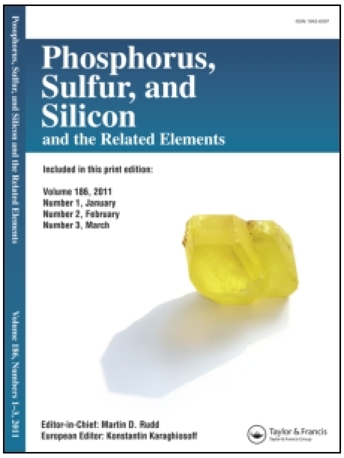

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BIS(SULFURDIIMIDO)SILICON AND GERMANIUM DERIVATIVES-CONFIGURATION IN SOLUTION AS STUDIED BY ^{1}H, ^{13}C, ^{15}N AND ^{29}Si-NMR SPECTROSCOPY

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BIS(SULFURDIIMIDO)SILICON AND GERMANIUM DERIVATIVES—CONFIGURATION IN SOLUTION AS STUDIED BY ^{1}H, ^{13}C, ^{15}N AND ^{29}Si-NMR SPECTROSCOPY

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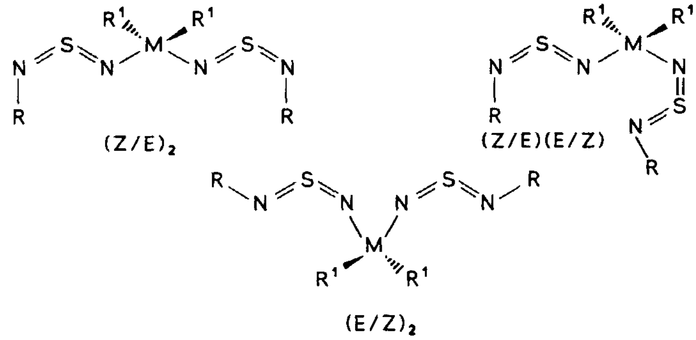
Bis(sulfurdiimido) compounds of the type $R^1R^2M(NSNR)_2$ (M = Si, Ge; R = ^{t}Bu, $SiMe_3$; R^1, R^2 = alkyl, aryl **1**–**7**) were studied by solution-state ^{15}N and ^{29}Si NMR spectroscopy in order to obtain information on their preferred configuration in solution. Chemical shifts δ^{15}N are sensitive towards substituents in E (deshielding) and Z (shielding) positions. The NMR data indicate that most of the compounds are fluxional, at least at room temperature, with respect to interconversion of configurational isomers [$(Z/E)_2$, $(E/Z)_2$, (Z/E)(E/Z)]. Furthermore, the reactivity of some bis(sulfurdiimido) silicon derivatives, $R^1R^2Si(NSNR)_2$, towards hexachlorodisilane was examined. For one product, **10a** ($R^1 = R^2$ = Me, R = ^{t}Bu), a solid-state ^{29}Si CP/MAS NMR spectrum was recorded.

Key words: Sulfur diimides, bis(sulfurdiimido) compounds, hexachlorodisilane, ^{15}N, ^{29}Si NMR spectroscopy, configurational isomerism.

INTRODUCTION

Sulfur diimides, R(NSN)R′, are important reagents in various active research areas.[1,2] Their synthetic potential is further enhanced if R and/or R′ are organometallic substituents,[3–5] and also if two or more RNSN groups are attached to a central element.[6,7] In continuing our studies on the configuration of sulfur diimides[8–10] and their reactivity towards hexachlorodisilane,[11] we report here on bis(sulfurdiimido) derivatives of silicon and germanium of the type $R^1R^2M(NSNR)_2$ (**1**–**7**). In principle, the fluxional character of the NSN system should give rise to an equilibrium between ten different configurational isomers. However, if R is a bulky substituent such as a ^{t}Bu or a $SiMe_3$ group, the presence of isomers with Z/Z configuration is unlikely as a result of steric repulsion, and E/E configurations will also not be favoured owing to interactions between the lone pairs of electrons at the nitrogen atoms. We did not observe any trace of a long-lived Z/Z or E/E isomer for sulfur diimides R(NSN)R′ with R = R′ = ^{t}Bu, $SiMe_3$ or R = ^{t}Bu and R′ = $SiMe_3$.[8b,8c,10b] Thus, we expect mainly three isomers, either with twice Z/E, twice E/Z, or Z/E and E/Z configuration as shown in Scheme I.

In our two series of compounds $R^1R^2M(NSNR)_2$ (R = ^{t}Bu: **1a**–**7a**; R = $SiMe_3$: **1b**–**7b**) only one silicon derivative, $Me_2Si(NSN^tBu)_2$ (**1a**), had been described previously[7b]; however, its configuration in solution had not been studied. We strive to determine the configurations of **1**–**7** in solution by using NMR data, in particular ^{15}N NMR data which had proved useful in previous studies.[8–10] Furthermore, we



SCHEME I Three preferred configurations of compounds $R^1R^2M(NSNR)_2$ (M = Si, Ge; R = ${}^tBu$, $SiMe_3$; the first letter, E or Z, refers to the position of the substituent R).

have investigated the reactivity of **1a**, **2a** and **1b** towards Si_2Cl_6 in order to compare with the analogous reaction of $Me_3Si(NSN){}^tBu$[11a] which gave quantitatively a diaminosulfane derivative via cleavage of the Si—Si bond of the disilane.

RESULTS AND DISCUSSION

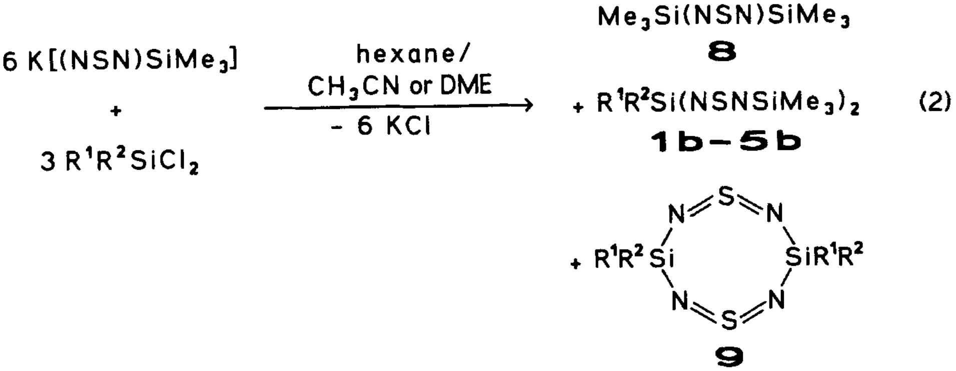
Synthesis of the Bis(sulfurdiimido)silicon and -germanium Derivatives

The reaction between the potassium salts K[(NSN)R] (R = ${}^tBu$, $SiMe_3$) and the dihalides, $R^1R^2MCl_2$, leads directly to the bis(sulfurdiimido) derivatives [Equation (1)].

$$2\ K[(NSN)R] + R^1R^2MCl_2 \xrightarrow[-78°C]{hexane} R^1R^2M(NSNR)_2 + 2\ KCl \quad (1)$$

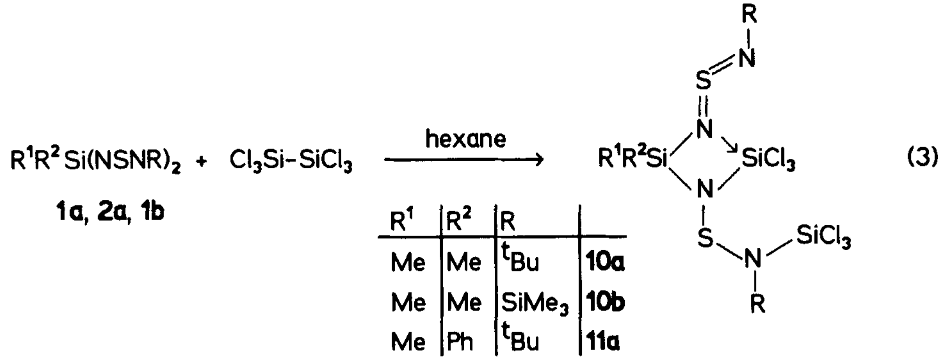
M	Si	Si	Si	Si	Si	Ge	Ge
R^1	Me	Me	Me	${}^tBu$	Ph	Me	Bu
R^2	Me	Ph	H	${}^tBu$	Ph	Me	Bu
R = ${}^tBu$	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
R = $SiMe_3$	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**

Addition of acetonitrile or 1,2-dimethoxyethane (DME) helps to improve the solubility of the potassium salts, K[(NSN)R] (R = ${}^tBu$, $SiMe_3$), and therefore accelerates the reactions. However, in the case of $K[(NSN)SiMe_3]$ and diorganodichlorosilanes, $R^1R^2SiCl_2$, both acetonitrile and DME favour the formation of by-products of the type **8** and **9** [Equation (2)]. Even in pure hexane the formation of these by-products cannot be completely suppressed (see Figure 1).



Reactivity of Bis(sulfurdiimido)silicon Derivatives Towards Hexachlorodisilane

Treatment of bis(N-*tert*-butylsulfurdiimido)dimethylsilane (**1a**) with hexachlorodisilane [Equation (3)], either in an equimolar ratio or in excess, gave a pale yellow



R^1	R^2	R	
Me	Me	^{t}Bu	**10a**
Me	Me	$SiMe_3$	**10b**
Me	Ph	^{t}Bu	**11a**

solid **10a** which was characterized by EI mass spectrometry, IR spectroscopy, ^1H, ^{13}C and ^{29}Si NMR in solution and solid-state ^{29}Si CP/MAS NMR spectroscopy. The analogous reaction was also carried out with **1b** and **2a**. According to the ^{29}Si NMR spectra in solution, the structure of the products **10b** and **11a** must be analogous to that of **10a**. Apparently, one of the sulfurdiimido groups reacts with Si_2Cl_6 in the same way as had been observed previously,[11] i.e. by oxidative cleavage of the Si—Si bond and reduction of sulfur(IV) to sulfur(II). The intramolecular N—Si coordination of one of the nitrogen atoms of the second sulfurdiimido group to one of the new $NSiCl_3$ substituents appears to protect the second sulfurdiimido group against further reaction with Si_2Cl_6. Obviously, the initial step of the reaction between sulfur diimides and Si_2Cl_6 requires the synchronous availability of both nucleophilic centres. The products are stable at room temperature for several days and can be stored at −20°C for longer periods without decomposition.

NMR Spectroscopic Results

The NMR data of the compounds **1–7** (Tables I and II) confirm the proposed composition of the bis(sulfurdiimido)silicon and -germanium derivatives. The ^{29}Si NMR data of **10** and **11** are listed in Table III.

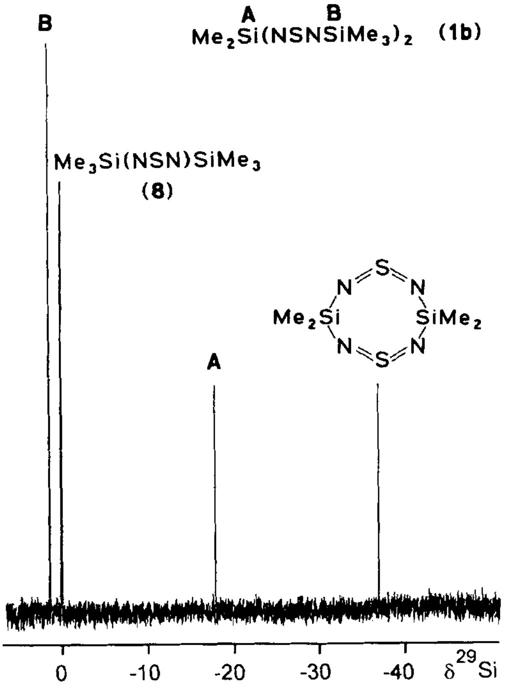


FIGURE 1 59.6 MHz ^{29}Si NMR spectrum of $Me_2Si(NSNSiMe_3)_2$ (**1b**) in toluene [d_8], measured at 298 K, recorded using the refocused INEPT pulse sequence with ^1H decoupling, based on $^2J(^{29}Si^1H)$.

^1H and ^{13}C NMR of bis(sulfurdiimido)silicon and -germanium compounds: As noted previously,[8b] the $\delta^1H(N^tBu)$ data serve to assign the presence of a preferred configuration of sulfur diimides bearing a ^{t}Bu group. A signal with δ^1H 1.25–1.65 or δ^1H 0.90–1.19 indicates the Z position or E position, respectively, of R = ^{t}Bu. The $\delta^{13}C(N^tBu)$ values appear to be less reliable in that respect. The corresponding data for R = $SiMe_3$ and for R^1 and R^2 cannot be used for configurational assignments.

^{15}N NMR of bis(sulfurdiimido)silicon and -germanium compounds: For the compounds under investigation three different methods are available for measuring and assigning ^{15}N NMR spectra at natural abundance: (i) inverse gated ^1H decoupling (for suppression of the NOE)[12]; (ii) direct measurement without ^1H decoupling, (iii) polarization transfer by using the refocused INEPT pulse sequence[13] with ^1H decoupling. The latter pulse sequence can be based on the long-range coupling constants $^3J(^{15}N^1H)$ in the range between 2–2.5 Hz for N^tBu and 1–1.8 Hz for all other groups (see Figures 2 and 3), and its successful application also serves to assign the ^{15}N NMR signals.

In the case of some bis(N-trimethylsilylsulfurdiimido) derivatives, e.g. **1b** or **2b**, 2D $^{15}N/^1H$ heteronuclear shift correlations (HETCOR) were crucial for the assignment of the ^{15}N NMR signals (see Figure 4).

As was pointed out,[10b] a $\delta^{15}N$ value of about −60 is typical of a ^{t}Bu group occupying the Z position in ^{t}Bu(NSN)$MR^1_2R^2$ ($MR^1_2R^2$ = organometallic fragment). Furthermore a ^{t}Bu group in the Z position forces the second substituent into the E

TABLE I

NMR data[a] of $R^1R^2M(NSN^tBu)_2$ (**1a**–**7a**)

Compound	%	δ^1H		$\delta^{13}C$		$\delta^{15}N$		$\delta^{29}Si$
		^tBu	MR^1R^2	^tBu	MR^1R^2	N^tBu	NM	SiR^1R^2
1a $Me_2Si(NSN^tBu)_2$								
$(Z/E)_2$	100	1.43	0.23	29.7	1.5	-56.3[b]	-71.8	-16.2
			(6.6)	62.2	(67.8)			
2a $MePhSi(NSN^tBu)_2$								
$(Z/E)_2$	100	1.44	0.49	29.8	0.5	n.m.	n.m.	-26.7
			7.20 m	62.4	[c]			
			7.60 m					
3a $MeHSi(NSN^tBu)_2$								
$(Z/E)_2$	100	1.38	0.23 d	29.8	0.8	-52.6[d]	-78.7	-34.1
			5.21 q	62.4				
4a $^tBu_2Si(NSN^tBu)_2$								
$(Z/E)_2$	100	1.44	0.98	29.7	20.8[e]	-55.1[f]	-82.1	-15.6
				61.9	27.8			
5a $Ph_2Si(NSN^tBu)_2$								
$(Z/E)_2$	100	1.48	7.18 m	29.7	[g]	n.m.	n.m.	-37.5
			7.73 m	62.7				
6a $Me_2Ge(NSN^tBu)_2$								
$(Z/E)_2$	50	1.34	0.51	28.8	2.7[h]	-57.5[i]	-50.0	—
				61.4				
(Z/E)(E/Z)	50	1.37	0.38	29.0	2.0[h]	-60.6	-53.7	—
		0.99		61.1		(Z)	(E)	
				31.4		+27.4	-130.0	
				60.0		(E)	(Z)	
7a $Bu_2Ge(NSN^tBu)_2$								
$(Z/E)_2$	50	1.45	0.82 t	29.0	[j]	-61.2[k]	-57.3	—
			1.18 m	61.5				
			1.54 m					
(Z/E)(E/Z)	50	1.50	0.82 t	29.1	[l]	-64.1	-57.3	—
		1.00	1.18 m	61.3		(Z)	(E)	
			1.54m	31.3		+22.0	-137.1	
				60.0		(E)	(Z)	

[a] In toluene [d_8], measured at -40°C; coupling constants in Hz : $^nJ(^{29}SiX)$ in (); n.m. = not measured; d = doublet, m = multiplet, q = quartet, t = triplet. The configurations of **2a** and **5a** are assumed to be analogous to that of **1a**, **3a** and **4a**.

[b] Measured at -30°C; $\delta^{14}N$(27°C) = -54.0 (N^tBu), -74.0 ($NSiMe_2$).

[c] $\delta^{13}C$ = 133.8 (ipso), 136.6 (ortho), 128.2 (meta), 130.2 (para).

[d] $\delta^{14}N$(27°C) = -48.0 (N^tBu), -82.0 (NSiMeH).

[e] $^1J(^{29}Si^{13}C)$ = 70.8 Hz.

[f] Measured at -50°C; $\delta^{14}N$(27°C) = -56.0 (N^tBu), -83.0 (NSi^tBu_2).

[g] $\delta^{13}C$ = 134.7 (ipso), 135.3 (ortho), 128.2 (meta), 133.4 (para).

[h] No assignment possible.

[i] Measured at -30°C.

[j] $\delta^{13}C$ = 14.0 (CH_3); 19.0, 26.0, 26.2 (CH_2).

[k] $\delta^{14}N$(27°C) = -65.0.

[l] $\delta^{13}C$ = 13.8 (CH_3); 18.2, 25.6, 26.0 (CH_2).

TABLE II

NMR data[a] of $R^1R^2M(NSNSiMe_3)_2$ (**1b**–**7b**)

Compound	δ^1H		$\delta^{13}C$		$\delta^{15}N$		$\delta^{29}Si$	
	$SiMe_3$	MR^1R^2	$SiMe_3$	MR^1R^2	$NSiMe_3$	NM	$SiMe_3$	SiR^1R^2
$Me_2Si(NSNSiMe_3)_2$ **1b**	0.22 (6.8)	0.35 (7.2)	0.8 (57.6)	1.3 (53.0)	-65.1 [b]	-54.7	+2.8	-16.2
$MePhSi(NSNSiMe_3)_2$ **2b**	0.22 (7.0)	0.58 (7.4) 7.20 m 7.70 m	0.9	0.5 [c]	-57.1 [d]	-62.2	+3.2	-27.7
$MeHSi(NSNSiMe_3)_2$ **3b**	0.17	0.29 d 5.29 q	1.0 (57.0)	0.2	-57.1	-63.9	+3.3	-36.1
$^tBu_2Si(NSNSiMe_3)_2$ **4b**	0.09	0.14	0.4	27.3 20.5	-64.6	n.o.	+2.4	-16.0
$Ph_2Si(NSNSiMe_3)_2$ **5b**	0.24 (6.8)	7.20 m 7.78 m	0.9 (57.2)	[e]	-57.8	-61.5	+3.6	-38.8
$Me_2Ge(NSNSiMe_3)_2$ **6b**	0.07	0.63	1.0	3.4	-54.8	-62.3	+1.3	—
$Bu_2Ge(NSNSiMe_3)_2$ **7b**	0.15	0.81 t 1.27 m 1.48 m	1.2 (57.8)	14.0 19.9 26.0 26.3	-56.0	-60.2	+1.2	—

[a] In C_6D_6, measured at +27°C; coupling constants in Hz : $^nJ(^{29}SiX)$ in (); n.o. = not observed; d = doublet, m = multiplet, q = quartet, t = triplet.

[b] In toluene[d_8], measured at -50°C; $\delta^{15}N(27°C)$ = -59.6 ($NSiMe_3$), -57.1 ($NSiMe_2$).

[c] $\delta^{13}C$ = 136.2 (ipso), 134.1 (ortho), 128.2 (meta), 130.3 (para).

[d] In toluene[d_8], measured at -30°C; $\delta^{15}N(27°C)$ = -59.7 ($NSiMe_3$), -60.7 (NSiMePh).

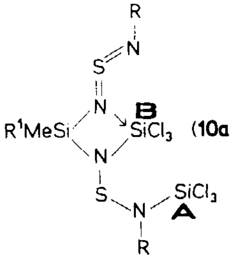
[e] $\delta^{13}C$ = 134.9 (ipso), 135.0 (ortho), 128.1 (meta), 130.5 (para).

position.[10b] These facts will not be changed if a group R^1 is replaced by a second NSN^tBu unit. Thus, the $\delta^{15}N(N^tBu)$ values of the compounds $R^1R^2Si(NSN^tBu)_2$ ($\delta^{15}N$ values range from −52 to −56) indicate the Z position of the ^tBu group in agreement with the $\delta^1H(N^tBu)$ data, and therefore, the configuration of **1a**, **3a** and **4a** is determined to be $(Z/E)_2$. Although ^{15}N NMR data for **2a** and **5a** are not available, ^1H and ^{13}C NMR data for the N^tBu group suggest that they also exist as $(Z/E)_2$ isomers. For all compounds **1a**–**5a** (M = Si), only one isomer was detected. Obviously the N^tBu group prefers the Z position if the second substituent is a silyl group. This is consistent with the data obtained for many other sulfur diimides of the type $^tBu(NSN)SiR^1_2R^2$ (see also Scheme II).[8b,10b]

The increased shielding of the $^{15}N(Si)$ nuclei in **4a** ($\delta^{15}N$ −82.1) with respect to **1a** ($\delta^{15}N$ −71.8) is caused by $R^1 = R^2 = {}^tBu$. In an analogous manner, the

TABLE III

^{29}Si NMR data[a] of



(10a,b, 11a)

Compound	δ^{29}Si SiMeR^1	 SiCl$_3$(A)	 SiCl$_3$(B)
10a (R^1 = Me, R = ^{t}Bu)[b]	+21.1	-26.6	-41.5
	(+23.2)	(-26.8)	(-41.8)
10b (R^1 = Me, R = SiMe$_3$)[c]	+24.2	-25.9	-41.5
11a (R^1 = Ph, R = ^{t}Bu)	+9.7	-26.4	-41.8

[a] In C_6D_6, measured at +27°C.

[b] δ^{29}Si CP/MAS values in ( ).

[c] δ^{29}Si = +6.8 (=NSiMe$_3$), +23.9 (SiMe$_3$).

^{15}N(Si)NMR signal of (^{t}Bu$_2$HSiN)$_2$S (δ^{15}N −72.0)[10b] is shifted towards lower frequencies as compared with (Me$_2$HSiN)$_2$S (δ^{15}N −64.0),[10b] and the same is true for ^{t}Bu$_2$Si(NSN)$_2$Si^{t}Bu$_2$ (δ^{15}N −94.9)[10a] relative to Me$_2$Si(NSN)$_2$SiMe$_2$ (δ^{15}N − 76.8).[10a]

In the case of the bis(sulfurdiimido)germanium derivatives **6a** and **7a**, it is evident from all NMR spectra that two isomers ($\approx$1:1) are present in solution, one with (Z/E)$_2$ and the other with (Z/E)(E/Z) configuration (see Scheme I). The δ^{15}N(N^{t}Bu) values between −57 and −64 are in support of the Z position, whereas the δ^{15}N-(N^{t}Bu) values between +22 and +27 are in the range typical of the E position.[10b] The δ^{15}N(Ge) values for the germyl group in Z position are −130.0 (**6a**) and −137.1 (**7a**), not far from δ^{15}N(Ge) = −128.7[10b] of (E/Z) ^{t}Bu(NSN)GeMe$_3$ (see Scheme II). The change from M = Si to M = Ge leads to an increasing amount of an isomer in which the ^{t}Bu group occupies the E position, both in ^{t}Bu(NSN)GeMe$_3$ and in the bis(sulfurdiimido)germanium derivatives **6a** and **7a**.

The bis(N-trimethylsilylsulfurdiimido) derivatives, R^{1}R^{2}M(NSNSiMe$_3$)$_2$ (**1b**–**7b**), are more mobile in solution than the corresponding N^{t}Bu compounds **1a**–**7a**. Most δ^{15}N values of **1b**–**7b** are typical averaged values which are markedly temperature-dependent, indicating fast Z/E $\rightleftarrows$ E/Z isomerization processes.[8c,10b] One example is the position of the ^{15}N(SiMe$_3$) resonance of **1b** at room temperature (δ^{15}N(SiMe$_3$) −59.6) and at −50°C (δ^{15}N(SiMe$_3$) −65.1). The increase in shielding at lower temperature can be interpreted as the result of a greater contribution from isomers in which the SiMe$_3$ group occupies the Z position. In contrast, at low temperature the ^{15}N(SiMe$_2$) signal of **1b** is shifted towards higher frequency, indicating an increasing

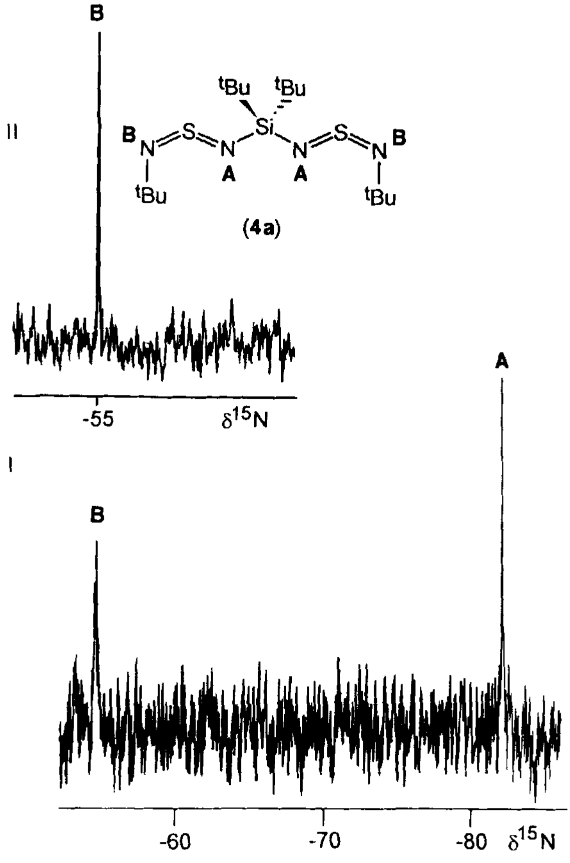


FIGURE 2 30.4 MHz ^{15}N NMR spectra of ^{t}Bu$_2$Si(NSN^{t}Bu)$_2$ (**4a**) in toluene[d$_8$]. I, Direct measurement without ^{1}H decoupling, measured at 223 K. II, Recorded using the refocused INEPT pulse sequence with ^{1}H decoupling, $^3J(^{15}N^1H)$ was assumed to be 2.2 Hz, measured at 243 K.

contribution from the isomers in which the SiMe$_2$ group prefers the E position. Altogether, this points towards a preference of the (Z/E)$_2$ configuration in **1b**.

^{29}Si NMR of bis(sulfurdiimido)silicon and -germanium derivatives: As can be seen from the small difference between δ^{29}Si(SiMe$_3$) values (Δ^{29}Si 0.7) for the isomers of ^{t}Bu(NSN)SiMe$_3$ (see Scheme II), ^{29}Si NMR is not particularly helpful for the configurational assignment. However, some other points can be made by comparing the δ^{29}Si(SiR^{1}R^2) values of R^{1}R^{2}Si(NSNR)$_2$ (**1a**,**b**–**5a**,**b**). Thus, the δ^{29}Si values of the compounds **1a** (δ^{29}Si −16.2), **1b** (δ^{29}Si −16.2) and **4a** (δ^{29}Si −15.6), **4b** (δ^{29}Si −16.0) differ only slightly from each other, although we are dealing with SiMe$_2$ and Si^{t}Bu$_2$ groups. Usually, the replacement of two methyl by two ^{t}Bu groups causes a reduced ^{29}Si nuclear shielding by ≥8 ppm [e.g. δ^{29}Si(Me$_2$HSiCl) +11.6 and δ^{29}Si(^{t}Bu$_2$HSiCl) +27.4; or δ^{29}Si(Me$_2$SiCl$_2$) +30.8 and δ^{29}Si(^{t}Bu$_2$SiCl$_2$) + 39.3); or δ^{29}Si(Me$_2$HSiN)$_2$S) −16.3 and δ^{29}Si((^{t}Bu$_2$HSiN)$_2$S) −1.1]. Interestingly, it was found that there is also only a small difference Δ^{29}Si between the comparable cyclic sulfur diimides R$_2$Si(NSN)$_2$SiR$_2$ (**9**) (R = Me: δ^{29}Si −35.2, and R = ^{t}Bu: δ^{29}Si −31.9).[10a]

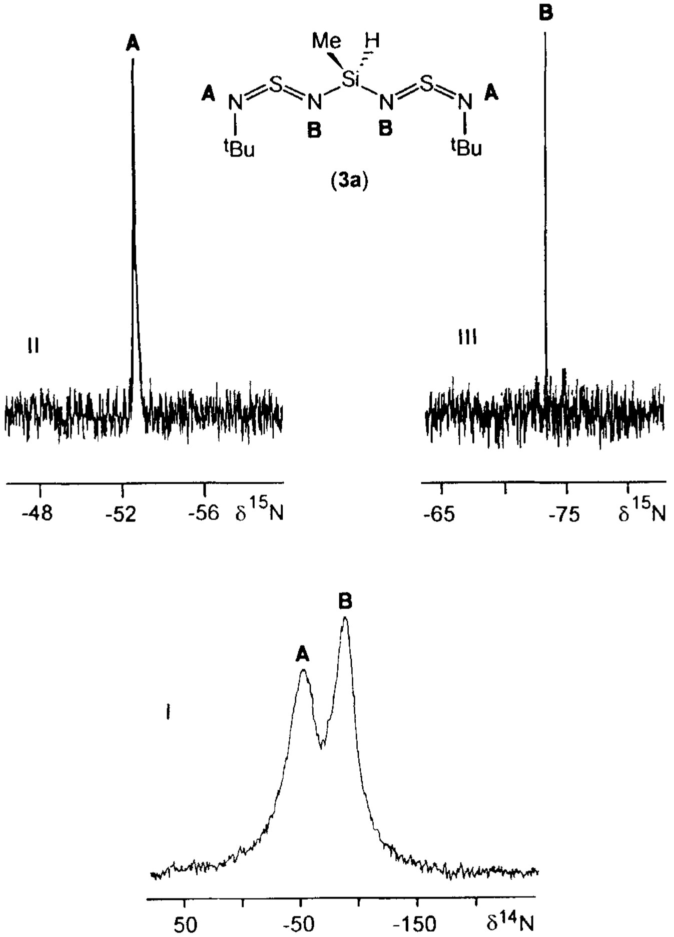


FIGURE 3 I, 21.7 MHz ^{14}N NMR spectrum of MeHSi(NSN^{t}Bu)$_2$ (**3a**) in toluene[d$_8$], measured at 298 K. II and III: 30.4 MHz ^{15}N NMR spectra of MeHSi(NSN Bu)$_2$ (**3a**) in toluene [d$_8$], measured at 243 K; recorded using the refocused INEPT pulse sequence with ^{1}H decoupling. II, $^3J(^{15}N^1H)$ was assumed to be 2.0 Hz. III, $^3J(^{15}N^1H)$ was assumed to be 1.3 Hz.

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 ^{t}Bu$_2$Si derivatives. It is further remarkable that the ^{29}Si NMR signals of the cyclic compounds are shifted by ≥ 16 ppm towards higher field than those of the corresponding non-cyclic compounds **1b** and **4b**. These differing δ^{29}Si values indicate the influence of the enforced Z/Z configuration on ^{29}Si nuclear shielding in the cyclic compounds as compared to the highly fluxional situation in the non-cyclic derivatives.

^{29}Si NMR of the products **10** *and* **11**, *obtained from the reaction between bis(sulfurdiimido)silicon derivatives and hexachlorodisilane*: Three ^{29}Si NMR signals are observed in each case, one at rather low frequency, typical of an N—SiCl$_3$ group with a penta-coordinated silicon atom, due to an additional coordinative N—Si bond, another one in the range typical of N—SiCl$_3$ groups[11] with a *tetra-*

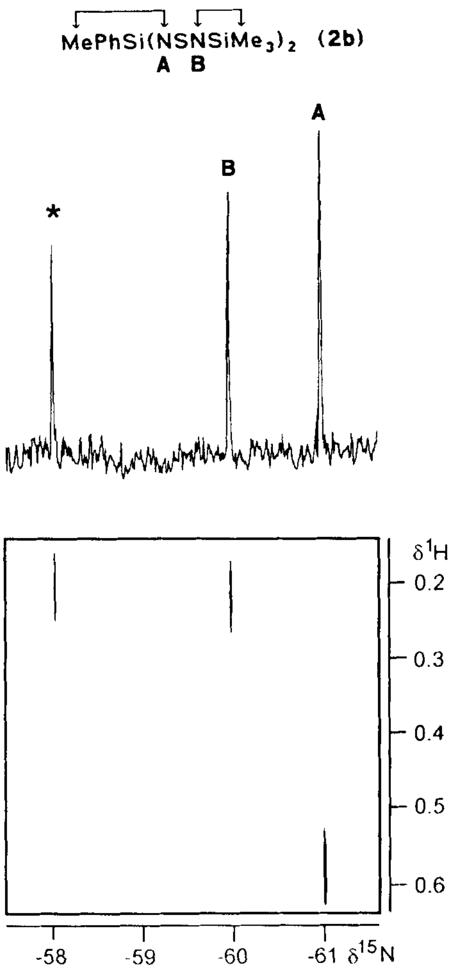
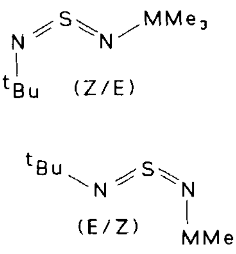


FIGURE 4 2D ^{15}N/^{1}H NMR spectrum of MePhSi(NSNSiMe$_3$)$_2$ (**2b**) in C$_6$D$_6$, measured at 298 K, $^3J(^{15}N^1H)$ was assumed to be 1.3 Hz (δ^1H(SiMe) = 0.56, δ^1H(SiMe$_3$) = 0.22); * = Me$_3$Si(NSN)SiMe$_3$ (δ^1H(SiMe$_3$) = 0.20); arrows on top of the formula indicate the path of polarisation transfer.



	δ^{15}N(N^{t}Bu)	δ^{15}N(NM)	δ^{29}Si
M = Si (95%)	-60.5	-65.9	1.7
M = Ge (70%)	-68.5	-46.0	--
M = Si (5%)	+34.1	-141.5	2.4
M = Ge (30%)	+17.1	-128.7	--

SCHEME II Configurational isomers and ^{15}N and ^{29}Si NMR data of the sulfur diimides ^{t}Bu(NSN)MMe$_3$,[10b] for comparison with the bis(sulfurdiimido)silicon and -germanium derivatives.

coordinated silicon atom, and finally the signal for the SiR^{1}R^2 group at fairly high frequency. By using INEPT, based on $^2J(^{29}Si^1H)$, only the latter ^{29}Si NMR signal was recorded. The ^{29}Si deshielding in the SiR^{1}R^2 group is caused by the adjacent nitrogen atom which is involved in donor-acceptor interactions[14] as proposed for the structures of **10** and **11**. The solid-state ^{29}Si CP/MAS spectrum of **10a** shows almost the same δ^{29}Si values as in solution, indicating that the structure in the solid state is comparable to that in solution.

EXPERIMENTAL

All compounds were handled in an atmosphere of dry argon, and carefully dried solvents were used for the syntheses and for the preparation of the samples for NMR measurements. Me_2SiCl_2, $MePhSiCl_2$, $MeHSiCl_2$, $^tBu_2SiCl_2$, Ph_2SiCl_2, Me_2GeCl_2 and Bu_2GeCl_2 were obtained as commercial products and used without further purification. The potassium salts K[(NSN)R] (R = ^{t}Bu, SiMe$_3$)[7c] were prepared according to literature procedures.

(a) Synthesis of Bis(tert-butylsufurdiimido) Compounds $R^1R^2M(NSN^tBu)_2$ (**1a–7a**)

General procedure: A solution of 3 mmoles $R^1R^2MCl_2$ (M = Si, Ge) in 20 ml hexane was added to a suspension of 6 mmoles K[(NSN)^{t}Bu] in 30 ml DME at −78°C. The mixture was stirred for 30 minutes at this temperature and then allowed to reach room temperature. After filtration the solvent was removed from the solution in the high vacuum. The products **1a–7a** are yellow to orange liquids, and the yields are in the range of 75–90%.

(b) Synthesis of bis(trimethylsilylsulfurdiimido) Compounds $R^1R^2M(NSNSiMe_3)_2$ (**1b–7b**)

General procedure: A suspension of 6 mmoles K[(NSN)SiMe$_3$] in 100 ml hexane was combined with a solution of 3 mmoles $R^1R^2MCl_2$ (M = Si, Ge) in 20 ml hexane at room temperature. The mixture was stirred for 7 days at room temperature, then filtered and the solvent removed from the solution in a high vacuum. All products were obtained as yellow liquids with yields between 60–75%.

(c) Reactions of Bis(sulfurdiimido)silicon Derivatives with Hexachlorodisilane: Synthesis of the Addition Compounds **10a,b** *and* **11a**

General procedure: A suspension of 2 mmoles $R^1R^2Si(NSNR)_2$ in 40 ml hexane was combined with a solution of either 2 mmoles, 4 mmoles or 20 mmoles, respectively, hexachlorodisilane in 30 ml hexane at 0°C. The mixture was allowed to reach room temperature and then stirred for an additional 24 hours. Finally the solvent was removed in a high vacuum.

10a (R^1 = R^2 = Me, R = ^{t}Bu): pale yellow powder; mp. 69–70°C; IR: ν_{as} (NSN) (hexane) = 1232 cm^{-1}, ν_s (NSN) (hexane) = 1047 cm^{-1}; δ^1H (C_6D_6, 25°C) [$^2J(^{29}Si^1H)$] = 0.66 [7.2] (SiMe$_2$); 1.35, 1.40 (^{t}Bu); δ^{13}C (C_6D_6, 25°C) = 5.9 (SiMe$_2$); 29.6, 30.9, 64.0, 63.3 (^{t}Bu); MS: m/z (%) = 504 (1.5; M$^+$-57), 386 (6), 350 (9), 252 (4), 192 (4), 139 (3), 93 (5), 57 (100), 41 (9).

10b (R^1 = R^2 = Me, R = SiMe$_3$): yellow oil; δ^1H (C_6D_6, 25°C) [$^2J(^{29}Si^1H)$] = 0.20 [6.8] (=NSiMe$_3$); 0.39 [6.8] (SiMe$_3$); 0.72 [7.2] (SiMe$_2$); δ^{13}C (C_6D_6, 25°C) [$^1J(^{29}Si^{13}C)$] = 0.5 [57.6] (=NSiMe$_3$); 3.3 [58.7] (SiMe$_3$); 6.0 (SiMe$_2$).

11a (R^1 = Me, R^2 = Ph, R = ^{t}Bu): yellow oil; δ^1 H (C_6D_6, 25°C) = 0.88 (SiMe); 1.26, 1.42 (^{t}Bu); 7.16 (m), 7.56 (m) (SiPh); δ^{13}C (C_6D_6, 25°C) = 5.6 (SiMe); 29.6, 31.0, 64.1, 64.3 (^{t}Bu); 135.0 (ipso), 134.3 (ortho), 128.3 (meta), 131.1 (para) (SiPh).

(d) Spectroscopic Studies

NMR instruments (all equipped with multinuclear units and variable-temperature control units) for liquid state measurements were JEOL FX 90Q (^{29}Si NMR), Bruker AC 300 and Bruker AM 500 (^{1}H, ^{13}C, ^{14}N, ^{15}N, ^{29}Si NMR). Chemical shifts are given with respect to Me$_4$Si (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$_4$Si (external: $\Xi(^{29}Si)$ = 19.867184 MHz) and liquid MeNO$_2$ (external: ^{14}N, ^{15}N, $\Xi(^{15}N)$ = 10.136767 MHz). 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 upon $^1J(^{13}C^1H)$ and $^2J(^{13}C^1H)$]. A Bruker MSL 300 instrument (equipped with a multinuclear double-bearing head) served for the solid state ^{29}Si CP/MAS NMR measurement; the sample was packed in an air-tight insert[15] fitting exactly into the commercial ZrO_2 rotor. The spectrum was run at two different spinning speeds for assignment of the isotropic $\delta^{29}Si$ values.

IR: Perkin-Elmer 9836. MS: EI-MS (70 eV) Varian MAT CH 7.

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