^{119}Sn, ^{15}N, ^{13}C, AND ^{1}H NMR STUDY OF THE INTRAMOLECULAR Sn–N DONOR–ACCEPTOR INTERACTION IN [2-(DIMETHYLAMINOMETHYL)-PHENYL]STANNANES

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Dedicated to Dr Dobroslav Snobl on the occasion of his 75th birthday.

^{119}Sn, ^{15}N, ^{13}C, and ^{1}H NMR spectra were studied for [2-(dimethylaminomethyl)phenyl]stannanes, $R^1R^2R^3R^4$Sn or $R^1R^2R^4_2$Sn, where R^1, R^2, and R^3 are 1-butyl, Cl or Br, the same or different, and R^4 is 2-(dimethylaminomethyl)phenyl. The occurrence of intramolecular interaction between the nitrogen and tin atoms was demonstrated based on changes in the characteristic values of the NMR parameters of these nuclides ($\delta(^{15}$N$)$, $\delta(^{119}$Sn$)$, $J(^{119}$Sn,^{15}N$)$), and their interrelations, as well as on the relatively high values of the coupling constants $^3J(^{119}$Sn,^{13}C(CH$_2$)).

Key words: Stannanes; Tin; Organotin(IV) compounds; [2-(dimethylaminomethyl)phenyl]stannanes; ^{119}Sn, ^{15}N,^{13}C, and ^{1}H NMR spectroscopy; $J(^{119}$Sn,^{15}N$)$; Tin–amine interaction.

The occurrence of the Sn–N intramolecular interaction in [2-(dimethylaminomethyl)phenyl]stannanes $R^1R^2R^3R^4$Sn or $R^1R^2R^4_2$Sn, where R^1, R^2 and R^3 are different organic substituents or halide atoms and R^4 is 2-(dimethylaminomethyl)phenyl, and hence formation of the corresponding azastannacycles or "C,N-chelates", has been proved many times in solids by using diffraction techniques. The extensive and systematic research carried out by Jastrzebski and his group[1,2] based on the synthesis of a numerous and well-selected groups of compounds and their detailed examination by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy suggests that this interaction is also preserved in the more or less isolated particles of these compounds as encountered in solutions. However, to our knowledge, there exists no evidence of such interaction based on NMR spectra of the nuclides directly involved.

The aim of this study was to fill this gap and present evidence of the occurrence of the Sn–N intramolecular interaction in [2-(dimethylaminomethyl)phenyl]stannanes $R^1R^2R^3R^4Sn$ (compounds **1**–**5**) and $R^1R^2R_2^4Sn$ (compounds **6**–**8**), where R^1, R^2, and R^3 are 1-butyl (Bu), Cl or Br, the same or different, and R^4 is 2-(dimethylaminomethyl)phenyl, based on their ^{119}Sn, ^{15}N, ^{13}C, and ^1H NMR spectra, with emphasis on the spectral parameters of the nuclides directly involved in this interaction, *viz.* ^{119}Sn and ^{15}N.
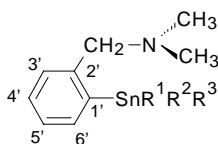
	R^1	R^2	R^3
1	Bu	Bu	Bu
2	Bu	Bu	Cl
3	Bu	Bu	Br
4	Bu	Cl	Cl
5	Br	Br	Br
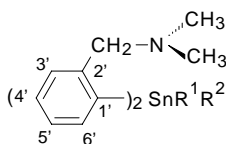
	R^1	R^2
6	Bu	Bu
7	Bu	Cl
8	Br	Br

$$Bu = \underset{1}{CH_2}\underset{2}{CH_2}\underset{3}{CH_2}\underset{4}{CH_3}$$

EXPERIMENTAL

Preparation of Compounds

Compounds **1**–**8** were synthesized by reacting 2-(dimethylaminomethyl)phenyllithium with the corresponding organotin halide following procedures published[2,3]. Substances **7** and **8** were also prepared by reacting 2-(dimethylaminomethyl)phenyllithium with anhydrous tin dichloride followed by oxidation with bromine or 1-chlorobutane[3]. The crude products were purified by vacuum distillation (compounds **1**–**4**, **6**, and **7**) or crystallization from boiling toluene (compounds **5** and **8**). The identity of the compounds was confirmed by elemental analysis (Table I) and analysis of their ^{119}Sn, ^{15}N, ^{13}C, and ^1H NMR spectra (Tables II and III).

Complexation of Butyltrichlorostannane with *N*,*N*-Dimethylbenzylamine

The complexation of butyltrichlorostannane with *N*,*N*-dimethylbenzylamine was monitored through changes in the $\delta(^{15}N)$ and $\delta(^{119}Sn)$ values in deuteriochlorofom solutions containing the two solutes in molar ratio *N*,*N*-dimethylbenzylamine : butyltrichlorostannane from 0.16 to 8.90 (starting concentration of the former reactant 0.85 mol l^{-1}) at 300 K. The solutions were measured 30 min after mixing, when the relevant spectral parameters did not change any longer.

NMR Spectra

^{119}Sn, ^{15}N, ^{13}C, and ^1H NMR spectra were measured on a Bruker AMX 360 instrument at 134.28, 36.56, 90.56, and 360.13 MHz, respectively, using a 5 mm tuneable broad-band probe at 300 K. The solutions were obtained by dissolving approximately 200 mg of the substance in 0.5 ml of deuteriochloroform or hexadeuteriodimethyl sulfoxide.

The reported ^1H and ^{13}C chemical shifts are relative to internal tetramethylsilane (δ 0.00 ppm), the ^{15}N and ^{119}Sn chemical shifts are relative to external nitromethane and tetramethylstannane, respectively, placed in coaxial capillaries (δ 0.0 ppm). Positive values denote downfield shifts. The $J(^{119}Sn, ^{15}N)$ coupling constants were read from the ^{15}N NMR spectra measured at a digital resolution better than 0.5 Hz/point. The 2D NMR spectra were measured conventionally using pulse sequences microprograms supplied by the spectrometer manufacturer.

RESULTS AND DISCUSSION

The parameters of the ^{119}Sn, ^{15}N, ^{13}C, and ^1H NMR spectra of the substances studied, *N,N*-dimethylbenzylamine and benzyltrimethylammonium iodide, are given in Tables II and III. The numbers of signals in the spectra and the NMR parameters are consistent with the composition of the compounds as determined by elemental analysis (Table I), as well as with their assumed structure (see below), thereby confirming their identity.

TABLE I
Analytical and physical data of compounds **1**–**8**

Compound	M.p. (b.p.), °C	Formula M.w.	Found/Calculated				
			% C	% H	% N	% Sn	% other
1	(170–173/200Pa)	$C_{21}H_{39}NSn$	58.27	9.37	3.83	27.93	–
		424.24	59.46	9.27	3.30	27.98	
2	(170–172/16Pa)	$C_{17}H_{30}ClNSn$	51.10	7.62	3.36	29.28	Cl: 8.27
		402.57	50.72	7.51	3.48	29.48	8.81
3	(170–173/9Pa)	$C_{17}H_{30}BrNSn$	46.02	6.48	3.27	26.46	Br: 17.15
		447.06	45.63	6.76	3.13	26.82	17.65
4	(170–172/9Pa)	$C_{13}H_{21}Cl_2NSn$	40.65	5.78	3.42	31.58	Cl: 18.52
		381.00	40.94	5.55	3.68	31.47	18.36
5	129–131	$C_9H_{12}Br_3NSn$	22.03	2.33	3.01	25.02	Br: 48.88
		490.75	22.01	2.46	2.85	24.43	48.24
6	(200–205/50Pa)	$C_{26}H_{42}N_2Sn$	62.02	8.66	6.12	23.47	–
		501.52	62.29	8.44	5.59	23.68	
7	(158–164/9Pa)	$C_{22}H_{33}ClN_2Sn$	55.53	7.17	5.84	23.53	Cl: 7.02
		480.13	54.98	6.93	5.83	24.97	7.28
8	245–247	$C_{18}H_{12}Br_2N_2Sn$	40.38	2.12	5.18	22.23	Br: 29.76
		533.83	40.46	2.27	5.25	22.46	29.57

TABLE II
^{13}C, ^{15}N, and ^{119}Sn NMR data of compounds **1**–**8** in CDCl$_3$ at 300 K

Compound	$\delta(^{15}N)$, ppm ($J(^{119}Sn,^{15}N)$, Hz)	$\delta(^{119}Sn)$ ppm	$\delta(^{13}C)$, ppm ($^{n}J(^{119}Sn,^{13}C)$, Hz)											
			C(1)	C(2)	C(3)	C(4)	CH$_3$	CH$_2$	C(1')	C(2')	C(3')	C(4')	C(5')	C(6')
dba[a]	−353.0						44.54	63.61	128.15	138.40	128.15	127.42	126.98	127.42
bta$^+$I^{-}[b]	−327.6						53.14	69.26	133.79	128.74	133.79	129.72	131.36	129.72
1	−351.9 (10.6)	−50.0	10.36 (349.2)	29.26 (18.5)	27.57 (58.9)	13.66	45.29	66.65 (15.9)	142.24 (430.1)	145.78 (24.5)	128.78 (37.7)	127.76 (29.4)	126.38 (44.7)	137.19 (32.7)
2	−348.0 (68.2)	−51.7	17.34 (499.1)	27.18 (29.7)	25.77 (98.5)	12.74 (c)	44.38	64.18 (22.8)	139.94 (642.2)	141.54 (36.41)	125.89 (53.8)	128.17 (13.7)	126.50 (59.8)	136.82 (37.9)
3	−347.3 (66.1)	−44.9	18.12 (487.6)	27.32 (29.9)	25.57 (83.8)	12.68 (c)	44.41	64.18 (23.73)	139.21 (611.0)	141.26 (35.3)	125.82 (51.0)	128.15 (12.61)	126.41 (60.9)	137.40 (39.1)
4	−346.2 (110.6)	−104.3	26.12 (686.9)	26.65 (42.6)	25.36 (136.8)	13.10 (c)	44.13	62.17 (32.6)	138.56 (874.1)	140.62 (47.1)	129.94 (72.7)	130.35 (18.92)	127.65 (86.9)	136.04 (64.1)
4[d]	−342.2	−270.7	34.12 (c)	27.91 (50.4)	25.37 (171.6)	13.76 (c)	45.25	62.48 (39.6)	148.19 (1 267.6)	138.78 (57.5)	126.91 (96.2)	128.73 (18.62)	127.40 (130.4)	133.57 (57.6)
5	−339.8 (113.8)	−414.5	c				44.87	60.60 (70.7)	136.95 (c)	138.56 (82.3)	128.08 (101.7)	132.27 (22.6)	129.11 (123.9)	135.62 (86.3)
6	−351.6 (9.5)	−83.9	12.23 (380.6)	29.09 (21.1)	27.60 (68.2)	13.69 (c)	45.04	66.36 (23.7)	142.93 (487.4)	145.53 (24.8)	126.24 (48.6)	127.59 (10.1)	128.65 (39.7)	137.24 (35.8)
7	−349.0 (44.4)	−118.1	18.67 (c)	27.31 (19.1)	26.12 (128.6)	13.01 (c)	44.80	64.76 (25.1)	142.07 (707.2)	142.64 (c)	126.43 (66.7)	128.21 (13.9)	127.43 (c)	135.74 (127.8)
8	−347.3	−271.2	c				46.86	63.46 (40.1)	140.62 (1 151.3)	140.71 (61.6)	128.03 (96.7)	130.21 (19.5)	128.11 (108.1)	135.46 (64.8)

[a] N,N-Dimethylbenzylamine; [b] benzyltrimethylammonium iodide; [c] not found; [d] hexadeuteriodimethyl sulfoxide.

TABLE III
$\delta(^1H)$ values of compounds **1**–**8** in $CDCl_3$ at 300 K

Compound	$\delta(^1H)$, ppm									
	H(1')	H(3')	H(4')/H(5')ᵃ	H(6')	CH₂	CH₃	H(1)	H(2)	H(3)	H(4)
dbaᵇ	7.23	7.21	7.21	7.23	3.27	2.11	–	–	–	–
bta⁺Tᶜ	7.69	7.51	7.51	7.51	4.85	3.27	–	–	–	–
1	–	7.14	7.14	7.49	3.34	2.11	1.52	1.35	1.01	0.88
2	–	7.13	7.25	8.21	3.56	2.27	1.70ᵈ 1.75ᵈ	1.36	1.36	0.88
3	–	7.12	7.24	8.25	3.59	2.31	1.68ᵈ 1.77ᵈ	1.38	1.38	0.87
4	–	7.18	7.45	8.14	3.71	2.39	1.89	1.79	1.44	0.93
5	–	7.23	7.47	8.05	3.81	2.52	–	–	–	–
6	–	7.13	7.13	7.55	3.21	1.86	1.51	1.34	1.24	0.85
7	–	7.18	7.25	7.89	3.21	1.98	1.69	1.55	1.38	0.86
8	–	7.26	7.36	8.21	3.31ᵈ 4.13ᵈ	2.22	–	–	–	–

ᵃ Centre of a multiplet; ᵇ *N,N*-dimethylbenzylamine; ᶜ benzyltrimethylammonium iodide; ᵈ anisochronous protons.

^{15}N NMR Spectra

The ^{15}N chemical shifts of all the compounds examined exhibit 1.1 to 13.2 ppm down-field shifts relative to the value of the unsubstituted *N,N*-dimethylbenzylamine. The differences $\Delta\delta(^{15}N)$ and the coupling constants $J(^{119}Sn,^{15}N)$ increase with the number of halogen atoms bonded to tin, hence, with increasing Lewis acidity of the central tin atom. For instance, in the **1** – **2** – **4** series, the $\Delta\delta(^{15}N)$ values are 1.1, 5.0, and 6.8 ppm, respectively, and the $J(^{119}Sn,^{15}N)$ values are 10.6, 68.2, and 110.6 Hz, respectively; in the **1** – **3** – **5** series, the corresponding values are 1.1, 5.7, and 13.2 ppm, and 10.6, 66.1, and 113.8 Hz, respectively. Similarly, in the **6** – **7** – **8** series the chemical shift differences are 1.4, 4.0, and 5.7 ppm, respectively, the $J(^{119}Sn,^{15}N)$ of **6** and **7** are 9.5 and 44.4 Hz, respectively (for compound **8**, the value was not determined).

Hence, it is reasonable to state that the $\delta(^{15}N)$ (or, better, the values and signs of $\Delta\delta(^{15}N)$) and $J(^{119}Sn,^{15}N)$ parameters give evidence of the occurrence of the intramolecular Sn–N donor–acceptor interaction in the molecules–molecular complexes and also provide a relative measure of this interaction.

Arguments in favour of this idea are based on the following experiments and reasonings:

a) Formation of the intramolecular Sn–N donor–acceptor bond is associated with a change in the valency of the nitrogen atom (from 3 to 4). The same valency change proceeds in the nitrogen quaternization, *e.g.* in the formation of the benzyltrimethylammonium ion. In this case, also, the valency change is accompanied by a downfield shift of the $\delta(^{15}N)$ value, which is relatively large, $\Delta\delta(^{15}N)) = 25.4$ ppm (Table II).

b) In parallel to the multinuclear NMR study of compounds **1–8**, ^{15}N and ^{119}Sn NMR spectroscopy was used to examine the equilibrium reaction of formation of the donor–acceptor complex of *N,N*-dimethylbenzylamine with butyltrichlorostannane.

$$(CH_3)_2NCH_2Ph + BuSnCl_3 \leftrightarrow [(PhCH_2)(CH_3)_2N\cdot SnBuCl_3)] \tag{A}$$

The plots in Fig. 1 show the dependences of the $\delta(^{15}N)$ and $\delta(^{119}Sn)$ values for mixtures of the two reactants on the composition, expressed through the molar ratio $n = c_N/c_{Sn}$ (c are starting molar concentrations; see Experimental).

The clear breaks in the plots indicate that in the $BuSnCl_3$–$(CH_3)_2NCH_2Ph$–$CDCl_3$ system, a single complex with the reactant molar ratio 1 : 1 is formed under the conditions used. The composition of the complex is also corroborated by the $\delta(^{119}Sn)$ values for solutions with molar ratios n higher than 1 (above –200 ppm), such values being characteristic of pentacoordinated butyltin compounds possessing the trigonal bipyramidal geometry of the central tin atom environment[4]. The upfield shift of the $\delta(^{119}Sn)$ values by approximately 250 ppm, associated with the change as shown in Eq. (*A*),

corresponds to the change in the coordination number of the butyltin compound from four to five[4].

The interrelation of the parameters $\delta(^{15}N)$ and $\delta(^{119}Sn)$ in the two plots in Fig. 1 is described by Eq. (*1*) (see Appendix):

$$n[\delta(^{15}N)_{obs} - \delta(^{15}N)_N] = \delta(^{119}Sn)_{obs} [\delta(^{15}N)_{SnN} - \delta(^{15}N)_N]/[\delta(^{119}Sn)_{SnN} - \delta(^{119}Sn)_{Sn}] -$$
$$- \delta(^{119}Sn)_{Sn} [\delta(^{15}N)_{SnN} - \delta(^{15}N)_N]/[\delta(^{119}Sn)_{SnN} - \delta(^{119}Sn)_{Sn}], \qquad (1)$$

where the subscripts obs, N, Sn, and SnN refer to the $\delta(^{15}N)$ or $\delta(^{119}Sn)$ shifts in the mixture, the two substrates, and the product of reaction (*A*) (1 : 1 complex), respectively. The plot of this equation in the coordinates $n[\delta(^{15}N)_{obs} - \delta(^{15}N)_N]$ *vs* $\delta(^{119}Sn)_{obs}$ is linear, with a slope of –0.085, determined by the ratio of the differences between the $\delta(^{15}N)$ values (–333.0 and –353.6 ppm) and between the $\delta(^{119}Sn)$ values (–235.0 and +6.1 ppm, ref.[4]) for the complex and the free components, and with an intercept which is the negative value of the slope multiplied by the $\delta(^{119}Sn)$ value of butyltrichlorostannane (0.52 ppm). The solid line in Fig. 2 is the plot of the dependence (*1*) constructed on the basis of the slope and intercept calculated from the limiting values; the circles show the observed pairs of the $\delta(^{15}N)_{obs}$ and $\delta(^{119}Sn)_{obs}$ values. This gives evidence that the two NMR parameters describe the same phenomenon, *i.e.*, both are measures of composition of the equilibrium mixture in reaction (*A*). The complexation process is associated with an increase in the coordination number of the tin atom (upfield shift of
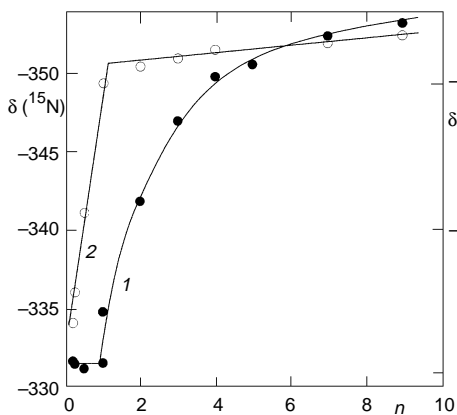

FIG. 1

Dependence of the $\delta(^{15}N)$ values (*1*) and $\delta(^{119}Sn)$ (*2*) in the BuSnCl$_3$–(CH$_3$)$_2$NCH$_2$Ph–CDCl$_3$ system on the $n = c_N/c_{Sn}$ molar ratio of the reacting components
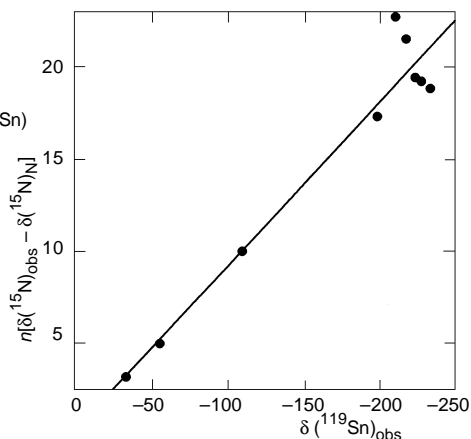
FIG. 2

Dependence of the value $n[\delta(^{15}N)_{obs} - \delta(^{15}N)_N]$ on $\delta(^{119}Sn)_{obs}$ in the BuSnCl$_3$–(CH$_3$)$_2$NCH$_2$Ph–CDCl$_3$ system

the $\delta(^{119}Sn)$ values) on the one hand, and, proportionally, with a change in the nitrogen atom valency (downfield shift of the $\delta(^{15}N)$ values). This situation is formally analogous (in the direction and magnitude of the $\delta(^{119}Sn)$ and $\delta(^{15}N)$ shifts) to the appearance of the Sn–N donor–acceptor interaction in compounds **1**–**8**.

c) The small yet significant shifts of the $\delta(^1H)$ values of the methyl and methylene groups bonded to the nitrogen atoms in (dimethylaminomethyl)arenes which are substituted in position 2 by an organometallic substituent are often used as evidence and even a measure of the M–N donor–acceptor interaction[1,2,5-7]. The $\delta(^1H)$ values of the methylene group and methyl groups in the dimethylaminomethyl moiety and the $\delta(^{15}N)$ values of compounds **1**–**5**, which contain only one such group, exhibit a linear correlation, the pairs of the parameters for *N,N*-dimethylbenzylamine and for the benzyltrimethylammonium cation constituting the end points of this correlation (Fig. 3).

Hence, it is clear that also in this case the two NMR parameters, $\delta(^1H)$ and $\delta(^{15}N)$, describe the same phenomenon. The parameters for compounds **6** to **8**, where the organotin fragment is bonded to two (dimethylaminomethyl)phenyl groups, depart slightly from the linear correlations, presumably due to the peculiarities of the bonding situation in these molecular complexes (see below).

^1H NMR Spectra

The ^1H NMR spectra of compounds **1**–**8** (Table III) served (in addition to elemental analysis) as a purity check of the compounds. In the aromatic spectral region, the signals of protons in positions 3′ and 6′ are separated in the form of broad doublets, whereas the signals of protons in positions 4′ and 5′ appear as coinciding multiplets. The protons 3′ and 6′ were resolved on the basis of the NOESY spectra where interaction between the protons of the NCH$_2$ group and the H(3′) proton is apparent. The assignment is borne out independently by the large coupling constant $^3J(^{119}Sn,^1H(6′))$.
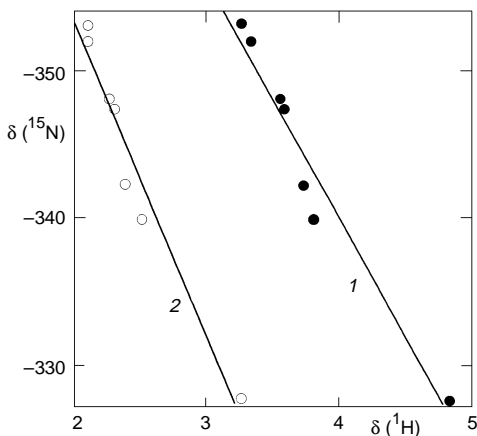

Fig. 3
Linear correlation of the $\delta(^1H,CH_2)$ (*1*) and $\delta(^1H,CH_3)$ (*2*) chemical shifts for the –CH$_2$N(CH$_3$)$_2$ substituent and the $\delta(^{15}N)$ chemical shifts for compounds **1**–**5**

The signals of the methylene groups $SnCH_2$ in compounds **2** and **3** and of the NCH_2 groups in compound **8** are anisochronous.

^{119}Sn and ^{13}C NMR Spectra

The increase in the strength of the intramolecular Sn–N interaction with increasing Lewis acidity of the central tin atom (decreasing number of Sn–C bonds) in the series under study is also confirmed by the relevant data of the ^{119}Sn and ^{13}C NMR spectra, particularly by the upfield shift of the $\delta(^{119}Sn)$ values of the compounds as compared with the unsubstituted analogues (see later), increase in the coupling constants $^1J(^{119}Sn,^{13}C)$, and the existence and growth of the coupling constants $J(^{119}Sn,^{13}C(CH_2))$.

   While for compounds **1** and **6** the $\delta(^{119}Sn)$ values exhibit upfield shifts of 8.3 and 18.0 ppm only as compared with the corresponding unsubstituted analogues (Bu$_3$SnPh, $\delta(^{119}Sn)$ –41.7 ppm, and Bu$_2$SnPh$_2$, $\delta(^{119}Sn)$ –65.9 ppm, ref.[8], respectively), for compounds **5** and **8** the differences from the unsubstituted analogues (PhSnBr$_3$, $\delta(^{119}Sn)$ –227.2 ppm, ref.[9], and Ph$_2$SnBr$_2$, $\delta(^{119}Sn)$ –71.8 ppm, ref.[10]) are as high as –187.3 and –199.4 ppm, respectively. In this context, it is noteworthy that a roughly 200 ppm upfield shift of the $\delta(^{119}Sn)$ value corresponds to an increase in the coordination number in monophenyltin(IV) and diphenyltin(IV) compounds from four to five[9,10]. A similar comparison of the $\delta(^{119}Sn)$ values between compounds **2**, **3**, **4**, and **7**, and their unsubstituted analogues could not be made because the values for the mixed butyl(halogeno)phenylstannanes are unavailable. Nevertheless, the $\delta(^{119}Sn)$ values of the triorganotin(IV) compounds **2**, **3**, and **7**, and the diorganotin(IV) compound **4** all display marked upfield shifts not only in comparison with tributyl(chloro)stannane ($\delta(^{119}Sn)$ +152.8 ppm, ref.[11]), the bromo derivative ($\delta(^{119}Sn)$ +126.3 ppm), and dibutyl(dichloro)stannane ($\delta(^{119}Sn)$ +126.3 ppm) but (except for compound **3**) also, to some extent, with chloro(triphenyl)stannane and dichloro(diphenyl)stannane (–44.7 ppm, ref.[12] and –26.7 ppm, ref.[10], respectively).

   Thus, all the data support the hypothesis that in solutions in non-coordinating non-polar solvents, all of the compounds studied occur in the form of molecular complexes with a more or less strong intramolecular Sn–N donor–acceptor bonding. The strength of this bonding increases with decreasing number of organic substituents at the tin atom, but even in diorganotin(IV) compounds, it is strong enough to resist the effect of coordinating solvents which occurs with the majority of chelate complexes (see, *e.g.*, ref.[13]). The change in the $\delta(^{119}Sn)$ value in compound **4** on replacing the non-coordinating deuteriochloroform solvent with the strongly coordinating hexadeuteriodimethyl sulfoxide, –166.4 ppm, implies a change in the coordination number of the central tin atom from five to six. This change is accompanied by a slight downfield shift of the $\delta(^{15}N)$ value, indicating preservation and even strengthening of the Sn–N donor–acceptor interaction rather than its vanishing. Hence, in solution in this polar solvent, compound **4**

occurs as a pseudo-octahedral complex derived from the initially trigonal bipyramidal chelate complex with an additional molecule of the solvent.

The coupling constants $^1J(^{119}Sn,^{13}C(1))$ and $^1J(^{119}Sn,^{13}C(1'))$ for compounds **1** and **6**, 349.2 and 380.6 Hz, respectively, and 430.1 and 487.4 Hz, respectively, are more typical of the tetragonal arrangement than of the trigonal bipyramidal arrangement of the bonding environment of the central tin atom in Bu_4Sn and Ph_4Sn (refs[14,15]). If we admit that molecular chelate complexes with weak Sn–N bonding interactions exist in solutions of such compounds in non-polar solvents, then the shape of the coordination polyhedron around the central tin atom can be formulated as an intermediate arrangement between the tetrahedron and the trigonal bipyramid, most probably kind of a strongly distorted tetrahedron. This is consistent with the average angles calculated based on the above $^1J(^{119}Sn,^{13}C)$ data[14,15]. The average C(Bu)–Sn–C(Bu) angle is approximately 109° in compound **1** and 112° in compound **6**, the average C(Ph)–Sn–C(Ph) angle in compound **6** is approximately 105°. It is noteworthy that virtually the same (rather pseudo-tetrahedral) arrangement around the central tin atom as considered for compound **1** is also present in some other tetraorganotin(IV) complexes, in the so-called C,N-chelate complexes, even in the solid state; this is the case, for instance, with (8-dimethylamino-1-naphthyl)triphenylstannane, where the C–Sn–C angles in the Ph_3Sn fragment are 114.4, 101.1, and 103.4°, average 106.3° (ref.[16]). With caution, a similar conclusion can also be drawn from a comparison of the assumed structure of compound **6** with that of diphenylbis[3-(2-pyridyl)-2-thienyl]stannane, derived from the single crystal diffraction data[17]. The coupling constants $^1J(^{119}Sn,^{13}C(1))$ and $^1J(^{119}Sn,^{13}C(1'))$ as well as the C(1)–Sn–C(1) and C(1')–Sn–C(1') angles in the triorganotin(IV) compounds **2**, **3**, and **7** calculated following refs[14,15] (about 124, 123, and 119°, respectively) are in agreement with the concept of a more or less distorted *trans*-trigonal bipyramidal arrangement of the bonding partners of the tin atom, as has been proved many times for similar species in the solid state as well as in solutions in non-polar solvents[1,2]. The concept of a trigonal bipyramidal geometry on the central tin atom in the C,N-chelate complexes **6**–**8** is not inconsistent with the presence of two nitrogen donor atoms manifesting themselves by a single signal in the ^{15}N NMR spectrum. This is apparently a consequence of the rapidly establishing exchange

$$N–Sn\cdots N \rightleftharpoons N\cdots Sn–N$$
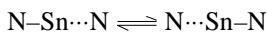
and hence, manifestation of a certain substituent flexibility in this complex. This is also borne out by the appreciably lower $\Delta\delta(^{15}N)$ values as compared with the remaining triorganotin(IV) compounds under study, which are probably arithmetic means of values for one coordinated and one non-coordinated nitrogen atom in the 2-(dimethylaminomethyl)phenyl substituent. The above interpretation corresponds to a shape

which is intermediate between a strongly distorted trigonal bipyramid (coordination number 5) and a distorted octahedron (coordination number 6 or, better, 5 + 1). Such an arrangement of the central tin atom environment which is in line with the above interpretation was confirmed by diffraction analysis of crystals of the analogous bis(8-dimethylamino-1-naphthyl)iodo(methyl)stannane[17]. The Sn···N distances in molecules of this complex in the solid state are conspicuously different: 253 and 310 pm (ref.[18]). The increase in the coupling constant $^1J(^{119}Sn,^{13}C(1'))$ for compound **4**, which is observed when the non-coordinating solvent $CDCl_3$ is replaced by the coordinating hexadeuteriodimethyl sulfoxide, only illustrates the change in the coordination of the central tin atom in the formation of the relatively stable complex of this compound with one molecule of the solvent. The coupling constant $^1J(^{119}Sn,^{13}C(1'))$, the C(1')–Sn–C(1') angle (about 148°), and the relatively low $\Delta\delta(^{15}N)$ value are consistent with the strongly distorted pseudo-octahedral arrangement (tin coordination number 4 + 2) of the coordination sphere of the central atom (the C–Sn–C angle in the analogous dibromobis(8-dimethylaminonaphthyl)stannane is 153.9° in the solid state[18]).

Indirectly but significantly, the existence and degree of the intramolecular Sn–N donor–acceptor interaction is also reflected by the coupling constants $^2J(^{119}Sn,^{13}C(NCH_2))$, which – like the coupling constants $^1J(^{119}Sn,^{13}C(1))$ or $^1J(^{119}Sn,^{13}C(1'))$ or $J(^{119}Sn,^{15}N)$ – increase with growing Lewis acidity of the compounds.

APPENDIX

The position of the single signal in the NMR spectrum of a system of two components which are in a rapidly establishing equilibrium (on the NMR time scale) is determined by the weighed average of the chemical shifts of the nuclide, *i.e.* the sum of products of the chemical shifts and relative concentrations of the two components[8]. Assuming that the dependences of the two parameters, $\delta(^{15}N)$ and $\delta(^{119}Sn)$, on the component concentration ratio both pertain to the same equilibrium, we have for equilibrium (*A*):

$$\delta(^{119}Sn)_{obs} = \delta(^{119}Sn)_{Sn}\,(c_{Sn}/c_{Sn}^0) + \delta(^{119}Sn)_{SnN}\,(c_{SnN}/c_{Sn}^0) \qquad (A1)$$

and similarly

$$\delta(^{15}N)_{obs} = \delta(^{15}N)_{N}\,(c_N/c_N^0) + \delta(^{15}N)_{SnN}\,(c_{SnN}/c_N^0)\,, \qquad (A2)$$

where the superscript 0 denotes the starting analytical concentrations of the substrates; the meaning of the remaining symbols is the same as in Eq. (*1*). By introducing from the balance equations

$$c^0_{Sn} = c_{Sn} + c_{SnN} \tag{A3}$$

$$c^0_N = c_N + c_{SnN} \tag{A4}$$

and rearranging, we obtain

$$\delta(^{119}Sn)_{obs} = [\delta(^{119}Sn)_{SnN} - \delta(^{119}Sn)_{Sn}]\, (c_{Sn}/c^0_{Sn}) + \delta(^{119}Sn)_{Sn} \tag{A5}$$

and

$$\delta(^{15}N)_{obs} = [\delta(^{15}N)_{SnN} - \delta(^{15}N)_{N}]\, (c_{SnN}/c^0_{N}) + \delta(^{15}N)_{N}\,. \tag{A6}$$

If Eqs (*A5*) and (*A6*) pertain to the same equilibrium, they can be combined by eliminating the c_{SnN} term, and after substituting

$$c^0_N = n c^0_{Sn} \tag{A7}$$

the interrelation of $\delta(^{15}N)$ and $\delta(^{119}Sn)$ is obtained in the form of Eq. (*1*).

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