253.2	51.0	d
(3)	3 551	233.5	44.0		250.2	46.6	22.7
(4)	2 832	229.6	34.4		261.7	45.0	7.6
(5)	3 505	233.5	44.3		251.3	46.6	17.7 ^{e}
(6)	2 810	225.9	34.0 ^{d}		c	c	9.2—7.7
(7)	2 841	c	c		c	c	c
(8)	2 702	247.0	41.0	c	247.0	41.0	c
(9)	2 688	244.9	41.2	c	242.6	39.7	16.0 ^{g}
(10)	1 208	248.8	32.8	6.5 ^{d}	248.8	32.8	6.5 ^{d}
(11)	2 748	241.9	39.7	15.0 ^{d,h}	241.9	39.7	15.0
(12)	2 533	230.4	32.0	c, j	259.4	c	c
(13)	764	c	c	c	c	c	c
(14)	<60 ^{l}	225.8	29.8	0.0	225.8	29.8	0.0
(15)	2 705	240.4	39.0	22.9	240.4	39.0	22.9
(16)	11 272	360.2	65.6	22.9 ^{k}	360.2	65.6	22.9
(17) ^{s}	4 262	267.2	56.5		374.6	56.6	40.5 ^{n}
(18)	3 153	c	c	c	c	c	c
(19)	3 199	262.4	48.8	18.7 ^{n}	354.8	44.6	39.7 ^{o}
(20)	2 260	271.8	47.3	14.5 ^{p}	344.5	35.5	41.6 ^{p}
(21)	4 470	c	c	41.2 ^{t}	c	c	41.2 ^{q}

^{a} $^1J(^{119}Sn\text{–}^{119}Sn)$, calculated from measured values of $^1J(^{119}Sn\text{–}^{117}Sn)$. ^{b} $^2J(^{119}Sn\text{–}C\text{–}C)$. ^{c} Not measured. ^{d} Uncertain. ^{e} $^3J(Sn\text{–}C_{3R'})$ 50.3 Hz. ^{f} $^3J(Sn\text{–}C_{3R'})$ 38.9 Hz. ^{g} $^3J(Sn\text{–}C_{3R'})$ 51.9 Hz. ^{h} $^3J(Sn\text{–}C)$ 51.1 Hz. ^{j} $^3J(Sn\text{–}C_{3R})$ 37.4 Hz. ^{k} $^3J(Sn\text{–}C)$ 71.8 Hz. ^{l} Not measurable with greater exactitude. ^{m} $^3J(Sn\text{–}C_{3R'})$ 45.0 Hz. ^{n} $^3J(Sn\text{–}C_{2R})$ 8.0, $^3J(Sn\text{–}C_{3R})$ 39.0 Hz. ^{o} $^3J(Sn\text{–}C_{3R'})$ 43.5 Hz. ^{p} $^3J(Sn\text{–}C_{3R})$ 55.9 Hz. ^{q} $^3J(Sn\text{–}C_{2R'})$ 4.6, $^3J(Sn\text{–}C_{3R'})$ 44.2 Hz. ^{r} $^3J(Sn\text{–}C)$ 48.5 Hz. ^{s} Lit.,^{10} $^1J(Sn\text{–}Sn)$ 4 240 ± 80 Hz.

Quoted values of $^nJ(Sn\text{–}C)$ refer to $^nJ(^{119}Sn\text{–}C)$ when the ^{119}Sn and ^{117}Sn satellites are resolvable.

TABLE 6

Tin–tin and tin–carbon coupling constants in octaorganotritins $R_3Sn\text{–}SnR'_2\text{–}SnR_3$ (in Hz)

Compound	$^1J(Sn\text{–}Sn)$ ^{a}	$^2J(Sn\text{–}Sn)$ ^{b}	$^1J(Sn\text{–}C_{1R})$ ^{f}	$^2J(Sn\text{–}C_{1R})$	$^2J(Sn\text{–}C_{2R})$	$^1J(Sn\text{–}C_{1R'})$ ^{f}	$^2J(Sn\text{–}C_{1R'})$	$^2J(Sn\text{–}C_{2R'})$
(22) ^{c}	2 873	763	238.2	44.1		179.4	25.0	
(23)	2 375	702	233.9	38.2		207.3	25.0	16.1
(24)	1 957	660	230.9	33.8		230.9	25.0	d
(25)	1 931	470	244.1	41.2	19.1	164.6	19.2	
(26)	1 481	418	241.0	35.4	19.5	194.7	19.3	12.9
(27)	1 153	392	237.0	30.8	20.4	219.6	19.0	d
(28)	1 366	262	251.6	36.7	e	147.0	13.2	
(29)	e	e	247.0	e	16.2	e	e	e
(30)	403	188	241.2	e	16.1	e	e	e
(32)	1 590	434	231.0	35.5	9.3 ^{g}	198.8	19.5	9.2 ^{h}
(33)	e	e	d	d	<5	d	d	d
(34)	2 273	670	374.3	43.5 ^{i}	40.0 ^{j}	d	d	10.2 ^{k}

^{a} $^1J(^{119}Sn\text{–}Sn^{119})$, measured directly or calculated from $^1J(Sn^{117}\text{–}Sn^{119})$. ^{b} $^2J(Sn^{119}\text{–}Sn^{119})$, calculated from $^2J(Sn^{119}\text{–}Sn^{117})$. ^{c} Lit.,^{10} $^1J(Sn^{119}\text{–}Sn^{119})$ 2 900 ± 50 Hz. ^{d} Not detected. ^{e} Not measured. ^{f} $^1J(^{119}Sn\text{–}C)$. ^{g} $^3J(Sn\text{–}C_{2R})$ 17.2, $^3J(Sn\text{–}C_{3R})$ 36.6 Hz. ^{h} $^3J(Sn\text{–}C_{2R'})$ 16.0, $^3J(Sn\text{–}C_{3R'})$ 36.6 Hz. ^{i} $^3J(Sn\text{–}Sn\text{–}Sn\text{–}C)$ 12.5 Hz. ^{j} $^3J(Sn\text{–}C_{3R})$ 45.8 Hz. ^{k} $^3J(Sn\text{–}C_{3R'})$ 42.4 Hz.

creasing electronegativity of R causes a shift to low field.

If we turn now to compounds (16)—(21), we find a typical shift value for the Ph$_3$Sn group of −140 p.p.m. Compound (16) is atypical since it contains pentaco-ordinate tin;[16] the high-field shift on going from

Bu$_6$Sn$_2$ to Bu$_4$Sn$_2$(OAc)$_2$ can be explained by a combination of two factors, the tendency of the electronegative acetate group to cause a shift to low field

[16] Though no structural data on Bu$_4$Sn$_2$(OAc)$_2$ are available, it has been shown that Ph$_4$Sn$_2$(OAc)$_2$ contains pentaco-ordinate tin, G. Bandoli, D. A. Clement, and C. Panattoni, *Chem. Comm.*, 1971, 1311.

being more than compensated by the well known high-field shift [13,17,18] observed when the tin atom increases its co-ordination number.

The tin chemical shifts of the triorganotin moieties in the octaorganonitritins correspond closely to the shifts of these groups in the ditins, e.g. Me_3Sn in Me_6Sn_2 −108.7, in Me_8Sn_3 −99.5 p.p.m. The tin shifts in the

TABLE 7

[13]C N.m.r. data for miscellaneous compounds referred to in the Discussion section

Compound	N.m.r. parameters [a]
Me_2SnEt_2	δ(Me) −12.74, δ(Et) 1.82, 10.85 p.p.m.; [1]J(Sn−Me) 300.0, [1]J(Sn−Et) 354.4 Hz
$Me_2SnPr^i{}_2$	δ(Me) −14.62, δ(Pr^i) 13.39, 21.64 p.p.m.; [1]J(Sn−Me) 276.5, [1]J(Sn−Pr^i) 373.6 Hz
$Et_2SnPr^i{}_2$	δ(Et) −0.97, 11.44, δ(Pr^i) 13.52, 22.16 p.p.m.; [1]J(Sn−Et) 292.6, [1]J(Sn−Pr^i) 338.2 Hz
$Me_3SnSiMe_3$	δ(Me$_3$Sn) −12.21, δ(Me$_3$Si) 0.48 p.p.m.; [1]J(Sn−Me) 244.8, [2]J(Sn−Me) 59 Hz
$Me_3SnGeMe_3$	δ(Me$_3$Sn) −11.50, δ(Me$_3$Ge) −0.33 p.p.m.; [1]J(Sn−Me) 250.0, [2]J(Sn−Me) 54.4 Hz

[a] Values of [1]J(Sn−C) refer to [1]J([119]Sn−C).

diorganotin groups are shifted to much higher field, e.g. Me_2Sn in Me_8Sn_3 −261.7 p.p.m.: however, each group R_2Sn again absorbs over a relatively small chemical shift range. Typical shifts are Me_2Sn −265, Et_2Sn −205, $Bu^i{}_2Sn$ −220, $Pr^i{}_2Sn$ −139 p.p.m.

Radeglia's treatment [14,15] predicts a high-field shift on going from R_3Sn in R_6Sn_2 to R_2Sn in $R_2Sn(SnR'_3)_2$, though the value calculated from his equations for the reduced paramagnetic shielding constant indicates that a correction of his f value (0.26) [15] may be required for the tin nucleus in R_2Sn, possibly due to variations in ΔE.

The relatively large variations in δ(SnR$_3$) or δ(SnR$_2$) with R are not so readily explained using Radeglia's model. Two factors are clearly involved, firstly the group electronegativity [19] of R and secondly deviations from tetrahedral geometry at tin, caused by steric crowding as well as electronic influences. In the hexa-alkylditin series, the compound with the largest $+I$ effect (lowest group electronegativity) and largest steric crowding at tin (largest deviations from tetrahedral geometry) is hexa-t-butylditin: we hope to be able to carry out an X-ray structural analysis of this compound shortly.

Carbon-13 Chemical Shifts.—It is now generally accepted that the carbon chemical shifts in alkyl groups are closely related to the charge density on the carbon atoms concerned, a low-field shift corresponding to an increased positive charge.[20] The 'reference shift' for methyltin compounds is Me_4Sn (−9.6 p.p.m.[1]). The methyl carbons in Me_3SnEt absorb at −11.0, in Me_3SnPr^i at −12.0 p.p.m.; however, in $Me_3SnSnMe_3$, $Me_3SnSnEt_3$, and $Me_3SnSnPr^i{}_3$, the shifts are −10.22, −9.40, and −8.66 p.p.m. respectively, although the $+I$ effects of all three SnR_3 groups are certainly larger

[17] P. J. Smith, R. F. M. White, and L. Smith, *J. Organometallic Chem.*, 1972, **40**, 341.
[18] J. D. Kennedy, W. McFarlane, and D. S. Rycroft, unpublished work quoted in ref. 13.

than that for Pr^i. A similar trend is seen in compounds Me_2SnR_2: R = Me, −9.6; Et, −12.74; Pr^i, −14.62; $SnMe_3$, −14.04; $SnEt_3$, −13.40; $SnPr^i{}_3$ −11.50 p.p.m. (shifts are given for the methyl carbons). Less data are available for corresponding series of ethyl- and isopropyl-tin compounds, but in general it appears that in ethyltin compounds a low-field shift is observed for the α-carbons and a high-field shift for the β-carbons, while in iso-propyltin compounds high-field shifts are observed for both α- and β-carbons when the $+I$ effect of the group attached to tin is increased.

The reasons for these somewhat complex trends in chemical shifts in the di- and tri-tins are unclear, particularly for the carbons which are at some distance from the 'perturbation site'; one factor involved is probably changes in ΔE caused by introduction of one or two tin nuclei into the tetra-alkyltin skeleton.

In compound (16), charge density variations are more clearly reflected: replacement of a butyl group by an electronegative acetate residue causes a large low-field shift for the α-carbons, though this is partially balanced by a high-field shift for the β- and γ-carbons.

Tin–Tin Coupling Constants.—Tables 3 and 5 contain values of [1]J([119]Sn−[119]Sn) and [2]J([119]Sn−[119]Sn): these were either calculated from the measured value of J([119−117]Sn) or obtained directly in the cases where a [119]Sn ··· [119]Sn AB spin system is present in the corresponding isotopomer.

It is generally accepted that the coupling mechanism in many spin systems is dominated by the Fermi contact mechanism; Pople and Santry have shown [12] that, for such an interaction, the coupling constant is given by equation (6) where $\psi_{ns}(0)$ is the valence s electron

$$^1J_{XY} = \frac{16\beta^2}{9\gamma_X\gamma_Y h} \cdot \psi^2_{ns(X)}(0) \cdot \psi^2_{ns(Y)}(0) \cdot \pi_{XY} \quad (6)$$

density at the nucleus and π_{XY} the mutual polarisability of the atoms X and Y. This equation is often used in the modified form in which π_{XY} is replaced by $\alpha^2(X)$-$\alpha^2(Y)(\Delta E)^{-1}$; α^2 represents the s character of the hybrid orbital used to form the X−Y bond and ΔE is an average excitation energy. The limitations of the modified equation have recently been discussed.[10,21]

It will be seen from Table 3 that [1]J([119]Sn−[119]Sn) varies between 11 272 [compound (16)] and <60 Hz [compound (15)]; the largest value for a hexa-alkylditin is 4 404 Hz [compound (1)]. The very low solubility of hexa-t-butylditin in organic solvents, plus the negative NOE (see below), has precluded exact determination of [1]J(Sn−Sn) for this compound: addition of $Cr(acac)_3$ helps to eliminate the NOE, but causes line broadening. It seems likely that [1]J(Sn−Sn) is negative in this compound. A very good linear correlation ($|r|$ 0.988) is found for compounds (1)—(14) between [1]J(Sn−Sn) and

[19] J. H. Letcher and J. R. van Wazer, *J. Chem. Phys.*, 1966, **44**, 815.
[20] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York and London, 1972.
[21] J. D. Kennedy, W. McFarlane, G. S. Pyne, and B. Wrackmeyer, *J.C.S. Dalton*, 1975, 386.

$\Sigma\sigma^*$, the sum of the Taft σ^* constants [22] of the six alkyl groups bound to the tin atoms. This suggests that the main factor involved in determining the value of $^1J(\text{Sn–Sn})$ in these compounds is Z_{eff}, the effective nuclear charge at the tin nucleus. This hypothesis appears at first glance to be supported by the very large value of ^1J in compound (16); replacement of two butyl groups in Bu_6Sn_2 by two electronegative acetoxy groups increases ^1J by a factor of 4.1. However, since this compound contains pentaco-ordinate tin,[16] it cannot properly be compared with compounds (1)—(14) where the tin atoms are tetraco-ordinate; we plan to investigate the variation of $^1J(\text{Sn–Sn})$ with the electron-attracting power of the acyloxy residue in compounds of the type $\text{R}_2\text{Sn}(\text{OCOR}')\text{SnR}_2(\text{OCOR}')$.

It has recently been shown [10] that $^1J(\text{Sn–Sn})$ is negative (ca. $-5\,000$ Hz) in complexed tris(trimethylstannyl)stannyl-lithium: this indicates that the modified form of equation (6) is invalid, since its application cannot lead to negative coupling constant values. The authors suggest that the main factor contributing to variations in $^1J(\text{Sn–Sn})$ is β_{SnSn}, the s overlap integral for the Sn–Sn bond, which in its turn must be sensitive to other factors to account for the wide variations in $^1J(\text{Sn–Sn})$ in the hexa-alkylditins. It is further suggested that the main factor affecting β_{SnSn} in these ditins is the bulk of the alkyl groups; this seems unlikely to be the only contributing factor, since $^1J(\text{Sn–Sn})$ correlates with the sum of the σ^* constants and not with the sum of the corresponding steric constants E_{s}.[22] The length of the tin–carbon bond also makes it unlikely that appreciable steric crowding at the tin atom will occur when methyl groups are replaced by ethyl or isopropyl groups. It seems clear that further work is required before a conclusion can be drawn as to which factors are most important in determining $^1J(\text{Sn–Sn})$ in organotins.

We do however find that $^1J(\text{Sn–Sn})$ in the tritins no longer correlates with the sum of the eight σ^* values for the alkyl groups, except where R (or R') is kept constant and R' (or R) varied. One can however treat a tritin as a derivative of a ditin in which one alkyl group has been replaced by a trialkyltin residue: from a plot of ^1J versus $\Sigma\sigma^*$ for the ditins it is then possible to calculate σ^* for the R_3Sn groups. For example, $^1J(\text{Sn–Sn})$ in Me_8Sn_3 (2 873 Hz) corresponds to $\Sigma\sigma^*$ -0.63; since $\sigma^*(\text{Me}) = 0$, $\sigma^*(\text{Me}_3\text{Sn})$ is also -0.63. Values obtained in this way are: $\sigma^*(\text{Me}_3\text{Sn})$ -0.63, -0.63, -0.59, mean -0.62; $\sigma^*(\text{Et}_3\text{Sn})$ -0.71, -0.68, -0.61, mean -0.67; $\sigma^*(\text{Pr}^i_3\text{Sn})$ -0.63, -0.62, mean -0.63. These values are based on the assumption that ^1J is only affected by electronic factors; this assumption will be discussed below in the light of σ^* values obtained from $^1J(\text{Sn–C})$.

Table 5 also contains the first reported values for $^2J(\text{Sn–Sn})$. When R or R' is kept constant, $^2J(\text{Sn–Sn})$ varies linearly with $^1J(\text{Sn–Sn})$ (and therefore with $\Sigma\sigma^*$ for the eight alkyl groups); though the number of data points available from this study is limited, it appears that deviations from linearity increase when R or R'

varies, in the order $\text{Me} < \text{Et} < \text{Pr}^i$. This could point to changes at the geometry of the central tin atom when the alkyl groups are varied, i.e. to the influence of steric as well as electronic factors on ^2J.

Tin–Carbon Coupling Constants.—In contrast to the large variations in $^1J(\text{Sn–Sn})$ in compounds (1)—(15), $^1J(\text{Sn–C})$ only varies between 225.9 and 261 Hz; for compounds of the type R_6Sn_2 ^1J varies only between 240.4 and 248.8 Hz, while the mean of the two ^1J values in compounds $\text{R}_3\text{SnSnR}'_3$ varies only between 241.9 and 244.9 Hz. The differences between the two ^1J values in the asymmetrical ditins can be explained on the basis of Bent's postulate.[23] In the trialkyltin residues of the tritins, a similar invariance of $^1J(\text{Sn–C})$ is found, the values ranging from 230.9 to 251.6 Hz. These values show no clear pattern, and are certainly not correlated with $^1J(\text{Sn–Sn})$.

The values of $^1J(\text{Sn–C})$ in the dialkyltin residues of the tritins, in contrast, vary over a range of almost 100 Hz. However, differences of this order are to be expected, as can be seen by comparing the ^1J values in compounds of the type $\text{R}_2\text{SnR}'_2$ (R = alkyl or trialkylstannyl). For example, $^1J(\text{Sn–Me})$ shows the following values in $\text{Me}_2\text{SnR}'_2$: R' = Me, 338; Et, 300; Pr^i, 277; SnMe_3, 179; SnEt_3, 165; SnPr^i_3, 147 Hz. Similar, though somewhat higher, values are found for $\text{Et}_2\text{SnR}'_2$ and $\text{Pr}^i_2\text{SnR}'_2$. As we have previously shown,[1] such variations in the tetra-alkyltin series can be accounted for on the basis of Bent's postulate; a linear variation exists in a series of closely related compounds between $^1J(\text{Sn–C})$ and σ^* for the alkyl group(s) concerned.

It should therefore be possible to obtain further values for $\sigma^*(\text{R}_3\text{Sn})$ from plots of $^1J(\text{Sn–C})$ against σ^*. For this purpose, ditins $\text{R}_3\text{SnSnR}'_3$ and tritins $\text{R}_2\text{Sn}(\text{SnR}')_3$ are considered as derivatives of tetra-alkyltins $\text{R}_3\text{SnR}''$ or $\text{R}_2\text{SnR}''_2$, σ^* being calculated from plots of $^1J(\text{Sn–C}_{1\text{R}})$ versus $\sigma^*(\text{R}'')$. In this way we have determined the following values from the ditin spectra: $\sigma^*(\text{Me}_3\text{Sn})$ -0.63, -0.57, -0.62, mean -0.61; $\sigma^*(\text{Et}_3\text{Sn})$ -0.70, -0.61, -0.69, mean -0.67; $\sigma^*(\text{Pr}^i_3\text{Sn})$ -0.72. From the tritin spectra, the following values are obtained: $\sigma^*(\text{Me}_3\text{Sn})$ -0.52, -0.49, -0.41, mean -0.51; $\sigma^*(\text{Et}_3\text{Sn})$ -0.57, -0.53, -0.44, mean -0.51; $\sigma^*(\text{Pr}^i_3\text{Sn})$ -0.62. It can be seen that the values obtained from $^1J(\text{Sn–Sn})$ in the tritins and $^1J(\text{Sn–C})$ in the ditins correspond fairly closely, while those from $^1J(\text{Sn–C})$ in the tritins are between -0.1 and -0.25 lower.

These σ^* values have been calculated on the assumption that the geometry at the tin atom is in each case tetrahedral: this is certainly not always so, but no exact information is at present available on bond lengths and angles in hexa-alkylditins or octa-alkyltritins. X-Ray crystal studies should help to clarify the situation.

It does however seem fairly clear that the σ^* values for trialkyltin residues are of the order of -0.6, varying

[22] R. W. Taft, jun., ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

[23] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

little with the nature of the alkyl groups. We have measured the ^{13}C spectra of $Me_3SnSiMe_3$ and $Me_3SnGeMe_3$ (Table 7), and on the basis of these measurements obtained the following Taft constants: $\sigma^*(Me_3Si)$ —0.65 and $\sigma^*(Me_3Ge)$ —0.62. These values seem reasonable in view of the very similar electronegativities of silicon, germanium, and tin; values for $\sigma^*(Me_3Si)$ of —1.1 and for $\sigma^*(Me_3Ge)$ of —0.8 have previously been determined from i.r. studies of organosilicon and organogermanium compounds.[24]

In the course of this work we have determined a large number of long-range coupling constant; the most interesting of these is probably the coupling $^2J(Sn-Sn-C)$. The values of this constant should reflect changes in $^1J(Sn-Sn)$ and $^1J(Sn-C)$; the correlation coefficient for the relation between $^1J(Sn-Sn)$ and $^2J(Sn-Sn-C)$ (the mean value of which is taken for mixed ditins) is 0.953, while in the mixed ditins the two values of $^2J(Sn-Sn-C)$ show the same variation pattern as does $^1J(Sn-C)$.

In the tritins the picture is more complex: the coupling $^2J(Sn-C_{1R})$ (Table 6) varies linearly with $^1J(Sn-Sn)$ when R or R' is constant; $^2J(Sn-C_{1R'})$ is invariant for constant R and variable R' [presumably because the opposing trends in $^1J(Sn-Sn)$ and $^1J(Sn-C_{1R'})$ cancel out], but varies linearly with $^1J(Sn-Sn)$ when R' is constant and R varied. A similar picture emerges when $^1J(Sn-C)$ and $^2J(Sn-Sn-C)$ are compared.

The Role of the Nuclear Overhauser Effect.—Since ^{119}Sn Fourier transform spectra of organotins must normally be recorded with proton noise decoupling (since the large tin–proton couplings would otherwise lead to the observation of extremely broad and complex signals), the occurrence of an NOE is possible.[25] Since for tin-119 (and tin-117) the magnetogyric ratio is

negative (—9.971 and —9.909 rad s^{-1} G^{-1} respectively) the NOE is also negative, the maximum value attainable being —1.34.

Lippmaa *et al.*[4] have shown that, for small organotin molecules such as Me_4Sn and trimethyltin halides, SR relaxation is dominant even below room temperature, so that only small NOEs are observed. We find that the NOE becomes important in the ditin series and in the tritins; for example, while it is very small for Me_6Sn_2 at room temperature, it attains a value of —1.0 (zero signal intensity) for Bu_6Sn_2 at +28 °C and for hexa-octylditin at +40 °C (an NOE of —1.0 corresponds to 75% DD relaxation). The low signal intensity at the operating temperature of the spectrometer is disadvantageous when tin–tin coupling constants are to be measured; while the thermal stability of the di- and tritins is such as to allow partial elimination of the NOE by heating to 80—100 °C (in a representative experiment, the signal intensity for Bu_6Sn_2 increased by a factor of 7 on raising the temperature from 40 to 100 °C), we have found that chromium tris(acetylacetonate) causes a similar reduction in the NOE at the spectrometer operating temperature. This relaxation reagent is also useful for other types of organotin compound; addition of $Cr(acac)_3$ often reveals the presence of small amounts of impurities in the sample under investigation, but normally has little effect on the chemical shift. We intend to carry out quantitative measurements of ^{119}Sn relaxation times T_1 in the near future.

[24] A. N. Egorochkin, N. S. Vyazankin, and E. N. Gladyshev, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1969, 1863.

[25] J. H. Noggle and R. E. Schirmer, ' The Nuclear Overhauser Effect,' Academic Press, New York and London, 1971.