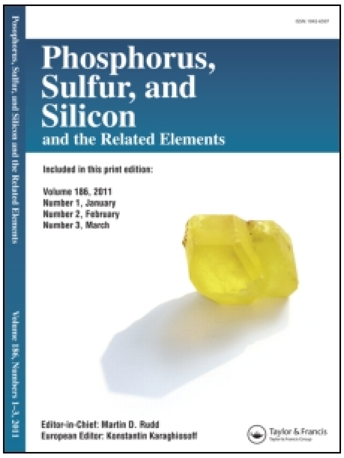

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BIS(SULFURDIIMIDO)TIN AND TRIS(SULFURDIIMIDO)SILICON, -GERMANIUM AND -TIN COMPOUNDS—STRUCTURE IN SOLUTION AND IN THE SOLID STATE AS DETERMINED BY MULTINUCLEAR MAGNETIC RESONANCE

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BIS(SULFURDIIMIDO)TIN AND TRIS(SULFURDIIMIDO)SILICON, -GERMANIUM AND -TIN COMPOUNDS—STRUCTURE IN SOLUTION AND IN THE SOLID STATE AS DETERMINED BY MULTINUCLEAR MAGNETIC RESONANCE

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Bis(sulfurdiimido)tin (**1a**–**5a**, **3b**, **4b**) and tris(sulfurdiimido)element compounds (element = Si, Ge, Sn; **6a**, **7a**,**b**–**9a**,**b**) were prepared and studied by multinuclear magnetic resonance in solution (^{1}H, ^{13}C, ^{15}N, ^{29}Si, ^{119}Sn NMR) and in the solid state (^{13}C, ^{15}N, ^{119}Sn CP/MAS NMR). All compounds are fluxional molecules in solution with respect to fast E/Z $\rightleftharpoons$ Z/E isomerization. In the case of N-*tert*-butyl derivatives, the configuration of the respective isomers could be assigned by low temperature NMR measurements. For example, in the case of ^{t}Bu$_2$Sn(NSN^{t}Bu)$_2$, **4a**, two configurational isomers are present in solution, but only one in the solid state. In the case of the tin compounds, all NMR data point towards association both in solution (at low temperature) and in the solid state, the tendency for association being greatest for n-butyl-tris(N-*tert*-butylsulfurdiimido)tin (**6a**).

Key words: Sulfur diimides, organometallic-substituted, organosilicon compounds, organogermanium compounds, organotin compounds, NMR, multinuclear, NMR, solid-state, CP/MAS.

INTRODUCTION

The structures of sulfur diimides, R(NSN)R′, have been discussed on the basis of various physical methods,[1] and their chemistry has been reviewed.[1,2] The chemistry of the NSN moiety[1,2] is further extended if one or both nitrogen atoms are bearing organometallic substituents,[3,4] and if two or more RNSN groups are linked to a central element.[5–8] In continuing our studies[8b,9–11] on the configuration of sulfurdiimido compounds, we now report on bis(sulfurdiimido)tin and tris(sulfurdiimido)silicon, -germanium and -tin compounds.

Ten different configurations are conceivable for compounds of the type R^1_2Sn(NSNR)$_2$ (**1a**–**5a**, **3b**, **4b**) assuming a rigid structure. For bulky substituents R such as ^{t}Bu or SiMe$_3$ the presence of isomers with the Z/Z configuration is unlikely due to steric effects, and the E/E configuration is not favoured for most combinations of substituents due to interactions between the lone pairs of electrons at the nitrogen atoms. Indeed, we did not observe any trace of a long lived Z/Z or E/E isomer in solution for sulfur diimides R(NSN)R′ with R = R′ = ^{t}Bu, SiMe$_3$ or R = ^{t}Bu and R′ = SiMe$_3$.[9] Therefore, we expect mainly three isomers for R^1_2Sn(NSNR)$_2$, the (Z/E)$_2$, the (E/Z)$_2$ and the (Z/E)(E/Z) isomer (see Scheme 1). This situation corresponds to that discussed in the case of bis(sulfurdiimido)silicon and -germanium compounds.[8b]

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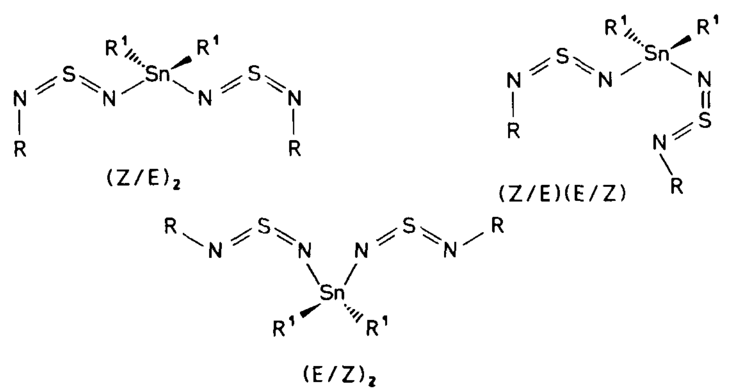
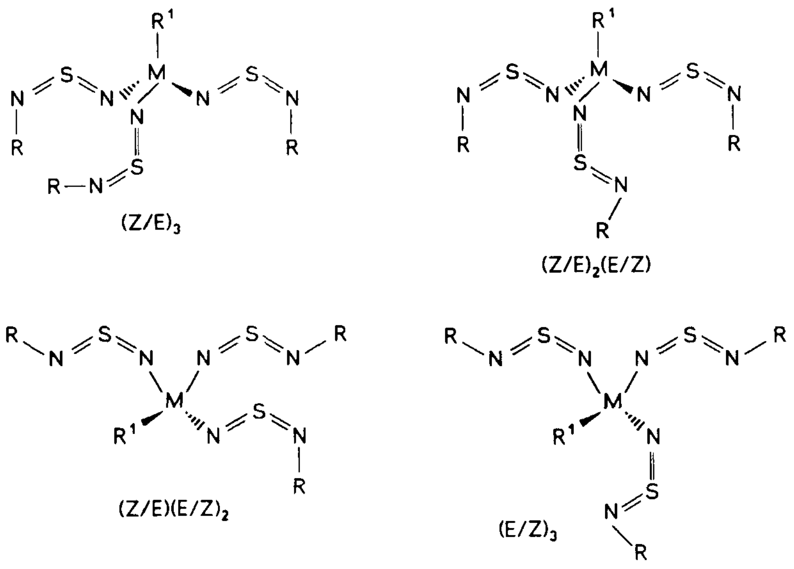
† Authors for correspondence.



Scheme 1.

The three most likely configurations of bis(sulfurdiimido)tin compounds, $R^1_2Sn(NSNR)_2$ (R = ^tBu, $SiMe_3$; the first letter E or Z refers to the position of the substituent R).



Scheme 2.

The four most likely configurations of tris(sulfurdiimido)element compounds $R^1M(NSNR)_3$ (R = ^tBu, $SiMe_3$; M = Si, Ge, Sn; the first letter E or Z refers to the position of the substituent R).

If the same arguments apply to tris(sulfurdiimido)element compounds, $R^1M(NSNR)_3$ (**6a**, **7a,b–9a,b**), we expect mainly the isomers (Z/E)$_3$, (Z/E)$_2$(E/Z), (Z/E)(E/Z)$_2$ and (E/Z)$_3$ (see Scheme 2).

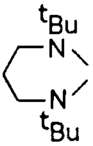
Although the compound $Me_2Sn(NSN^tBu)_2$ (**1a**) was described previously,[8a] its configuration in solution was not studied as yet. We strive to determine the configuration of bis- and tris(sulfurdiimido) compounds in solution by means of NMR spectroscopy, in particular ^{15}N and ^{119}Sn NMR, and to compare this information, wherever possible, with data for the solid state. For this reason ^{119}Sn cross polarization magic angle spinning (CP/MAS) NMR spectra were measured for the solid compounds **1a**, **4a** and **6a**, as well as ^{13}C and ^{15}N CP/MAS NMR spectra in the case of **4a**.

RESULTS AND DISCUSSION

Synthesis of the $R_2^1Sn(NSNR)_2$ and $R^1M(NSNR)_3$ Compounds

The reaction between the potassium salt K[(NSN)R] (R = ^{t}Bu, $SiMe_3$) and a tin dihalide, $R_2^1SnCl_2$, leads directly to the corresponding bis(sulfurdiimido)tin compound [Equation (1)].

$$2\ K[(NSN)R] + R_2^1SnCl_2 \xrightarrow[-78^\circ C]{hexane/DME} R_2^1Sn(NSNR)_2 + 2\ KCl \qquad (1)$$

R^1	Me	Et	^{n}Bu	^{t}Bu	
R = ^{t}Bu	**1a**	**2a**	**3a**	**4a**	**5a**
R = $SiMe_3$	-	-	**3b**	**4b**	-

Addition of 1,2-dimethoxyethane (DME) helps to improve the solubility of the potassium salts, K[(NSN)R] (R = ^{t}Bu, $SiMe_3$), and thus accelerates the reaction. In general the compounds with R = $SiMe_3$, e.g., **3b**–**4b**, are less stable than the compounds with R = ^{t}Bu, **1a**–**5a**. They decompose in the course of several hours even when kept at −20°C.

In an analogous manner [Equation (2)] tris(sulfurdiimido)element compounds are obtained from the reaction of the potassium salt K[(NSN)R] (R = ^{t}Bu, $SiMe_3$) with an alkylelement trichloride, R^1MCl_3.

$$3\ K[(NSN)R] + R^1MCl_3 \xrightarrow[-78^\circ C]{hexane/DME} R^1M(NSNR)_3 + 3\ KCl \qquad (2)$$

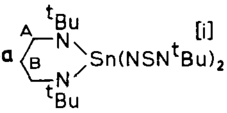
R^1	^{n}Bu	Me	^{t}Bu	Me
M	Sn	Si	Si	Ge
R = ^{t}Bu	**6a**	**7a**	**8a**	**9a**
R = $SiMe_3$	-	**7b**	**8b**	**9b**

NMR Spectroscopic Results

The NMR data of the compounds **1a**–**5a**, **3b**, **4b**, **6a** and **7a,b**–**9a,b** are listed in Tables I–III. ^{15}N NMR spectra have been measured by using one of the following methods: (i) ^{1}H inverse-gated decoupling for suppression of the NOE,[12] (ii) direct measurement without ^{1}H decoupling, (iii) direct measurement with ^{1}H decoupling and (iv) application of the refocused INEPT pulse sequence[13] with ^{1}H decoupling (polarization transfer based on $^3J(^{15}N^1H)$). Owing to long longitudinal relaxation

TABLE I

NMR data[a] of bis(sulfurdiimido)tin compounds (**1a–5a**, **3b**, **4b**)

Compound	$\delta^{13}C$		$\delta^{119}Sn$	$\delta^{15}N$		
	${}^{t}Bu$; $SiMe_3$	R^1_2Sn	$(\delta^{29}Si)$	NR[b]	NSn	[c]
1a $Me_2Sn(NSN^{t}Bu)_2$ [d] $(E/Z)_2$	31.5/59.4	1.6	-17.2	---	---	--
2a $Et_2Sn(NSN^{t}Bu)_2$ [e] $(E/Z)_2$	31.7/59.1	9.7 [33.8] 13.5	-16.0	+8.0 (E)	-114.4 (Z)	A, C
3a ${}^{n}Bu_2Sn(NSN^{t}Bu)_2$ [f] $(E/Z)_2$	31.7/59.0	[g]	-19.1	+8.4 (E)	-113.6 (Z)	A, B
4a ${}^{t}Bu_2Sn(NSN^{t}Bu)_2$ [h] (Z/E)(E/Z)	29.4/60.9 32.0/59.4	30.0/37.2 [231.8]	-65.2	-58.2 (Z) +12.1 (E)	-53.3 (E) -124.9 (Z)	A, C
$(E/Z)_2$	32.1/59.1	30.1/37.8	-42.8	+14.0 (E)	-124.4 (Z)	
5a  (Z/E)(E/Z)	29.4/61.5 32.3/60.4	29.0/49.8 29.5 (A) 41.5 (B)	-218.7	---	---	--
3b ${}^{n}Bu_2Sn(NSNSiMe_3)_2$ [j]	0.8 {57.8}	[k]	-28.3 (+1.6)	-58.0	-47.9	A, B
4b ${}^{t}Bu_2Sn(NSNSiMe_3)_2$ [l]	1.3 {56.7}	30.1/38.0 [444.7]	-65.1 (-0.1)	-48.4	-60.3	A, B

[a] In toluene[d_8]; measured at -40°C; coupling constants in Hz : ${}^{n}J({}^{119}Sn{}^{13}C)$ in [], ${}^{1}J({}^{29}Si{}^{13}C)$ in { }; br. = broad.

[b] R = ${}^{t}Bu$, $SiMe_3$.

[c] ${}^{15}N$ NMR methods : **A** = refocused INEPT pulse sequence with ${}^{1}H$ decoupling; **B** = ${}^{1}H$ inverse-gated; **C** = direct measurement, ${}^{15}N\{{}^{1}H\}$; **D** = direct measurement, ${}^{1}H$ coupled.

[d] Measured at -60°C; additional signals at this temperature: $\delta^{13}C$ = 29.6, 61.2 (${}^{t}Bu\{Z\}$), 31.5, 59.4 (${}^{t}Bu\{E\}$), -0.1 (Me_2Sn); $\delta^{119}Sn$ = -30.0 (br.), -180.0 (br.), -208.0 (br.); $\delta^{14}N$(27°C) = +9.0, -29.0, -120.0 (all resonances broad); $\delta^{119}Sn$ (27°C) = 28.0 (br.); $\delta^{119}Sn$(0°C) = -17.4 (br.); $\delta^{119}Sn$(-40°C) = -18.8, -21.0, -204.0 (br.); $\delta^{119}Sn$(CP/MAS) = -120.0.

[e] Additional signals at -40°C: $\delta^{13}C$ = 29.5, 60.1 (${}^{t}Bu$ {Z}), 32.0, 58.9 (${}^{t}Bu$ {E}), 10.1 [39.2], 14.7 (Et_2Sn); $\delta^{119}Sn$ measured at -60°C; additional signals at -60°C: $\delta^{119}Sn$ = -67.2 (br.), -133.2 (br.); $\delta^{15}N$ = -42.6, -65.8, -106.1; $\delta^{14}N$ (27°C) = +10.0, -59.0, -114.0 (all resonances broad); $\delta^{119}Sn$(27°C) = -25.8; $\delta^{119}Sn$(-30°C) = -19.5, -51.9, -113.8.

TABLE I (*Continued*)

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[f] Additional signals at -40°C: $\delta^{13}C$ = 29.4, 60.6 (^tBu(Z)), 31.7, 59.4 (^tBu(E)), 14.0 (CH_3), 20.5, 26.8, 27.5 (CH_2); $\delta^{119}Sn$ = -35.3 (br.); $\delta^{15}N$ = -49.3; $\delta^{14}N$ (27°C) = +10.0, -66.0, -129.0 (all resonances broad); $\delta^{119}Sn$(27°C) = -31.5 (br.); $\delta^{119}Sn$(0°C) = -23.6, -32.9; $\delta^{119}Sn$(-30°C) = -20.0, -35.7; $\delta^{119}Sn$ (-50°C) = -20.0, -53.8, -120.4 (br.), -177.5 (br.), -217.4 (br.).

[g] $\delta^{13}C$ = 13.9 (CH_3), 21.0, 27.0, 27.5 (CH_2).

[h] Measured at -60°C; $\delta^{14}N$(27°C) = +7.0, -61.0, -117.0 (all resonances broad); $\delta^{15}N$(CP/MAS) = -54.7 (N^tBu (Z)), -49.5 (NSn (E)), +15.9 (N^tBu (E)), -119.4 (NSn (Z)); $\delta^{119}Sn$(27°C) = -74.0; $\delta^{119}Sn$ (-20°C) = -71.2, -49.1; $\delta^{119}Sn$ (-40°C) = -69.1, -46.1; $\delta^{119}Sn$(CP/MAS) = -67.8; $\delta^{13}C$(CP/MAS) = 30.7, 31.8, 60.8 (^tBu), 31.0, 339, 38.3, 38.8 (Si^tBu).

[i] Measured at -60°C; $\delta^{14}N$(27°C) = -48.0, -307.0 (both resonances broad); $\delta^{119}Sn$ (27°C) = -234.0; $\delta^{119}Sn$(-30°C) = -223.4.

[j] Measured at +27°C; $\delta^{14}N$(27°C) = -58.0 ($h_{1/2}$ = 310 Hz); $\delta^{15}N$(-50°C) = -57.8 ($NSiMe_3$), -46.6 (NSn, br.); $\delta^{119}Sn$(-30°C) = -17.4.

[k] $\delta^{13}C$ = 13.6 (CH_3), 21.3 [450.0], 26.9 [80.7], 27.8 [26.2] (CH_2).

[l] Measured at +27°C; $\delta^{14}N$(27°C) = -57.0 (br.); $\delta^{29}Si$ (-20°C/-40°C) = +0.3; $\delta^{29}Si$(-60°C/-80°C) = +0.5; $\delta^{119}Sn$(-20°C) = -57.3; $\delta^{119}Sn$(-60°C) = -50.6; $\delta^{119}Sn$(-80°C) = -49.3.

times $T_1(^{15}N)$ the direct measurements required much spectrometer time and were not successful in all cases. A further problem is the broadening of the ^{15}N resonances due to dynamic processes which also prevents the straightforward application of polarization transfer pulse sequences. The refocused INEPT pulse sequence[13] based on $^3J(^{15}N^1H)$ ~ 2.0–2.5 Hz for $=N^tBu$ and ~ 1.0–1.8 Hz for $=NSiMe_3$, $=NSiMe$ and $=NGeMe$ proved to be valuable for these moieties. In the case of $=NSnR^1_2$ groups, polarization transfer was not efficient, possibly because of rather small coupling constants $^3J(^{15}N^1H)$ and/or dynamic effects. Solid state CP/MAS ^{15}N NMR spectra were extremely difficult to record, mainly due to inefficient cross polarization as a result of unfavourable $T_{1\rho}$ values. Therefore, only the ^{15}N CP/MAS NMR spectrum of **4a** could be measured (see Figure 1B), whereas in the other cases, e.g. for **6a**, the signal-to-noise ratio was insufficient for assigning all ^{15}N resonance signals.

a) Bis(sulfurdiimido)tin Compounds (1a–5a, 3b, 4b)

^{15}N NMR: We have recently found that the ^{15}N nucleus linked to the *tert*-butyl group in E position is markedly deshielded as compared with that linked to a *tert*-butyl group in Z position (e.g., $\delta^{15}N$ of $^tBu(NSN)^tBu$: −6.6 (E) and −105.9 (Z)).[8b,9a,9c] The $\delta^{15}N$ values of the N atoms bound to a *tert*-butyl group in E position of **2a**–**4a** (between +8.0 and +14.0; see Table I) show that this is also true for bis(N-*tert*-butylsulfurdiimodo)tin compounds. If the second substituent is not a *tert*-butyl group,

TABLE II

NMR data[a] of n-butyl-tris(N-*tert*-butylsulfurdiimido)tin (**6a**)

Temperature	δ^{1}H ^{t}Bu	 ^{n}Bu	δ^{13}C ^{t}Bu	 ^{n}Bu	δ^{119}Sn
+27°C [b]	1.24 (br.)	0.79 (t) 1.24 (br.) 1.63 (m)	31.4 (br.) 60.6 (br.)	13.7 26.5 [102.9] 27.4 [40.5] 30.3	-167.5
-50°C [c]	1.59 (Z) 1.05 (E) 0.93 1.19	0.94 1.14 1.78	28.5/60.9 (Z) 31.4/60.1 (E) 31.0 32.1 59.6 59.7 61.8	14.2 29.6 [d] 31.3	-320.7

[a] In toluene[d_8]; coupling constants in Hz: $^{n}J(^{119}Sn^{13}C)$ in [ ]; br. = broad; t = triplet; m = multiplet.

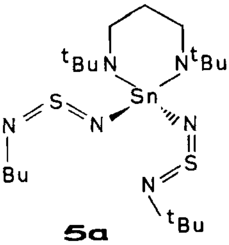
[b] NMR data of the monomer ^{n}BuSn(NSN^{t}Bu)$_3$; additional ^{119}Sn resonance at -513.0 (DME·^{n}BuSn(NSN^{t}Bu)$_3$).

[c] NMR data of the dimer [^{n}BuSn(NSN^{t}Bu)$_3$]$_2$; δ^{119}Sn(CP/MAS) = -320.7; δ^{15}N (CP/MAS) = -70.4, -83.6, -103.4, -123.7, the signal-to-noise ratio was insufficient for assigning all ^{15}N resonances.

[d] Two signals coincide.

the deshielding for the E-substituted ^{15}N nucleus is less significant, and the shielding of the Z-substituted ^{15}N nucleus (δ^{15}N(Z-*tert*-butyl group) ≈ -60) is also less extreme.

It has been shown that stannyl groups prefer the Z position and force a *tert*-butyl group into the E position.[9c] Isomers with the *tert*-butyl group in E position are also favored in the bis(N-*tert*-butylsulfurdiimido)tin compounds **1a**–**5a**. Consistent NMR spectroscopic evidence points towards the presence of only two isomers with (Z/E)(E/Z) or (E/Z)$_2$ configuration (see Scheme 1). In the case of the compounds **1a**–**3a**, the (E/Z)$_2$ configuration is preferred, whereas an isomer with (E/Z)$_2$ configuration can have only a minor share in the case of the di-*tert*-butyltin derivative **4a**. Compound **4a** exists mainly as (Z/E)(E/Z) isomer, and compound **5a** as (Z/E)(E/Z) isomer exclusively.



5a

TABLE III

NMR data[a] of tris(sulfurdiimido) compounds, $R^1M(NSNR)_3$ (**7a**, **b**–**9a**, **b**)

Compound	$\delta^{13}C$		$\delta^{29}Si$		$\delta^{15}N$		
	^tBu; $SiMe_3$	MR^1	SiR^1	$SiMe_3$	N^tBu; $NSiMe_3$	NM	[b]
7a $MeSi(NSN^tBu)_3$ [c] $(Z/E)_3$	29.6 62.6	1.0 {61.0}	-43.2	--	-52.7 (Z)	-78.1 (E)	A
8a $^tBuSi(NSN^tBu)_3$ [d] $(Z/E)_3$	29.5 62.6	18.8 25.6	-42.0	--	-50.4 (Z)	-84.6 (E)	A, D
9a $MeGe(NSN^tBu)_3$ [e] $(Z/E)_3$	28.7 62.1	2.0	---	--	-56.8 (Z)	-63.2 (E)	C
$(Z/E)_2(E/Z)$	28.8 61.8 31.2 60.9	3.1	---	--	-60.2 (Z) +28.6 (E)	-67.7 (E) -143.7 (Z)	
7b $MeSi(NSNSiMe_3)_3$ [f]	0.8 {58.0}	1.1 {57.5}	-45.0	+4.0	-59.8	-56.7	A
8b $^tBuSi(NSNSiMe_3)_3$ [g]	0.7	28.8 25.2	-44.5	+4.0	-62.9	-77.2	A
9b $MeGe(NSNSiMe_3)_3$ [h]	0.8 {57.8}	4.9	---	+2.8	-56.2	-62.8	A

[a] In toluene[d_8]; ^{15}N NMR spectra measured at -50°C (**7a**–**9a**) or at +27°C (**7b**–**9b**); ^1H, ^{13}C and ^{29}Si NMR spectra measured at +27°C; coupling constants in Hz: $^1J(^{29}Si^{13}C)$ in { }; $^2J(^{29}Si^1H)$ in ( ).

[b] See Footnote [c] Table I.

[c] δ^1H = 1.45 (^tBu), 0.40 (7.2) (SiMe).

[d] δ^1H = 1.46 (^tBu), 1.04 (Si^tBu).

[e] ^1H and ^{13}C NMR spectra measured at -40°C;
$(Z/E)_3$ isomer: δ^1H = 1.42 (^tBu), 0.72 (GeMe);
$(Z/E)_2(E/Z)$ isomer: δ^1H = 1.45 ($^tBu\{Z\}$), 0.98 ($^tBu\{E\}$), 0.46 (GeMe);
additional signals: δ^1H = 1.37 ($^tBu\{Z\}$), 0.95 ($^tBu\{E\}$), 0.58 (GeMe); $\delta^{13}C$ = 28.6,62.6 ($^tBu\{Z\}$), 31.0, 60.9 ($^tBu\{E\}$), 6.0 (GeMe).

[f] δ^1H = 0.22 (6.8) ($SiMe_3$), 0.47 (SiMe).

[g] δ^1H = 0.25 ($SiMe_3$), 1.08 (Si^tBu).

[h] δ^1H = 0.11 ($SiMe_3$), 0.86 (GeMe).

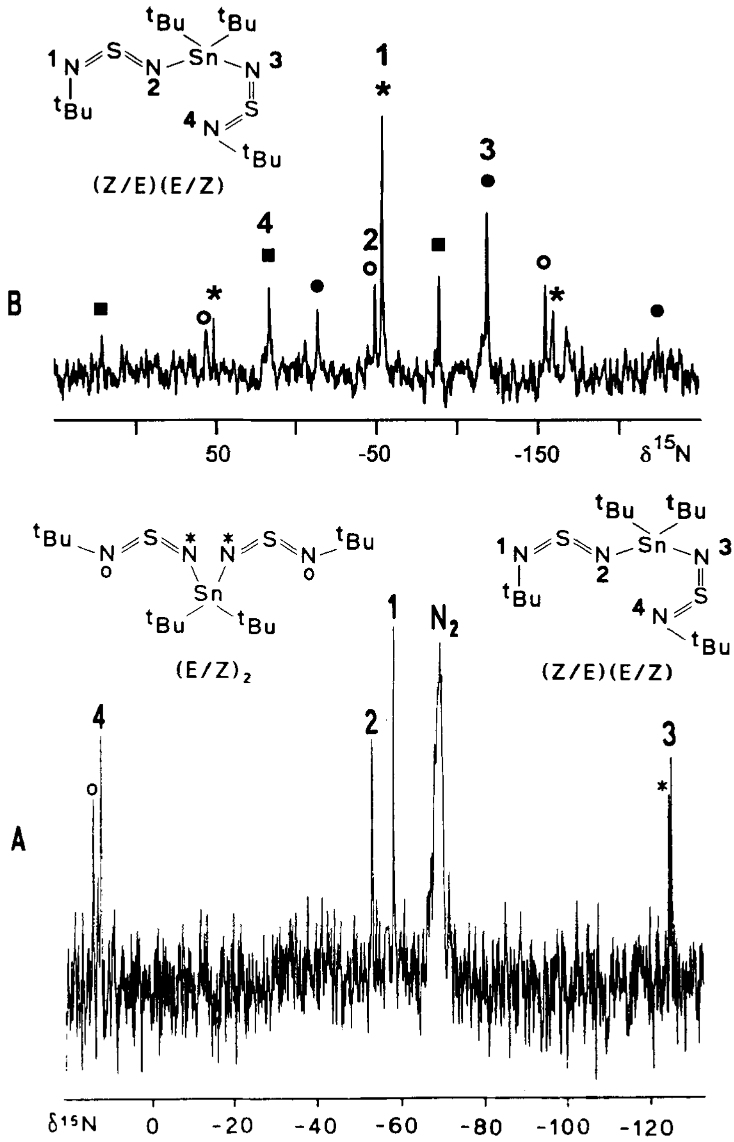


FIGURE 1 (A) 30.4 MHz ^{15}N NMR spectrum of ^{t}Bu$_2$Sn(NSN^{t}Bu)$_2$ (4a), measured in toluene[d$_8$] at 213 K, direct measurement: ^{15}N{^{1}H}. The resonances of the (Z/E)(E/Z) isomer are marked by numbers (1–4), those of the (E/Z)$_2$ isomer by * and o. (B) 30.4 MHz ^{15}N CP/MAS NMR spectrum of ^{t}Bu$_2$Sn(NSN^{t}Bu)$_2$ (4a), 11092 scans, recycle delay 5 s, contact time 20 ms, spinning speed 3208 Hz, temperature 298 K. The isotropic shifts of the different ^{15}N nuclei are marked by numbers (1–4), spinning side bands are marked by: *, o, ● and ■.

It appears that the configuration of bis(N-*tert*-butylsulfurdiimido)tin compounds depends mainly on the steric requirement of the substituent R^1. Bulky groups R^1 attached to the tin atom (see **4a** and **5a**) cause the preferential formation of the (Z/E)(E/Z) isomer. This is supported by a comparison of the solution- and solid-state NMR data of **4a**. In solution **4a** adopts the (E/Z)$_2$ and the (Z/E)(E/Z) configuration.

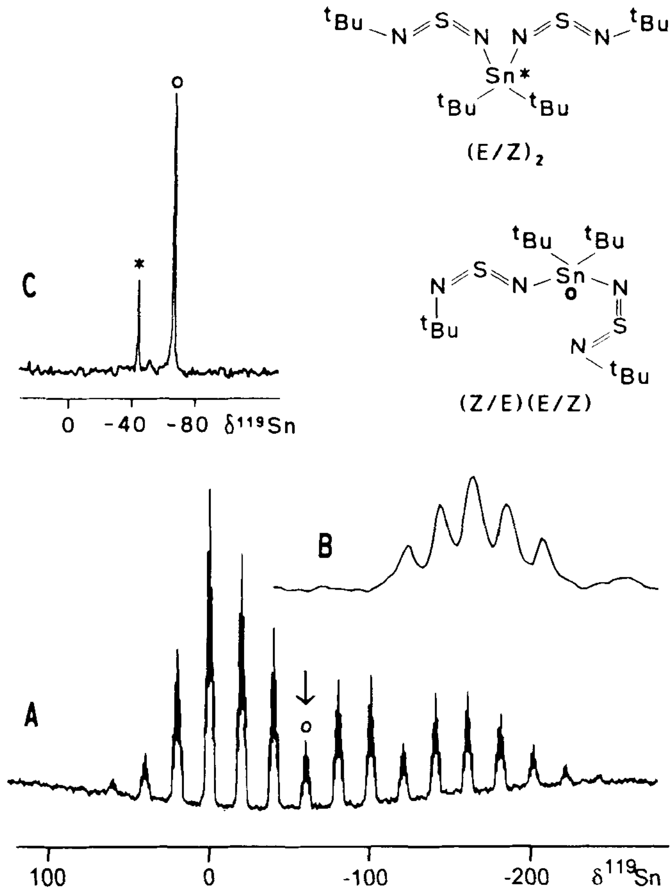


FIGURE 2 (A) 111.9 MHz ^{119}Sn CP/MAS NMR spectrum of ^{t}Bu$_2$Sn(NSN^{t}Bu)$_2$ (**4a**), 1872 scans, recycle delay 5 s, contact time 2000 μs, spinning speed 2253 Hz, temperature 298 K. The isotropic shift is marked by an arrow. (B) Spreading of the centreband. (C) 33.6 MHz ^{119}Sn NMR spectrum of ^{t}Bu$_2$Sn(NSN^{t}Bu)$_2$ (**4a**), measured in toluene[d$_8$] at 213 K.

In contrast, only the (Z/E)(E/Z) isomer is observed in the solid-state NMR spectra (see Figures 1 and 2 and Table I).

In solution, most sulfur diimides are highly fluxional molecules, with respect to fast E/Z ⇌ Z/E interconversion,[9b] in particular if the nitrogen atoms bear an organometallic substituent. This is also evident for the compounds R$^1_2$Sn(NSNSiMe$_3$)$_2$ **3b**–**4b**. The δ^{15}N value of the NSiMe$_3$ group in **3b** in the temperature range of +27°C to −50°C (−58.0 ± 0.2) is a typical averaged value, indicating fast E/Z ⇌ Z/E interconversion.[9b] On the other hand the δ^{15}N value of the NSn^{n}Bu$_2$ moiety in **3b** (−47.9 at +27°C; −46.6 at −50°C) seems to indicate a preference of the E position for this group. However, the broadened ^{15}N NMR signals point to dynamic processes (E/Z ⇌ Z/E interconversion) both at room temperature and at −50°C. In contrast the ^{15}N(NSiMe$_3$) nucleus is deshielded in **4b** (−48.4) as compared with **3b** (−58.0), and this suggests major contributions to the equilibrium from isomers with the N-trimethylsilyl group in E position. On the other hand, the value δ^{15}N(NSn^{t}Bu$_2$) = −60.3 suggests preference of the Z position for this moiety. This would be in

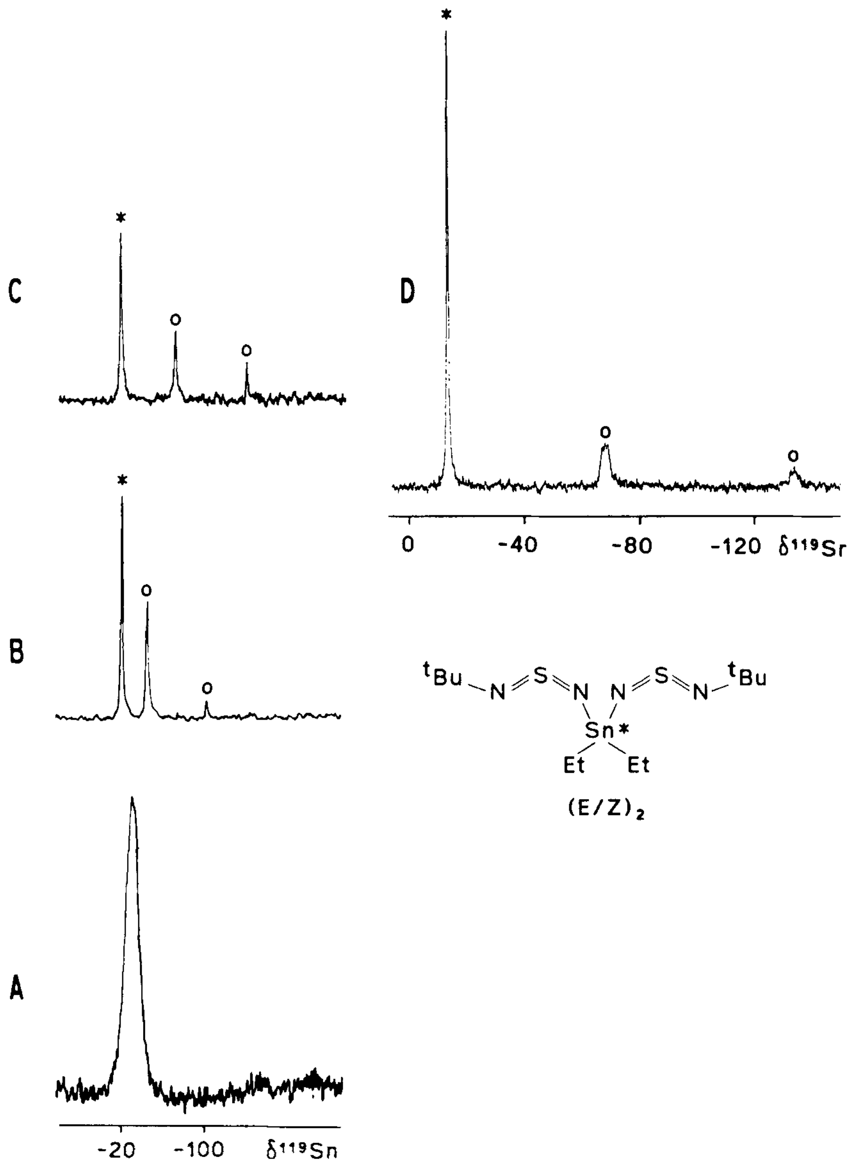


FIGURE 3 ^{119}Sn NMR spectra of $Et_2Sn(NSN^tBu)_2$ (**2a**), measured in toluene[d_8]; the ^{119}Sn resonances of the associated species are marked by o. (A) 33.6 MHz, measured at 298 K. (B) 33.6 MHz, measured at 253 K. (C) 33.6 MHz, measured at 213 K. (D) 111.9 MHz, measured at 213 K.

agreement with the generally observed trend that stannyl groups prefer the Z position. In consequence it seems likely that the dominant configuration of **4b** in solution is $(E/Z)_2$.

^{119}*Sn NMR*: All ^{119}Sn NMR spectra were recorded using inverse-gated ^{1}H decoupling for suppression of the NOE.[12] As pointed out before, two isomers, (Z/E)(E/Z) and $(E/Z)_2$, were observed in solution for **4a** and only one isomer, (Z/E)(E/Z), was

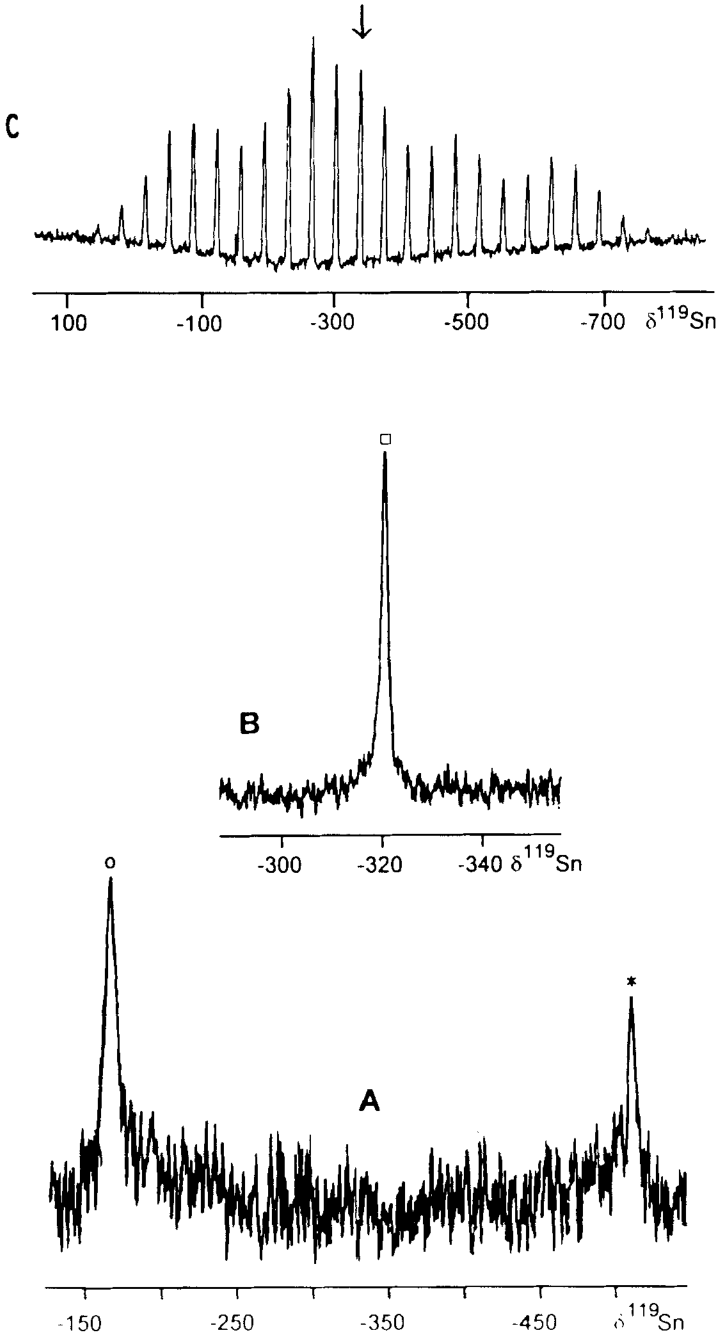
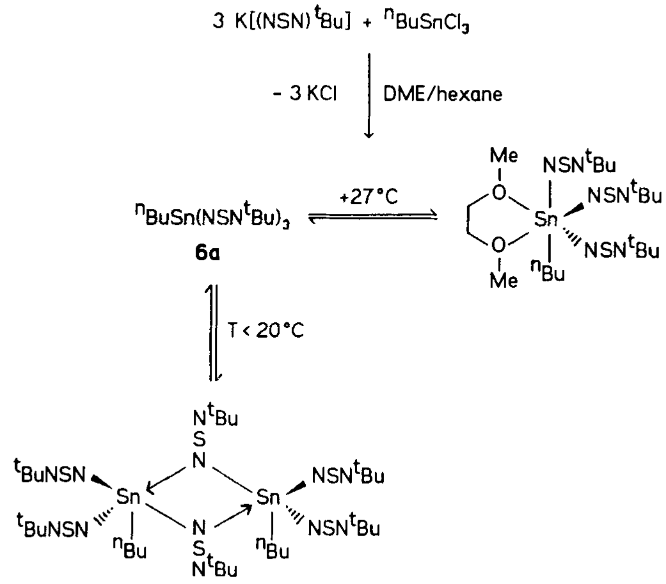


FIGURE 4 (A) 111.9 MHz ^{119}Sn NMR spectrum of ^{n}BuSn(NSN^{t}Bu)$_3$ (marked by ○) and DME·^{n}BuSn(NSN^{t}Bu)$_3$ (marked by *), measured in toluene[d$_8$] at 298 K, recorded with the ^{1}H inverse-gated pulse sequence. (B) 111.9 MHz ^{119}Sn NMR spectrum of [^{n}BuSn(NSN^{t}Bu)$_3$]$_2$ (marked by □), measured in toluene[d$_8$] at 223 K, recorded with the ^{1}H inverse-gated pulse sequence. (C) 111.9 MHz ^{119}Sn CP/MAS NMR spectrum of [^{n}BuSn(NSN^{t}Bu)$_3$]$_2$, 10292 scans, recycle delay 5 s, contact time 3000 μs, spinning speed 3994 Hz, temperature 298 K. The isotropic shift is marked by an arrow.



Scheme 3.

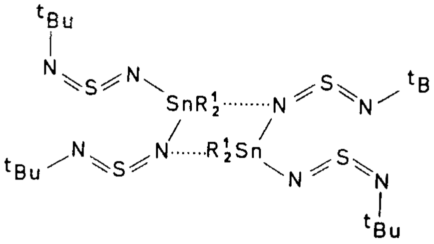
Products of the reaction between K[(NSN)^{t}Bu] and n-butyltin trichloride

identified in the solid-state. The δ^{119}Sn values of the (Z/E)(E/Z) isomer in solution (−65.2) and in the solid-state (−67.8) are almost identical (see Figure 2).

The signal-to-noise ratio in the ^{15}N NMR spectrum of **4a** was insufficient for reliable assignment of $^{117/119}$Sn satellites. However, the solid-state ^{119}Sn CP/MAS NMR spectrum of **4a** (see Figure 2) shows a pattern which arises to a small extent from non-averaged dipolar ^{119}Sn—^{14}N interactions[14] and mainly from scalar ^{119}Sn—^{14}N coupling [$^1J(^{119}\mathrm{Sn}^{14}\mathrm{N}) \approx 153$ Hz; calcd. $^1J(^{119}\mathrm{Sn}^{15}\mathrm{N}) \approx 225$ Hz].

The temperature dependence of the δ^{119}Sn values of **1a–3a** is remarkable. For all compounds rather broad ^{119}Sn resonances are observed at room temperature indicating fast E/Z ⇌ Z/E isomerization processes. At lower temperatures the signals of the (E/Z)$_2$ isomers remain fairly sharp and show only the usual slight shift with temperature (±4 ppm between 0°C and −50/−60°C). The situation is different for the resonances which are most probably those of the (Z/E)(E/Z) isomers. For all compounds the $\Delta\delta^{119}$Sn between 0°C and −50/−60°C is about 20 ppm indicating other processes in addition to configurational isomerization. In the case of **3a** the ratio of the (E/Z)$_2$ to the (Z/E)(E/Z) isomer is roughly 1:1 at 0°C. At −50°C the portion of the (Z/E)(E/Z) isomer decreases and new resonances at lower frequencies are observed in the ^{119}Sn NMR spectrum. The latter are probably due to compounds with five-coordinated tin atoms. Obviously the (Z/E)(E/Z) isomer has a high tendency to form dimers or oligomers. The interconversion of the isomers and the dimerization process must be rather slow as compared to the NMR time scale. In consequence we can observe the signals of both species in the ^{119}Sn NMR spectra for all compounds **1a–3a** (see Figure 3). Furthermore the δ^{119}Sn values of the (Z/E)(E/Z) isomer and the associated species are extremely concentration and temperature dependent, and it seems worth noting that the ^{119}Sn nuclear relaxation behavior in the associated compounds varies significantly with the applied magnetic field strength (see Figure 3).

A likely explanation for the formation of five-coordinated tin compounds is association involving a nitrogen atom linked to the R^1_2Sn group and the tin atom of a second bis(sulfurdiimido)tin molecule.



In solution, both four- and five-coordinated tin species are detectable, in contrast the solid-state ^{119}Sn CP/MAS NMR spectrum of **1a** proves that only the associated compound with a five-coordinated tin atom exists in the solid-state ($\delta^{119}Sn \approx -120$).

The fast decomposition of the compounds $R^1_2Sn(NSNSiMe_3)_2$ (**3b–4b**) makes the situation worse for ^{119}Sn NMR studies. The $\delta^{119}Sn$ value of $^tBu_2Sn(NSNSiMe_3)_2$ (**4b**) at room temperature (−65.1) differs considerable from that at −80°C (−49.3), indicating either changes in the contributions to fast E/Z ⇌ Z/E interconversion at 27°C or association. In accord with the ^{15}N NMR data, the $\delta^{119}Sn$ value is regarded as representative for the Z position of the stannyl group, especially as it fits very well to the $\delta^{119}Sn$ value (−42.8) of the $(E/Z)_2$ isomer of $^tBu_2Sn(NSN^tBu)_2$ (**4a**). It seems that the $(E/Z)_2$ isomer has a major share in the case of **4b**. Nevertheless, weak association cannot be completely ruled out for this molecule.

b) *n-Butyl-tris(N-tert-butylsulfurdiimido)tin* (**6a**)

Two ^{119}Sn resonances, $\delta^{119}Sn$ −167.5 and −513.0, are observed for **6a** in solution at room temperature. The $\delta^{119}Sn$ value of −167.5 is in the expected range for four-coordinated tin atoms and corresponds to the compound $^nBuSn(NSN^tBu)_3$ (**6a**). In contrast the $\delta^{119}Sn$ value of −513.0 is typical of a six-coordinated tin atom.[15] In principle there are two possibilities leading to an increase of the coordination number of the tin atom: (i) intramolecular association via the free electron pairs at the N atoms of the NSN system and (ii) coordination of 1,2-dimethoxyethane (DME) which is used as a solvent in the synthesis. When further DME is added only the signal at $\delta^{119}Sn$ −513.0 remains, indicating that this resonance is due to the DME coordinated complex $^nBuSn(NSN^tBu)_3 \cdot DME$. If DME is replaced by tetrahydrofuran as a solvent only the four-coordinated tin species is found at room temperature. This suggests that the chelate effect is the driving force for the strong coordinate Sn-DME interaction. At temperatures below −20°C, in the presence or absence of DME, only one ^{119}Sn resonance (−320.7) is observed in the typical range for five-coordinated tin atoms.[15] The $\delta^{119}Sn$ CP/MAS value (−336.4) corresponds very well to the low temperature solution-state value (see Figure 4).

Obviously **6a** forms a dimer at lower temperature (see Figure 4 and Scheme 3). This is the usual tendency for an increase in the coordination number of tin with an increasing number of electronegative substituents.

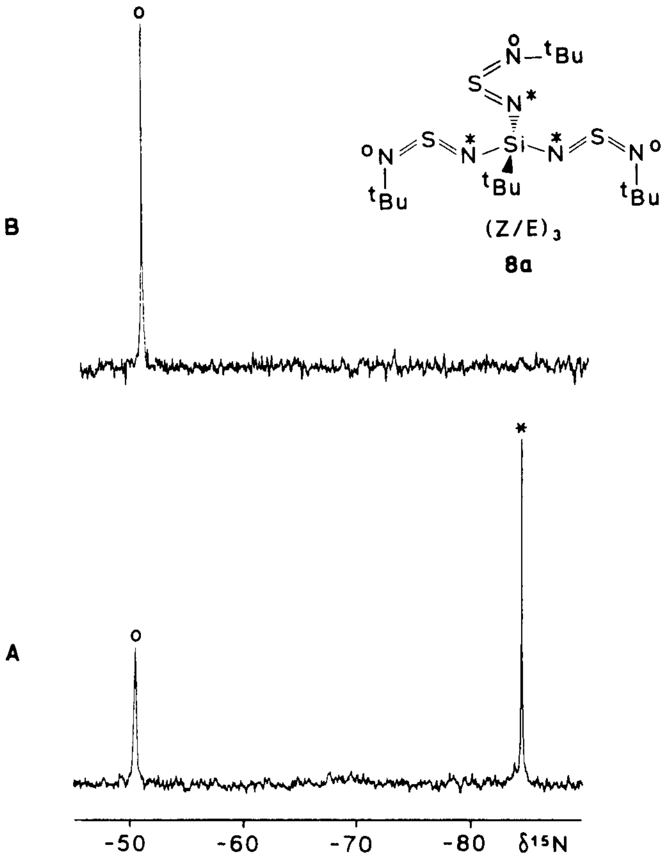
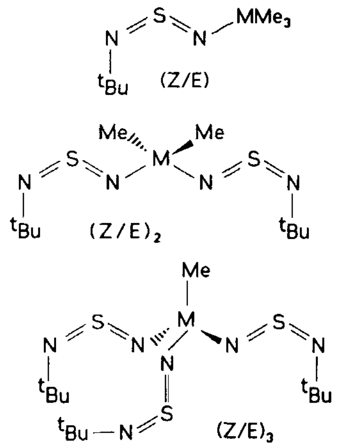


FIGURE 5 30.4 MHz ^{15}N NMR spectra of $^tBuSi(NSN^tBu)_3$ (**8a**), measured in toluene [d_8] at 223 K. (A) Direct measurement: ^1H coupled. (B) Recorded with the refocused INEPT pulse sequence, $^3J(^{15}N^1H)$ was assumed to be 2.2 Hz.

c) *Tris(sulfurdiimido)silicon and -germanium Compounds* (7a,b–9a,b)

^{15}*N NMR*: All solution-state NMR data support the $(Z/E)_3$ configuration (see Scheme 2) for the tris(N-*tert*-butylsulfurdiimido)silicon compounds **7a** and **8a**. The ^{15}N (N^tBu) resonances are found in the typical range for N atoms attached to a ^tBu group in Z position, and the $\delta^{15}N(Si)$ values are characteristic for N atoms linked to a silyl substituent in E position (see Figure 5). The increased shielding of the $^{15}N(NSi)$ nuclei in **8a** (−84.6) with respect to **7a** (−78.1) is caused by the substituent $R^1 = {}^tBu$.[8b,9c,16]

In the case of methyl-tris(N-*tert*-butylsulfurdiimido)germanium **9a**, it is evident from all NMR spectra that at least two isomers (~2:1) are present in solution, one with $(Z/E)_2(E/Z)$ and the other with $(Z/E)_3$ configuration (see Scheme 2). The δ $^{15}N(N^tBu)$ values between −57 and −60 are in support of the Z position, whereas the $\delta^{15}N(N^tBu)$ value of +28.6 is typical of the E position.[9c] The value $\delta^{15}N(NGe)$ = −143.7 is characteristic for a germyl group in Z position. Thus, the change from M = Si to M = Ge leads to an increasing amount of isomers with the ^tBu group in



	δ^{15}N(=N^{t}Bu)	δ^{15}N(=NM)	δ^{29}Si
M = Si	-60.5	-65.9	+1.7
M = Ge	-68.5	-46.0	--
M = Si	-56.3	-71.8	-16.2
M = Ge	-57.5	-50.0	--
M = Si	-52.7	-78.1	-43.2
M = Ge	-56.8	-63.2	--

Scheme 4.

Configurational (Z/E), (Z/E)$_2$ and (Z/E)$_3$ isomers of sulfurdiimido silicon and germanium compounds with ^{15}N and ^{29}Si NMR data.

E position, in the mono(sulfurdiimido) derivative ^{t}Bu(NSN)GeMe$_3$ as well as in bis(sulfurdiimido)- and tris(sulfurdiimido)germanium compounds. An increasing number of sulfurdiimido groups attached to the central metal leads to a shift towards higher frequencies of the ^{15}N(N^{t}Bu{Z}) resonances of the (Z/E)$_x$ isomers. On the other hand the ^{15}N(NM{E}) NMR signals are shifted towards lower frequencies (see Scheme 4).

The tris(N-trimethylsilylsulfurdiimido)silicon and -germanium derivatives **7b**–**9b** possess a more fluxional character in solution than the corresponding N^{t}Bu compounds **7a**–**9a**. The δ^{15}N values of **7b**–**9b** are typical averaged values indicating fast Z/E $\rightleftharpoons$ E/Z isomerization processes (see Figure 6). The better shielding of the ^{15}N nuclei in **8b** relative to **7b** can be interpreted as a result (i) of the presence of R^1 = ^{t}Bu instead of R^1 = Me, and (ii) of a greater contribution from isomers in which the SiMe$_3$ groups occupy the Z position and the Si^{t}Bu group the E position.

^{29}*Si NMR*: The δ^{29}Si(SiR^1) values of the compounds **7a** (−43.2), **7b** (−45.0) and **8a** (−42.0), **8b** (−44.5) differ only slightly from each other (see Table III). Usually, the replacement of a methyl by a ^{t}Bu group causes a reduced ^{29}Si nuclear shielding by ~5 ppm (e.g., δ^{29}Si(MeSiCl$_3$) 12.2 and δ^{29}Si(^{t}BuSiCl$_3$) 17.8, or δ^{29}Si(Me$_3$SiCl) 30.2 and δ^{29}Si(Me$_2{}^t$BuSiCl) 35.5). Interestingly, it was found that there is also only a small difference Δ^{29}Si in the compounds R$^1_2$Si(NSN^{t}Bu)$_2$ (R^1 = Me: δ^{29}Si −16.2, and R^1 = ^{t}Bu: δ^{29}Si −15.6,[8b] R$^1_2$Si(NSNSiMe$_3$)$_2$ (R^1 = Me: δ^{29}Si −16.2, and R^1 = ^{t}Bu: δ^{29}Si −16.0[8b]) and in the cyclic sulfur diimides R$_2$Si(NSN)SiR$_2$ (R = Me: −35.2, and R = ^{t}Bu: −31.9[16]). It is conceivable that the small Δ^{29}Si values are related to the wider S—N—Si bond angles in the case of the Si^{t}Bu derivatives.

Comparing the different sulfurdiimido compounds, there is a systematic shift of the ^{29}Si(SiMe$_3$) resonance towards lower frequencies with increasing number of

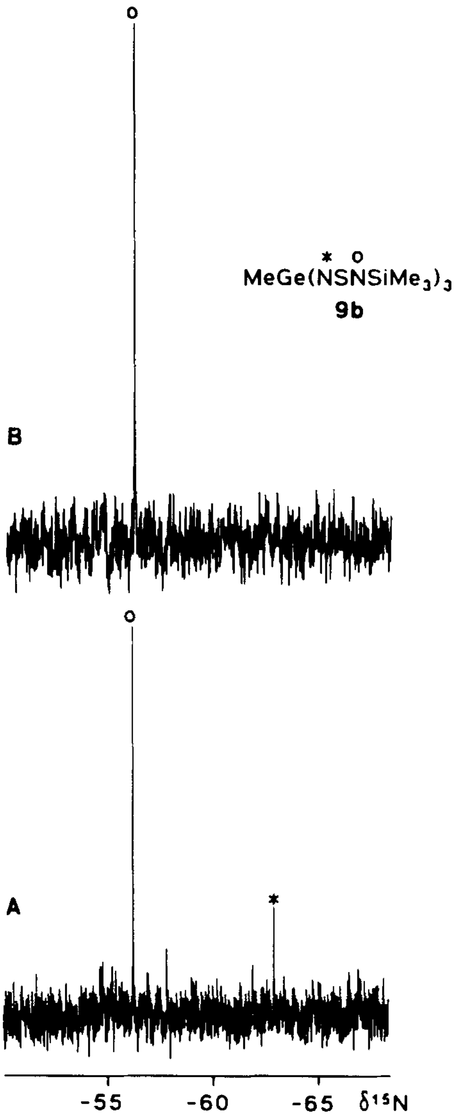


FIGURE 6 50.4 MHz ^{15}N NMR spectra of $MeGe(NSNSiMe_3)_3$ (**9b**), measured in toluene[d_8] at 300 K, recorded with the refocused INEPT pulse sequence. (A) $^3J(^{15}N^1H)$ was assumed to be 1.3 Hz. (B) $^3J(^{15}N^1H)$ was assumed to be 1.8 Hz.

$NSNSiMe_3$ groups attached to the central element [$Me_3M(NSN)SiMe_3$: $\delta^{29}Si$ 1.6 (M = Si), 0.1 (M = Ge)[9a]; $Me_2M(NSNSiMe_3)_2$: $\delta^{29}Si$ 2.8 (M = Si), 1.3 (M = Ge)[8b]; $MeM(NSNSiMe_3)_3$: $\delta^{29}Si$ 4.0 (M = Si), 2.8 (M = Ge)]. On the other hand, the ^{29}Si nuclear shielding increases with an increasing number of sulfurdiimido groups linked to silicon [$Me_3Si(NSN)SiMe_3$: $\delta^{29}Si$ 1.6[9a]; $Me_2Si(NSNSiMe_3)_2$: $\delta^{29}Si$ −16.2[8b]; $MeSi(NSNSiMe_3)_3$: $\delta^{29}Si$ −44.5], which is the usual trend for the influence exerted by electronegative substituents.

EXPERIMENTAL

All compounds were handled in an atmosphere of dry argon, and carefully dried solvents were used for syntheses and preparation of the samples for NMR measurements. $K[(NSN)R]$ (R = ^{t}Bu, $SiMe_3$),[8a] Me_2SnCl_2, Et_2SnCl_2, $^nBu_2SnCl_2$, Bz_2SnCl_2,[17] $^tBu_2SnCl_2$[18] and $[CH_2N(^tBu)_2]_2SnCl_2$[19] were prepared according to literature procedures.

Bis(sulfurdiimido)tin Compounds $R^1_2Sn(NSNR)_2$ (R = ^{t}Bu, **1a–5a**; *R = $SiMe_3$,* **3b–4b**)*, and tris(sulfurdiimido) Compounds $R^1M(NSNR)_3$ (M = Sn, R = ^{t}Bu,* **6a**; *M = Si, Ge, R = ^{t}Bu,* **7a–9a**; *R = $SiMe_3$,* **7b–9b**)

General procedure: A suspension of 6 mmol of a potassium sulfurdiimido salt, $K[(NSN)R]$, in 30 ml DME was added to the corresponding molar amount of the respective element dichloride or trichloride (3 mmol $R^1_2SnCl_2$, 2 mmol R^1MCl_3) in 20 ml of hexane at −78°C. The mixture was stirred for 30 minutes at −78°C and then allowed to reach room temperature. After filtration the solvent was removed in high vacuum.

All compounds are yellow to orange oils or solids. The yields range from 70 to 90% for the N-*tert*-butyl compounds and from 30 to 70% for the N-trimethylsilyl compounds.

$Et_2Sn(NSN^tBu)_2$ (**2a**); $C_{12}H_{28}N_4S_2Sn$; M = 411.202 g/mol.
EI-MS: m/z (%) = 383 (25) [M^+-28], 327 (13), 295 (20), 271 (13), 179 (12), 104 (24), 84 (98), 57 (22), 49 (100).
$^nBuSn(NSN^tBu)_3$ (**6a**); $C_{16}H_{36}N_6S_3Sn$; M = 527.388 g/mol.
EI-MS: m/z (%) = 471 (2.5) [M^+-57], 411 (8), 104 (96), 58 (100), 41 (29).
$MeSi(NSN^tBu)_3$ (**7a**); $C_{13}H_{30}N_6S_3Si$; Me = 394.703 g/mol.
EI-MS: m/z (%) = 379 (2) [M^+-15], 348 (5), 323 (35), 277 (30), 267 (50), 211 (100), 165 (140), 136 (39), 91 (26), 61 (98%), 57 (68), 43 (62).
$^tBuSi(NSN^tBu)_3$ (**8a**); $C_{16}H_{36}N_6S_3Si$; M = 436.784 g/mol.
EI-MS: m/z (%) = 436 (3) [M^+], 379 (100) [M^+-57], 238 (22), 182 (27), 136 (14), 57 (33).

NMR instruments (all equipped with multinuclear units and variable-temperature control units) for liquid state measurements were JEOL FX 90Q (^{119}Sn NMR), Bruker ARX 250, Bruker AC 300 and Bruker AM 500 (^{1}H, ^{13}C, ^{14}N, ^{15}N, ^{29}Si, ^{119}Sn NMR). Chemical shifts are given with respect to Me_4Si (internal) for δ^1H and δ^{13}C (δ^{13}C(toluene[d_8]) = 20.4, $\delta^{13}C(C_6D_6)$ = 128.0), Me_4Si (external: δ^{29}Si = 0, Ξ^{29}Si = 19.867184 MHz), liquid $MeNO_2$ (external: δ^{14}N, δ^{15}N = 0, Ξ^{15}N = 10.136767 MHz) and Me_4Sn (external: δ^{119}Sn = 0, Ξ^{119}Sn = 37.290665 MHz). A Bruker MSL 300 instrument (equipped with a multinuclear double-bearing probe head) served for solid state ^{13}C, ^{15}N and ^{119}Sn CP/MAS NMR measurements; the samples were packed in air-tight inserts[20] fitting exactly into the commercial ZrO_2 rotors. The spectra were run at two different spinning speeds for assignment of the isotropic δ values.

The assignment of ^{1}H and ^{13}C resonances to the different isomers is based upon 2D^{13}C/^{1}H heteronuclear shift correlations [based on $^1J(^{13}C^1H)$ and $^2J(^{13}C^1H)$].

Mass spectra: EI-MS (70eV), Varian MATCH 7.

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