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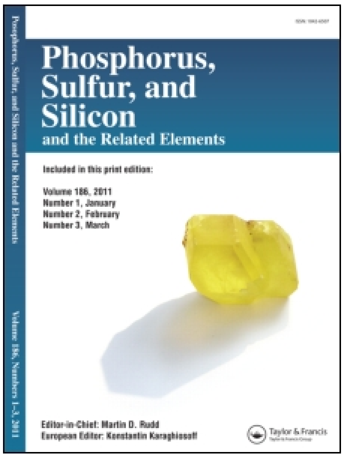

Phosphorus, Sulfur, and Silicon and the Related Elements

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SULFUR DIIMIDES BEARING DIALKYLBORYL AND BIS(AMINO)BORYL SUBSTITUENTS-STUDIED BY MULTINUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Reactions of metallated sulfur diimides, K(NSN)R (R = ^{t}Bu, $SiMe_3$, P^tBu_2) and K(NSN)K, with various boron chlorides $R^1{}_2BCl$ (R^1 = ^{t}Bu, ^{c}pent, Et_2N, $^iPr_2N$), $[CH_2N(R^1)]_2BCl$ (R^1 = Me, ^{n}Bu, ^{i}Pr, ^{t}Bu) and $R^1R^2NBCl_2$ ($R^1 = R^2$ = Et, iPr ; $R^1 = PhCH_2$, R^2 = ^{t}Bu; $R^1 = PhCH_2$, R^2 = Ph) lead to the corresponding boryl-substituted sulfur diimides **2 – 8**, **9a – 20a**, **9b**, **11b – 13b**, **17b** and **15c**.The sulfur diimides $(Et_2N)_2B(NSN)SiMe_3$ (**11b**) and $(^iPr_2N)_2B(NSN)^tBu$ (**12a**) react with hexachlorodisilane by cleavage of the Si-Si bond to give the new bis(amino)sulfanes **21b** and **22a**, in which the nitrogen atoms bear additional $SiCl_3$ substituents. A complete NMR spectroscopic study was carried out for the known cyclic sulfur diimide $^iPr_2B(NSN)_2BN^iPr_2$ (**1**). All non-cyclic compounds were studied by ^1H, ^{11}B, ^{13}C and ^{15}N NMR at variable temperature aiming for configurational assignment. The ^{15}N NMR data, in particular, suggest that in most cases almost linear N=S-B units are preferred with a perpendicular arrangement of the plane of the boryl group with respect to the NSN plane.

Keywords: Boron; Sulfur diimides; NMR spectroscopy

INTRODUCTION

The structure of sulfur diimides, R(NSN)R′, in solution has been discussed on the basis of various physical methods [1]. In principle, sulfur diimides with two different substituents R and R′ can exist in the form of four con-

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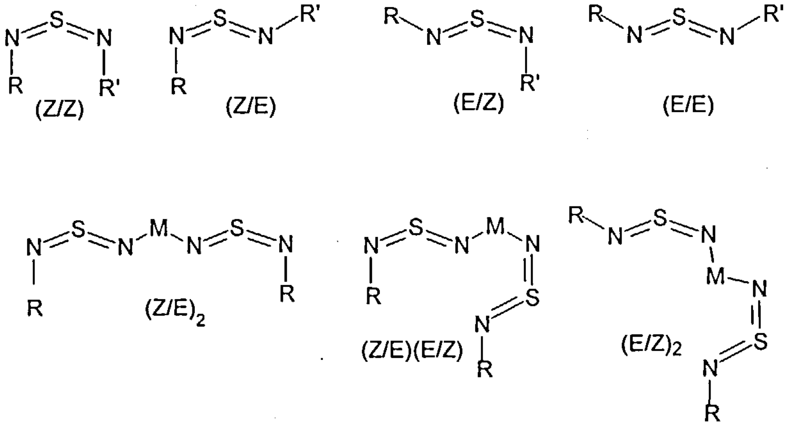
figurational isomers (Scheme 1) which, in fact, have all been found in the solid state [2–5], although it appears that in most cases the Z/E or E/Z isomers are preferred in solution [1]. In the case of bis(sulfurdiimido) compounds, e.g. $M(NSNR)_2$, ten different configurational isomers are possible. If the less favored Z/Z and E/E configurations are excluded, three isomers remain (Scheme 1) with either twice Z/E, twice E/Z, or Z/E and E/Z configuration.

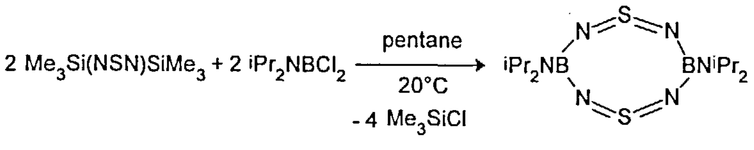


SCHEME 1

It is well known that sulfur diimides are highly fluxional in solution with respect to E/Z-Z/E isomerization [1]. Our previous studies have indicated that ^{15}N NMR spectra provide the most conclusive information on the configuration of sulfur diimides [6–9]. We now report studies pertaining to symmetrically and unsymmetrically substituted sulfur diimides bearing dialkylboryl and bis(dialkylamino)boryl groups.

So far only two non-cyclic sulfur diimides bearing diazaborolidinyl groups have been prepared [10], and one cyclic derivative **1** [11] was characterized by X-ray structural analysis. We have repeated the synthesis of **1** [Eq. (1)] in order to obtain a complete set of NMR data of a boryl-substituted sulfur diimide with a defined Z/Z configuration.

Furthermore, we have prepared (Scheme 2) a series of 25 sulfur diimides (**2 – 8, 9a – 20a, 9b, 11b – 13b, 17b** and **15c**) mainly for NMR spectroscopic studies. The reactivity of the sulfur diimides **11b** and **12a** towards Si_2Cl_6 was studied for comparison with previous results where cleavage of the Si-Si bond had been observed [12].



1

(1)

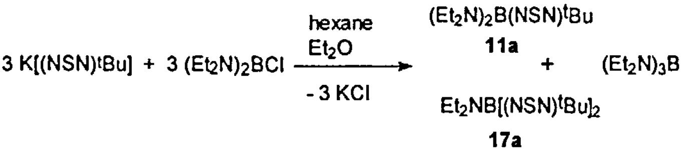
EQUATION 1

2. RESULTS AND DISCUSSION

2.1 Synthesis of boryl-substituted sulfur diimides

The reaction of the potassium salts K[(NSN)R] (R = ^tBu, $SiMe_3$, P^tBu_2) and K(NSN)K with various boron chlorides leads to the boryl-substituted sulfur diimides **2 - 8, 9a – 16a, 9b, 11b – 13b** and **15c** (Scheme 2). In an analogous manner the bis(sulfurdiimido)boranes **17a – 20a** and **17b** are obtained by the reaction of K(NSN)R (R = ^tBu, $SiMe_3$) with the corresponding aminoboron dichloride

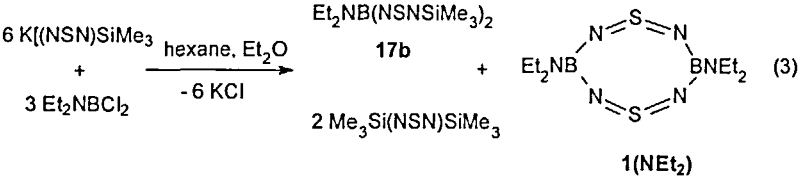
A solvent mixture of ether/hexane (2:3) proved to be necessary for the syntheses shown in Scheme 2. In the case of the reactions with bis(diethylamino)boron chloride, additional compounds besides the expected products are observed [Eq. (2)]. The product distribution depends on the temperature; at lower temperature **11a** is the main product, whereas in boiling hexane **17a** is the main product. Independently it was shown that isolated **11a** can be converted into **17a** by heating for 3 days at 80°C in benzene[d_6].



$$3\ K[(NSN)^tBu] + 3\ (Et_2N)_2BCl \xrightarrow[-3\ KCl]{\text{hexane}\ Et_2O} \begin{matrix} (Et_2N)_2B(NSN)^tBu \\ \mathbf{11a} \\ Et_2NB[(NSN)^tBu]_2 \\ \mathbf{17a} \end{matrix} + (Et_2N)_3B \qquad (2)$$

EQUATION 2

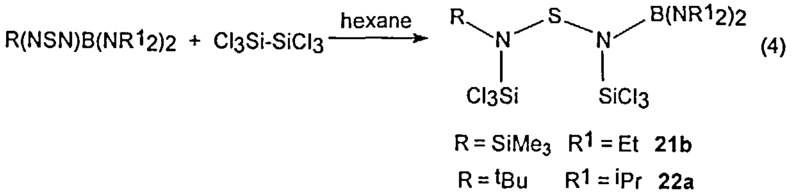
Tris(diethylamino)borane is also formed in the reaction of $K(NSN)SiMe_3$ with bis(diethylamino)boron chloride, in addition to the desired unsymmetrically substituted sulfur diimide **11b** and the symmetrically substituted ones. Tris(diethylamino)borane is the main product in the reaction of K(NSN)K with bis(diethylamino)boron chloride. As a consequence of these symmetrization processes, the reaction of K[(NSN)SiMe$_3$] with diethylaminoboron dichloride leads to the eight-membered ring **1(NEt$_2$)**as a side product [Eq. (3)].



EQUATION 3

2.2 Reactivity of boryl-substituted sulfur diimides towards hexachlorodisilane

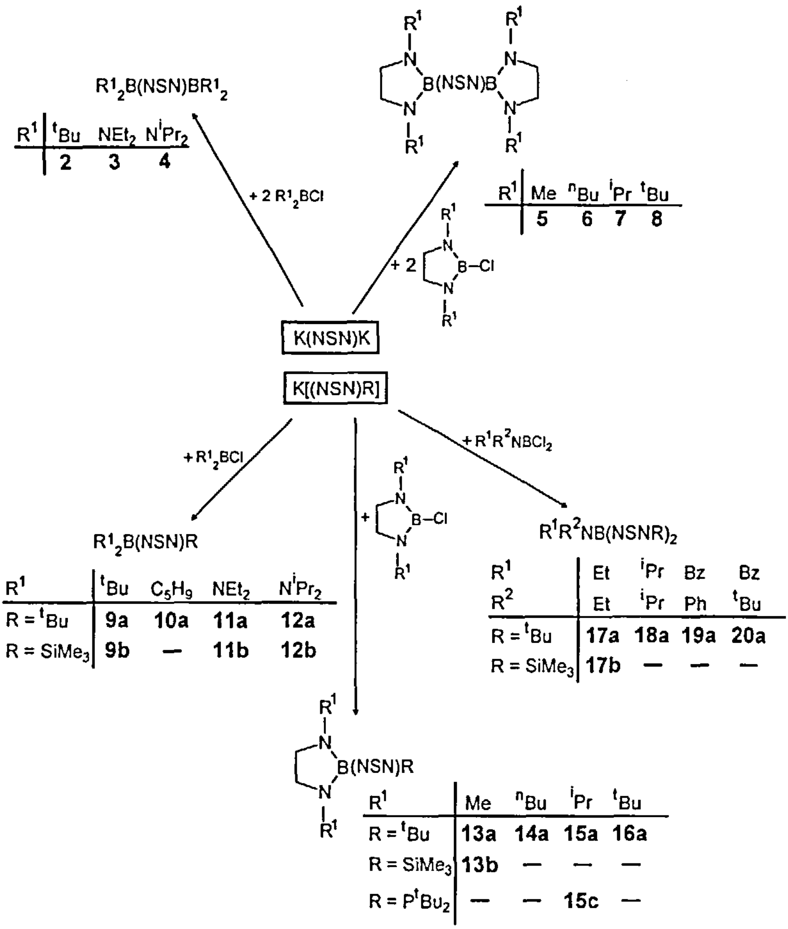
Treatment of the boryl-substituted sulfur diimides **11b** and **12a** with hexachlorodisilane in an equimolar ratio leads directly to the corresponding diaminosulfanes [Eq. (4)].



EQUATION 4

2.3 NMR spectroscopic results

The complete sets of NMR data of all compounds are listed in Tables I - VI. ^{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 [13], (ii) direct measurement with ^{1}H decoupling and (iii) application of the refocused INEPT pulse sequence [14] with ^{1}H decoupling (polarization transfer based on $^{3}J(^{15}N^{1}H)$). Application of the latter pulse sequence, based on



SCHEME 2

$^3J(^{15}N^1H) \approx 2.0 - 2.5$ Hz for N^tBu and $\approx 1.5 - 1.8$ Hz for $NSiMe_3$, allowed to observe selectively the ^{15}N resonance signals of these moieties.

2.3.1 Dialkylboryl-substituted sulfur diimides (2, 9a, 9b, 10a)

^{15}N NMR – The $\delta^{15}N(NSiMe_3)$ value of $^tBu_2B(NSN)SiMe_3$ (**9b**) (-132.8) is rather close to that of the E/Z isomer of $^tBu(NSN)SiMe_3$ (-141.5) where

the $SiMe_3$ group occupies the Z position [9a]. Similarly, the $\delta^{15}N(N^tBu)$ value of $tBu_2B(NSN)^tBu$ (**9a**) (-101.2) corresponds to the $\delta^{15}N[N^tBu(Z)]$ value (-105.9 [9a]) of $^tBu(NSN)^tBu$ (Figure 1). This assignment is also based upon nitrogen shielding calculations of sulfur diimides by the GIAO method [15], the comparison of nitrogen shielding in sulfur diimides and N-sulfinylamines, R(NSO) [8a, 16], and the results of CNDO/S calculations of nitrogen nuclear shielding in N-sulfinylamines [16]. This suggests that the ^tBu group in **9a** and the Me_3Si group in **9b** are in the Z positions. Therefore, the boryl groups should either be in E positions or a linear arrangement SNB is preferred.

TABLE I NMR data[a] of $R(NSN)BR^1_2$ (2, 9a,b, 10a)

Compound	δ^1H		$\delta^{13}C$		$\delta^{11}B$	$\delta^{15}N$		*[c]*
	R	*R¹*	*R*	*R¹*	*[b]*	*NB*	*NR*	
$R = BR^1{}_2$;	---	1.05	---	28.6	51.8	-89.1	---	A
$R^1 = {}^tBu$				24.4	(400)	(4.0)	---	
2 [d]								
$R = {}^tBu$	1.29	0.96	28.3	27.8	49.0	-63.4	-101.2	A, B
$R^1 = {}^tBu$			58.9	22.7	(180)	(3.0)	(3.0)	
9a [e]								
$R = SiMe_3$	0.07	0.86	0.8	28.3	49.0	-38.2	-131.8	A, B
$R^1 = {}^tBu$	[7.2]			23.3	(300)	(3.6)	(3.4)	
9b [f]								
$R = {}^tBu$	1.24	1.29	29.7	27.1	50.5	n.m.	n.m.	---
$R^1 = C_5H_9$		1.47	60.1	27.2	(800)			
10a [g]		1.63		28.8				
				29.5				

[a] Coupling constants $^2J(^{29}Si^1H)$ in Hz in [ ]; br = broad, $h_{1/2}$ [Hz] in ( ); n.m. = not measured.

[b] In C_6D_6; measured at +25°C.

[c] Methods to record ^1H decoupled ^{15}N NMR spectra: **A**: direct measurement, **B**: refocused INEPT pulse sequence [14]; **C**: inverse-gated ^1H decoupling [13].

[d] In toluene[d_8], measured at –50°C; δ values at 25°C: $\delta^1H = 1.02$; $\delta^{13}C = 29.1, 24.5$; $\delta^{14}N = -86.0$.

[e] In toluene[d_8], measured at –40°C; δ values at 25°C: $\delta^1H = 1.00$ (B^tBu), 1.35 (^tBu); $\delta^{13}C = 29.5, 23.0$ (br) (B^tBu), 30.0, 60.3 (^tBu); $\delta^{14}N = -64.0, -101.0$.

[f] In toluene[d_8], measured at –50°C; δ values at 25°C $\delta^1H = 0.07$ ($SiMe_3$), 0.86 (B^tBu); $\delta^{13}C = 1.1$ ($SiMe_3$), 29.0, 23.5 (br) (B^tBu); $\delta^{29}Si = +0.8$; $\delta^{14}N = -39.0, -128.0$; $\delta^{15}N(-70°C) = -31.8$ (=NB), –132.8 (=$NSiMe_3$).

[g] In toluene[d_8], measured at +25°C; $\delta^{14}N = -64.0$; δ values at –70°C: $\delta^1H = 0.96, 1.03, 1.25$ (^tBu), 1.20 (CH), 1.40, 1.69 (CH_2); $\delta^{13}C = 29.0, 59.8, 31.1, 61.3, 61.4, 31.6, 59.4$ (^tBu), 32.4 (CH), 26.9, 27.1, 28.7, 29.3 (CH_2).

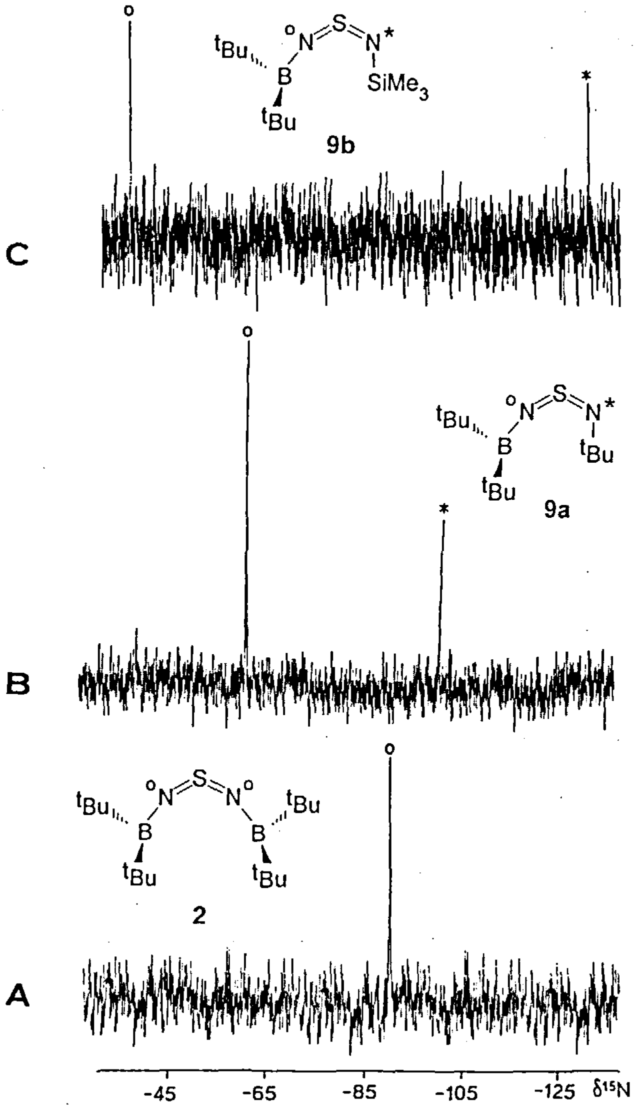
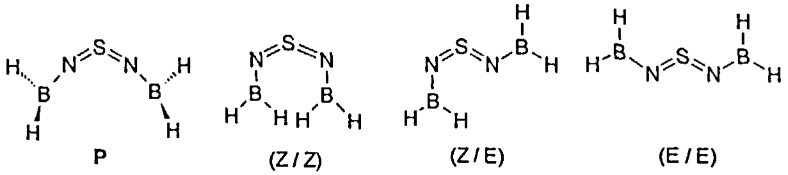


FIGURE 1: A 30.5 MHz $^{15}N\{^{1}H\}$ NMR spectrum of $^{t}Bu_2B(NSN)B^{t}Bu_2$ (**2**) in toluene[d_8], recorded at −50°C; B 30.5 MHz $^{15}N\{^{1}H\}$ NMR spectrum of $^{t}Bu(NSN)B^{t}Bu_2$ (**9a**) in toluene[d_8], recorded at −40°C; C 30.5 MHz $^{15}N\{^{1}H\}$ NMR spectrum of $Me_3Si(NSN)B^{t}Bu_2$ (**9b**) in toluene[d_8], recorded at −50°C

The electron deficient boron atom can have π interactions with the NSN cumulene system which would require the boryl group to remain in plane with the NSN plane [Scheme 3, (Z / Z), (Z / E) or (E / E) configurations]. Energetically more favorable π interactions will result from BN(pp)π bonding involving the lone pair of electrons at each nitrogen atom of the NSN system. This would lead to a linear S=N=B arrangement in which the boryl group is oriented perpendicular to the NSN plane. The conformation **P** (Scheme 3) for the parent compound $H_2B(NSN)BH_2$ is suggested as a compromise: the H_2B planes are oriented almost perpendicular to the NSN plane, and the S=N=B fragments are almost linear, slightly bent towards Z/Z positions [17].

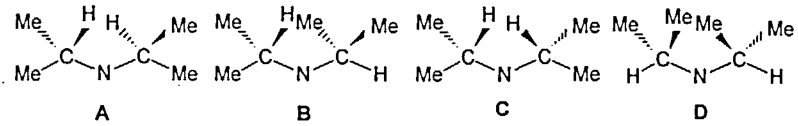


SCHEME 3

This means that the structures of boryl-substituted sulfur diimides are fundamentally different from those of other sulfur diimides (see also Scheme 1). Only in cyclic compounds such as **1**, the structures will be directly comparable with the (Z/Z) isomer (Scheme 1 and 3). It seems very likely that the SNB units in **2**, **9a** and **9b** adopt a conformation analogous to **P**. The influence of a ^{t}Bu or a $SiMe_3$ group on the ^{15}N(B) resonance is similar as in other sulfur diimides (see Table I and Figure 1). *^{11}B NMR* – The ^{11}B resonance signals of **2**, **9a**, **9b** and **10a** are shifted by ca. 25 ppm towards lower frequencies as compared to those of the corresponding dialkylboron chlorides. Considering the similar electronegativities of Cl and the NSN unit, changes in the energies of the σ bonding framework in the vicinity of the boron atom should be small. Thus, the marked increase in ^{11}B nuclear shielding must be ascribed mainly to BN(pp)π interactions which are most favorable in the configuration **P** (Scheme 3). In the cases of **2**, **9a** and **9b**, the line widths of the ^{11}B resonances are in the expected range ($h_{1/2}$ = 180 – 400 Hz), indicating that these compounds are monomeric in solution. In contrast, the fairly large line width of the ^{11}B NMR signal of **10a** ($h_{1/2}$ = 800 Hz) may be due to equilibria involving associated species, although the δ^{11}B value has not changed as compared to **9a**.

2.3.2 3,7-Bis(diisopropylamino)-3H, 7H-1λ^4,5λ^4-dithia-, 2,4,6,8-tetraza-3,7-diborocine (1)

In the heterocycle **1** the Z/Z configuration is enforced by the ring size as shown by an X-ray structural analysis [11]. The diffraction data reveal disorder of the isopropyl groups. Four different conformers of the di(isopropyl)amino group are conceivable (**A** - **D**), but the conformers **C** and **D** should be less favored due to steric effects.



SCHEME 4

At lower temperature (below –20°C) the ^1H and ^{13}C NMR spectra show two signals for the CH groups. Below –60°C four doublets for the Me groups are observed in the ^1H NMR spectrum, two of which coincide by chance. In accordance, four $^{13}C(Me)$ resonances are detected in the ^{13}C NMR spectrum. This is in agreement with reported data [11] and indicates hindered rotation about the B-N$^iPr_2$ bonds. However, at –90°C the ^{13}C NMR spectrum clearly shows the presence of a second conformer for which also two $^{13}C(CH)$ and four $^{13}C(Me)$ resonances are observed (Figure 2). The ratio of the two conformers is approximately 1:2. This doubling of the signals is caused by a hindered rotation about the N-C bonds in the N$^iPr_2$ groups. These features are also reflected in the ^{15}N NMR spectrum at –50°C. It shows two $^{15}N(N{=}S)$ resonances for each conformer (Figure 3). At –20°C, when the rotation about the N-C bonds is still fast, only one ^{15}N resonance is detected. The ^{15}N NMR signal of the amino nitrogen atoms is shifted by about 30 ppm towards higher frequencies as compared to the corresponding tris(amino)borane, $B(N^iPr_2)_3$ (see Table II), typical of BN(pp)π bonding [18]. This is in agreement with the result of the X-ray structure analysis [11] which indicates strong BN(pp)π interactions between boron and the exocyclic nitrogen atoms.

The solid-state 30.4 MHz ^{15}N CP/MAS NMR spectrum of **1** shows at least two $^{15}N(N{=}S)$ resonances. Unfortunately, the signals are extremely broad, probably as the result of unresolved ^{15}N-^{11}B scalar and dipolar coupling, and effects exerted by the ^{11}B quadrupolar moment. Therefore, the signal-to-noise ratio is insufficient for a reliable assignment of the actual number of ^{15}N resonances.

TABLE II NMR data [a] of $^{i}Pr_2NB(NSN)_2BN^{i}Pr_2$ (**1**) at different temperatures and of **1**(NEt_2) [b]

δ^{1}H		*δ^{13}C*		*δ^{15}N*		*temp.*
Me	*CH*	*Me*	*CH*	*=NS*	*N^{i}Pr*	*[°C]*
1.23 (d)	3.61 (sp)	22.9	47.5	---	---	+25
1.21 (d)	3.58 (br)	22.9 (11.3)	47.5 (35)	---	---	0
1.19 (d)	3.56 (br)	22.4 (64)	46.2 (320)	-73.4 (14)	-260.2	-20
1.19 (br)	3.45 (br)	22.1 (96)	44.9 (150)	---	---	-30
	3.60 (br)		49.5 (150)			
1.16 (br)	3.29 (br)	22.1 (br)	43.7 (60)	---	---	-40
	3.81 (br)	24.9 (70)	50.2 (60)			
1.09 (br)	3.21 (br)	21.1 (43)	43.6 (28)	-73.7 (12)	-259.8	-50
1.19 (br)	3.83 (br)	22.1 (25)	50.2 (24)	-75.4 (12)		
		23.1 (13)	44.7*	-73.1*		
		24.8 (37)	49.4*	-76.8*		
1.07 (br)	3.21 (br)	20.7	43.4 (15)	---	---	-60
1.20 (br)	3.83 (br)	21.0	50.0 (13)			
		21.9	44.6*			
		24.6	49.3*			
1.00 (d)	3.16 (sp)	20.4	43.0	---	---	-90
	3.77 (sp)	20.7	49.8			
1.22 (d)		21.5				
1.14(d)		24.3				
		20.3*	43.2*			
		21.7*	49.9*			
		21.9*				
		24.6*				

[a] Measured in CD_2Cl_2 ; $\delta^{11}B(+25°C) = 22.8$; $\delta^{14}N(+25°C) = -77.0, -255.0$; $h_{1/2}$ in ( ); (br) = broad; d = doublet; sp = septet; the signals of the minor conformer are marked by *.

[b] **1**$(NEt_2)_1$ measured in toluene[d_8]; ^{1}H, ^{11}B, ^{13}C and ^{14}N NMR spectra recorded at +25°C; $\delta^{1}H = 0.86, 2.82$ (NEt_2); $\delta^{13}C = 15.5, 42.1$ (NEt_2); $\delta^{11}B = 24.5$; $\delta^{14}N = -71.0$ (=NB), -288.0 (NEt); $\delta^{15}N(-40°C) = -75.3$ (=NB); $\delta^{15}N(-60°C) = -75.5$ (=NB).

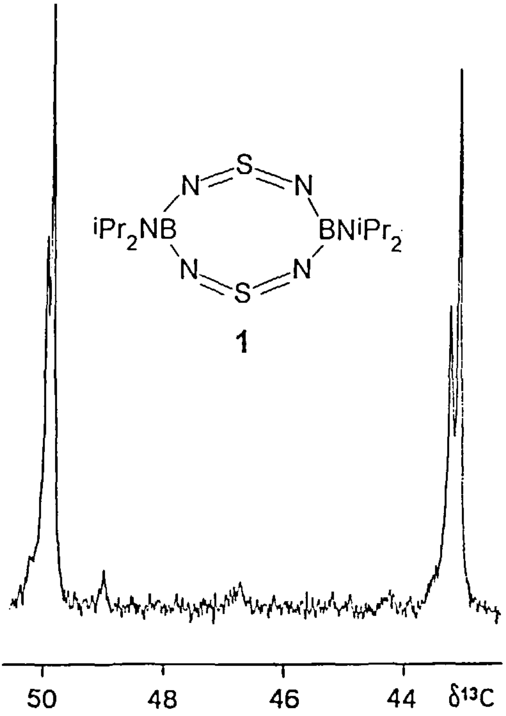


FIGURE 2 NCH region of the 75.4 MHz ^{13}C NMR spectrum of $^{i}Pr_2NB(NSN)_2BN^{i}Pr_2$ (1) in CD_2Cl_2, recorded at −90°C

The ^{11}B nuclear shielding in **1** (δ^{11}B 22.8) is greater than in $^{i}Pr_2NBCl_2$ (δ^{11}B 30.2), where the strength of BN(pp)π bonding should be comparable with that in **1**. It is therefore possible that π interactions between the boron p_z orbital and the NSN cumulene π system also contribute to increased ^{11}B nuclear shielding.

2.3.3 Aminoboryl-substituted sulfur diimides (3 – 8, 11a – 16a, 11b- 13b, 15c)

The ^{15}N resonances of the amino nitrogen atoms are shifted about 30 ppm towards higher frequencies as compared to the corresponding tris(amino)borane, $B(NR_2)_3$ (Tables III and IV), in accordance with

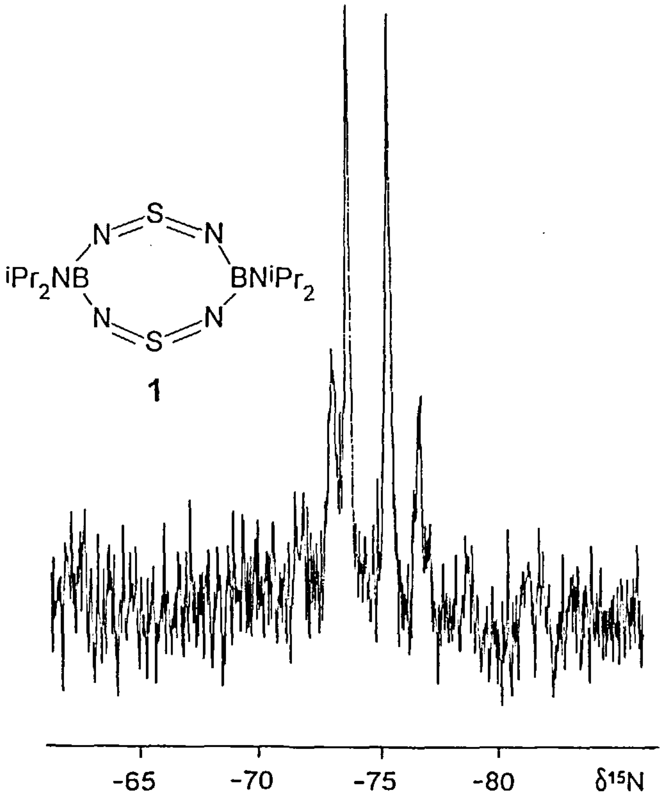


FIGURE 3 NSN part of the 30.5 MHz $^{15}N\{^{1}H\}$ NMR spectrum of $^{i}Pr_2NB(NSN)_2BNPr_2$ (**1**) in CD_2Cl_2, recorded at −50°C

BN(pp)π bonding [18]. The $\delta^{14}N$ values of **6** correspond to the literature values [10b]

In contrast to the dialkylboryl-substituted sulfur diimides **9a**, **9b** and **10a** (Table I), the $\delta^{15}N(R)$ data of **11a,b** and **12a,b** (Table III) indicate a fluxional structure of the sulfur diimides in which both the ^{t}Bu and the Me_3Si group prefer the Z positions (averaged $\delta^{15}N$ values are −74 for $N^{t}Bu$ and −84 for $NSiMe_3$ groups; see e.g.Figure 4). In general, the Z positions seem to be energetically favored for the non-boryl substituent. Since BN(pp)π interactions with the amino nitrogen atoms dominate, the almost linear SNB arrangement as in **P** (Scheme 3) is not necessarily the most likely conformation.

TABLE III NMR data[a] of R(NSN)BR^1_2 (**3, 4, 11a,b, 12a,b**)

Compound	$\delta^{13}C$		$\delta^{11}B$	$\delta^{15}N$			*[b]*
	R	*R¹*		*=NR*	*=NB*	*B-N*	
R = BR^1R^2	--	15.7	26.0	---	-78.7	-314.8	**A**
R^1 = NEt_2	--	42.2					
3 [c]							
R = BR^1R^2	30.9	23.9	29.6	-84.1	-50.9	-289.5	**A, B**
R^1 = N^iPr_2	60.1	46.1					
4 [d]							
R = ^tBu	30.5	15.8	26.2	-76.5	-59.9	-317.3	**B, C**
R^1 = NEt_2	60.2	42.0					
11a [e]							
R = ^tBu	30.9	23.9	29.6	-84.1	-50.9	-289.5	**A, B**
R^1 = N^iPr_2	60.1	46.1					
12a [f]							
R = $SiMe_3$	1.5	15.6	26.0	-85.8	-59.2	-313.2	**A, B**
R^1 = NEt_2	(57.0)	42.0					
11b [g]							
R = $SiMe_3$	1.6	23.8	27.6	-84.3	-34.8	-290.4	**A, B**
R^1 = N^iPr_2	(53.8)	46.2					
12b [h]							

[a] Solutions in C_6D_6, ^{11}B and ^{13}C NMR spectra recorded at +25°C; coupling constants $^1J(^{29}Si^{13}C)$ in Hz in ( ); d = doublet; t = triplet; q = quadruplet; sp = septet.

[b] See footnote [c] Table I.

[c] ^{15}N NMR spectrum recorded at –50°C, in toluene[d_8]; δ values at 25°C: δ^1H= 0.97 (CH_3 t), 2.90 (CH_2, q); $\delta^{14}N$ = –77.6, –316.6.

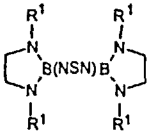
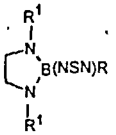
[d] ^{15}N NMR spectrum recorded at –50°C, in toluene[d_8]; δ values at 25°C: δ^1H= 1.19 (CH_3, d), 3.51 (CH, sp); $\delta^{14}N$ = –65.0, –250.0.

[e] ^{15}N NMR spectrum recorded at –40°C, in toluene[d_8]; δ values at 25°C: δ^1H= 1.40 (^tBu), 0.96 (CH_3, t), 2.89 (CH_2,q); $\delta^{14}N$ = –63.0, –288.0.

[f] ^{15}N NMR spectrum recorded at –60°C, in toluene[d_8]; 6 values at 25°C: δ^1H= 1.60 (^tBu), 1.20 (CH_3, d), 3.50 (CH, sp); $\delta^{14}N$ = –78.0, –308.0; $\delta^{13}C$(-80°C) = 30.1, 59.7 (^tBu), 23.2 (CH_3), 45.3 (CH).

[g] ^{15}N NMR spectrum recorded at –60°C, in toluene[d_8]; δ values at 25°C: δ^1H= 0.17 ($SiMe_3$), 0.97 (CH_3, t), 2.85 (CH_2, q); $\delta^{14}N$ = –58.0 (=$NSiMe_3$),-79.0 (=NB), -317.0 (NEt_2); $\delta^{29}Si$ = –2.0.

[h] ^{15}N NMR spectrum recorded at –40°C, in toluene[d_8]; δ values at 25°C: δ^1H= 0.21 ($SiMe_3$), 1.10 (CH_3, d), 3.39 (CH, sp); $\delta^{14}N$ = –41.0, –278.0; $\delta^{15}N$ = –80.5 (=$NSiMe_3$); $\delta^{29}Si$ = –1.2.

TABLE IV : NMR data[a] of  **(5-8)** and  **(13a-16a, 13b, 15c)**

Compound	$\delta^{13}C$			$\delta^{11}B$	$\delta^{15}N$			*[b]*
	CH_2	*R^1*	*R*		*=NB*	*=NR*	*NR^1*	
R^1 = Me	50.7	33.4	--	25.5	-91.0	---	-328.8	A
5 [c]				(90)	(3.6)		(8.0)	
R^1 = ^{n}Bu	47.9	14.4	--	26.7	-87.3	---	-317.7	C
6 [d]		20.6		(210)	(5.4)		(6.1)	
		32.0						
		46.5						
R^1 = ^{i}Pr	45.2	21.9	--	26.8	-83.3	---	-304.9	C
7 [e]		41.8		(125)	(3.9)		(6.6)	
R^1 = ^{t}Bu	51.3	30.6		25.6	-61.0	---	-294.1	A
8[f]		44.3		(250)	(7.1)		(5.8)	
R^1 = Me, R = ^{t}Bu	50.6	33.3	29.9	26.0	-86.8	-66.7	-329.9	A, B
13a [g]			60.9	(120)	(5.0)	(2.5)	(5.5)	
R^1 = ^{n}Bu, R = ^{t}Bu	47.5	14.0	29.7	26.4	-77.2	-69.8	-318.8	B, C
14a [h]		20.0	61.1	(240)	(4.6)	(3.8)	(5.8)	
		31.7						
		45.9						
R^1 = ^{i}Pr, R = ^{t}Bu	45.0	21.3	29.8	25.6	-77.2	-70.4	-305.3	B, C
15a [i]		41.8	60. 9	(170)	(3.6)	(2.2)	(4.7)	
R^1 = ^{t}Bu, R = ^{t}Bu	51.0	30.5	30.4	26.2	-59.3	-73.6	-294.4	B, C
16a [j]		44.1	60.6	(230)	(4.5)	(2.9)	(4.8)	
R^1 = Me, R = $SiMe_3$	50.5	33.2	0.8	25.5	-75.2	-82.0	-329.1	A, B
13b [k]			(56.5)	(120)	(3.2)	(1.8)	(4.5)	
R^1 =^{i}Pr, R = P^tBu_2	45.0	21.8	28.4	25.4	-80.1	-75.9	-306.0	C
15c [l]		41.6	34.9	(260)	(7.3)	(5.0)	(8.7)	

[a] In toluene[d_8] ^1H, ^{11}B, ^{13}C, ^{14}N and ^{29}Si NMR spectra recorded at +25°C, ^{15}N NMR spectra recorded at –50°C (other δ values determined at 25°C, if not stated otherwise); coupling constants $^1J(^{29}Si^{13}C)$ in Hz in ( ); d = doublet; m = multiplet; sp = septet; t = triplet.

[b] See footnote [c]Table I.

[c] δ^1H= 2.32 (CH_3) 2.85 (CH_2); $\delta^{14}N$ = –89.0, –326.0.

[d] δ^1H= 0.76 (CH_3, t), 1.14 (CH_2, m), 1.18 (CH_2, m), 2.76 (CH_2, t), 2.95 (CH_2); $\delta^{14}N$ = –77.0, –304.0.

[e] δ^1H= 0.87 (CH_3, d), 3.31 (CH, sp), 2.87 (CH_2); $\delta^{14}N$ = –78.0, –296.0.

[f] δ^1H= 1.19 (^{t}Bu), 2.98 (CH_2). $\delta^{14}N$ = –70.0, –294.0.

[g] δ^1H= 1.41 (^{t}Bu), 2.41 (CH_3), 2.93 (CH_2); $\delta^{14}N$ = –65.0 (N^tBu), –88.0 (NB), –334.0 (NMe).

[h] δ^1H= 1.41 (^{t}Bu), 0.79 (CH_3, t), 1.18 (CH_2, m), 1.25 (CH_2, m), 2.75 (CH_2, t), 2.96 (CH_2); $\delta^{14}N$ = –80.0, –295.0.

[i] δ^1H= 1.38 (^{t}Bu), 0.92 (CH_3, d), 3.26 (CH, sp), 2.93 (CH_2); $\delta^{14}N$ = –76.0, –299.0.

[j] δ^1 H = 1.39 (^{t}Bu), 1.06 (N^tBu), 2.93 (CH_2); $\delta^{14}N$ = –62.0, –265.0.

[k] δ^1H= 0.07 ($SiMe_3$), 2.32 (CH_3), 2.86 (CH_2); $\delta^{14}N$ = –79.0, –337.0; $\delta^{29}Si$ = –0.7; $\delta^{15}N$(+25°C and –20°C) = –80.8 ($NSiMe_3$).

[l] $^1J(^{31}P^{13}C)$ = 25.6 Hz, $^2J(^{31}P^{13}C)$ = 15.8 Hz; δ^1H= 1.06 (P^tBu_2, 11.7 Hz), 0.96 (CH_3, d), 3.32 (CH, sp), 2.94 (CH_2); $\delta^{14}N$ = –72.0, –300.0; $\delta^{31}P$(+25°C) = 89.2, $^1J(^{31}P^{15}N)$ = 59.8 Hz, IE = 62.4 ppb; $\delta^{31}P$(-40°C) = 85.9.

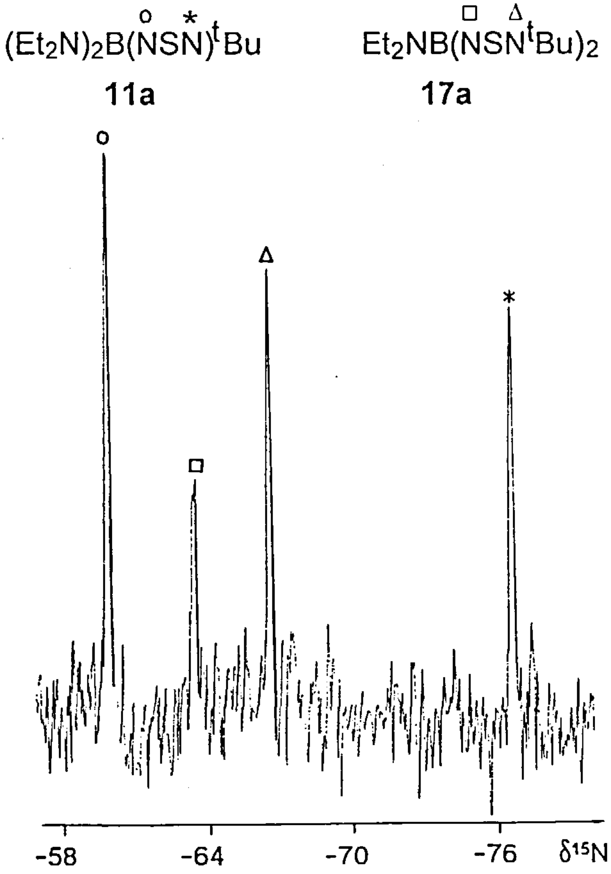


FIGURE 4: NSN part of the 30.5 MHz $^{15}N\{^{1}H\}$ NMR spectrum of a mixture of $(Et_2N)_2B(NSN)^{t}Bu$ (**11a**) and $Et_2NB(NSN^{t}Bu_2)_2$ (**17a**) in toluene[d_8], recorded at −50°C

In the series of sulfur diimides bearing cyclic diaminoboryl substituents (**5** – **8**, **13a**- **16a**) the $\delta^{15}N(=NB)$ values of **8** (-61.0) and **16a** (-59.3) are remarkable. The $^{15}N(=NB)$ resonances of these compounds with ^{t}Bu groups at the amino nitrogen atoms are shifted by ca. 30 ppm towards higher frequencies as compared to those of the corresponding Me-derivatives (**5** and **13a**). This large effect indicates a change in the local electronic structure of the =NB-nitrogen atom. The most likely explanation invokes steric interactions which force the diazaborolidinyl group with the most bulky substituents from the Z position towards the linear SNB arrangement or even into the E position.

Compound **15c** is another example of phosphorus-nitrogen compounds [8b, 19, 20]where the application of Hahn-echo extended (HEED [19]) polarization transfer pulse sequences is promising. These experiments afford the coupling constant $^1J(^{31}P,^{15}N) = 59.8$ Hz and the isotope induced chemical shift $^1\Delta^{15/14}N(^{31}P) = -62.4$ ppb at natural abundance of ^{15}N (Figure 5). The $\delta^{31}P$ value and the coupling constant $^1J(^{51}P,^{15}N)$, determined at room temperature, point towards Z/E-isomerization of the P^tBu_2 group in **15c.** At lower temperature the ^{31}P NMR signal is shifted to lower frequencies close to the range which was found typical of the E positions of P^tBu_2 groups [8b]. However, the $\delta\,^{15}N$ value (-75.9; determined at –50°C) does not support this structural assignment, since $\delta^{15}N$ around –35 would be expected by comparison with other sulfur diimides bearing the P^tBu_2in Z positions [8b]. Therefore, this question cannot be settled without further structural information.

The $\delta^{11}B$ values of **5 – 8, 11a - 16a, 11b - 13b** and **15c** are in the expected range [21].

2.3.4 Bis(sulfurdiimido)aminoboryl compounds (17a – 20a, 17b)

All $\delta^{15}N(NR)$ (R = ^tBu, $SiMe_3$) values point towards the Z position for the substituent R (see Table V) in the compounds **17a – 20a** and **17b.** At low temperature the ^1H, ^{13}C and ^{15}N NMR spectra of **18a, 19a** and **20a** show the presence of two different $=N^tBu$ groups, both occupying the Z position (Figure 6). In addition, the ^{15}N NMR spectra at low temperature reveal the existence of two different =NB nitrogen atoms as well. In the cases of **19a** and **20a,** this can be readily explained by the presence of two different substituents (benzyl / phenyl and benzyl / ^tBu) at the amino nitrogen atom and hindered rotation about the B-N(amino) bond (**19a:** $\Delta G^{\#} = 51.6 \pm 1$ kJ/mol). In the case of **18a**, the appearance of the same phenomenon requires a different explanation. The energy of activation $\Delta G^{\#} = 43.6 \pm 1$ kJ/mol is significantly lower than for the dynamic process in **19a.** However it is well comparable with $\Delta G^{\#} = 45.6 \pm 1$ kJ/mol ($\Delta G^{\#} = 46.4$ [11]), the energy of activation determined for the rotation about the N-C bond in **1** (vide supra). Therefore, the NMR signals for different $=N^tBu$ and N^iPr groups in **18a** at low temperature must be ascribed to particular conformations of the ^iPr groups (Scheme 4). There are reports on analogous dynamic properties of diisopropylamides or -thioamides for which a vary-

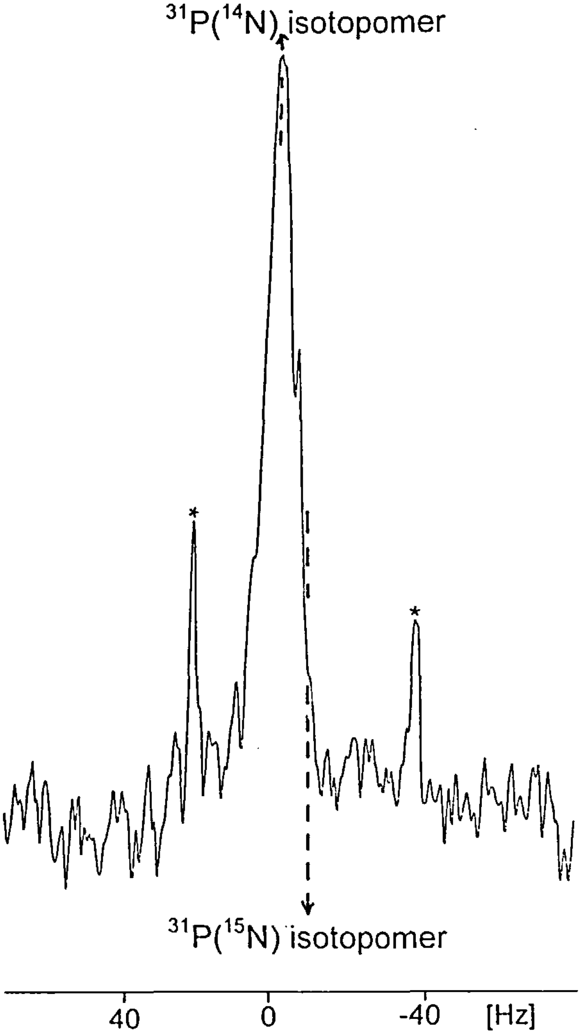


FIGURE 5 121.5 MHz ^{31}P NMR spectrum (INEPT-HEED, ^{1}H decoupled) of tBu$_2$P(NSN)B[N(^{i}Pr)CH$_2$-]$_2$ (**15c**) at 25°C in toluene[d$_8$] (HE delay 0.11 s); 16 scans; $^{1}J(^{31}P^{15}N) = 59.8$ Hz; $^{1}\Delta^{15/14}N(^{31}P) = -62.4$ ppb. Asterisks indicate ^{15}N satellites

ing number of conformations of ^{i}Pr groups has been observed [22]. In principle, restricted rotation about the B-N(sulfur diimide) bond is also conceivable for **18a.** However, this would cause the presence of additional isomers in the cases of **19a** and **20a** which were not observed.

TABLE V : NMR data [a] of $R^1R^2NB(NSNR)_2$ **(17a-20a, 17b)**

Compound	$\delta^{13}C$			$\delta^{11}B$	$\delta^{15}N$			*[b]*
	R	R^1	R^2		*=NR*	*=NB*	NR^1R^2	
R = ^{t}Bu	30.1	16.0	--	25.5	-66.6	-63.6	-287.6	**B, C**
$R^1 = R^2 =$ Et	61.3	41.4		(320)				
17a [c]								
R = ^{t}Bu	29.0	21.2	--	25.3	-61.8	-57.3	-269.1	**C**
$R^1 = R^2 = {}^i$Pr	60.2	48.1		(215)	-72.5	-68.8		
18a [d]	29.3	23.9						
	61.3	43.0						
R = ^{t}Bu	28.3	54.6	[f]	26.0	-68.4	-69.6	-278.1	**B, C,**
R^1 = Bz, R^2 = Ph	60.9			(335)		-71.0		**D**
19a [e]	28.4				-60.9			
	61.6							
R = ^{t}Bu	28.9	49.6	30.6	27.0	-63.7	-57.2	-282.2	**C**
R^1=Bz	61.5	142.6	54.6	(500)	-73.1	-68.5		
$R^2 = {}^t$Bu	29.0	125.9						
20a [g]	60.4	128.0						
		125.8						
R = $SiMe_3$	1.1	15.7	--	24.6	-77.8	-59.6	-284.5	**B, C**
$R^1 = R^2 =$ Et	[59.1]	41.4		(295)				
17b [h]								

[a] ^1H, ^{11}B, ^{13}C and ^{14}N NMR spectra recorded at +25°C (a) in toluene[d_8]: **10a,b, 11a**, (b) in CD_2Cl_2 : **12a, 13a**; ^{13}C NMR spectra recorded (a) at −50°C, in CD_2Cl_2: **12a,b**, (b) at −70°C, in toluene[d_8]: **11a**, in CD_2Cl_2 **13a**; ^{15}N NMR data at −40°C: **10a, 13a**, all others at −50°C (other δ values were determined at 25°C, if not stated otherwise); coupling constants $^1J(^{29}Si^{13}C)$ in Hz in [ ]; $h_{1/2}$ [Hz] in ( ); br = broad; d = doublet; q = quadruplet; sp = septet; t = triplet.

[b] *See footnote [c]Table I; D: two dimensional heteronuclear* $^{15}N/^1H$ *shift correlation* (based on $^3J(^{15}N^1H)$).

[c] δ^1 H = 1.40 (^{t}Bu), 0.93 (CH_3, t), 2.89 (CH_2, q); $\delta^{14}N$ = −68.0, −285.0.

[d] δ^1H= 1.52 (^{t}Bu), 1.18 (CH_3, d), 3.53 (CH, sp); δ^1H(-70°C) = 1.37, 1.44 (^{t}Bu), 1.00, 1.18 (CH_3, d), 3.16, 3.63 (CH, sp); $\delta^{13}C$(+25°C) = 30.5, 61.5 (^{t}Bu), 23.5 (CH_3), 46.4 (CH); $\delta^{14}N$ = −73.0, −269.0; $\delta^{15}N$(-70°C) = −59.6, −65.1, −72.7, −75.8, −272.6.

[e] δ^1H= 1.52 (^{t}Bu), 4.79 (CH_2), 7.16, 7.30 (Ph); δ^1H(-50°C) = 1.41, 1.59 (^{t}Bu), 4.81 (CH_2), 7.14, 7.27 (Ph); $\delta^{13}C$(+25°C) = 29.7, 61.7 (^{t}Bu), 54.7 (CH_2), 140.3, 146.4 (C^i), 124.7, 126.7 (C^P), 127.4, 127.7, 128.2, 128.4 ($C^{o/m}$) ; $\delta^{14}N$ = −69.5, −284.0.

[f] Other $\delta^{13}C$ data: 139.4 (Ph, C^i), 145.0 (Bz, C^i), 124.3, 126.6 (C^P), 126.8, 127.2, 128.2, 128.3 ($C^{o/m}$).

[g] δ^1H= 1.24 (B-N^{t}Bu), 1.35 (^{t}Bu, br), 4.30 (CH_2), 7.02, 7.13 (Ph); δ^1H(-70°C) = 1.24 (B-N^{t}Bu), 1.31, 1.50 (^{t}Bu), 4.26 (CH_2), 7.18, 7.26 (Ph); $\delta^{13}C$(+25°C) = 31.6, 55.1 (B-N^{t}Bu), 30.4, 61.3 (^{t}Bu), 50.4 (CH_2), 143.1 (C^i), 126.7 (C^o), 128.5 (C^m), 126.4 (C^P).

[h] δ^1H= 0.26 ($SiMe_3$), 0.94 (CH_3, t), 2.90 (CH_2, q); $\delta^{14}N$ = −71.0, −288.0; $\delta^{15}N$ = −77.0 ($NSiMe_3$).

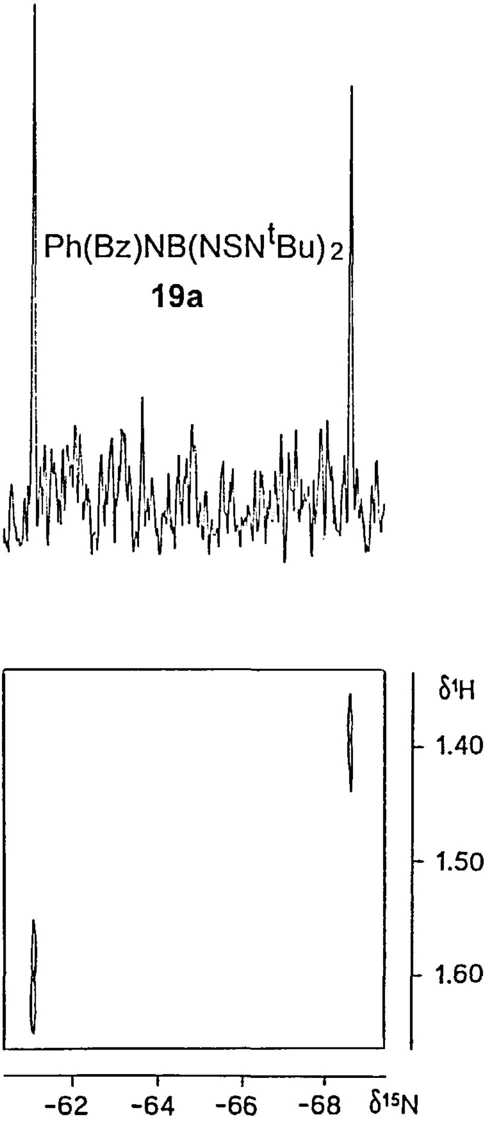
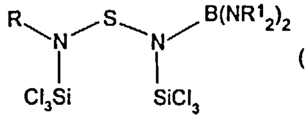


FIGURE 6 =N^{t}Bu region of the 2D{^{15}N^{1}H} NMR spectrum of Ph(PhCH$_2$)NB(NSNtBu$_2$)$_2$ (19a) in CD$_2$Cl$_2$, recorded at −50°C; ^{3}J(^{15}N^{1}H) was assumed to be 2.2 Hz

2.3.5 Diaminosulfanes (21b, 22a)

The ^{29}Si NMR spectra of **21b** and **22a** show two signals each, at lower frequencies, in the typical range of N-SiCl$_3$ groups [12]. In the case of **21b**, there is an additional signal at higher frequency (see Table VI). By using the INEPT pulse sequence, based on $^2J(^{29}Si^1H)$, only the latter NMR signal of the Me$_3$Si group was recorded. The observed $\delta^{15}N$ values are in the typical region for aminoboranes.

TABLE VI : NMR data[a] of



(21b, 22a)

Compound	δ^1H		$\delta^{13}C$		$\delta^{11}B$	$\delta^{29}Si$		$\delta^{15}N$	
	R	*R^1*	*R*	*R^1*		*R*	*SiCl$_3$*	*NR*	
R=SiMe$_3$	0.47	1.06	3.12	15.2	33.5	+22.5	-25.4	-315.0	-324.5
R^1 = Et		3.06		42.7			-27.3		-328.5
21b									
R = ^{t}Bu	1.36	0.97	29.7	23.3	31.0	---	-25.1	-308.8	-289.5
R^1 = ^{i}Pr		3.18	62.0	47.1			-26.1		-323.0
22a									

[a] ^{1}H, ^{13}C, ^{11}B and ^{29} Si NMR spectra recorded at +25°C, ^{15}N NMR spectra recorded at -50°C in toluene[d$_8$], assignment of the ^{15}N resonances is based upon refocused INEPT [14] experiments.

3. EXPERIMENTAL

All compounds were handled in an atmosphere of dry argon, and carefully dried solvents were used for the synthesis and for the preparation of the samples for NMR measurements. The potassium salts K(NSN)K[23], K[(NSN)R] (R = ^{t}Bu, SiMe$_3$, P^{t}Bu$_2$) [24], ^{i}Pr$_2$NB(NSN)$_2$BN^{i}Pr$_2$ (**1**) [11], Me$_3$Si(NSN)SiMe$_3$ [25], ^{t}Bu$_2$BCl [26], (cyclo-C$_5$H$_9$)$_2$BCl [27], (R$_2$N)$_2$BCl (R = Et, ^{i}Pr) [28], R$_2$NBCl$_2$ (R = Et, ^{i}Pr) [29], BzRNBCl$_2$ (R = Ph, ^{t}Bu) [30] and 1, 3-dialkyl-2-chloro-1, 3,2-diazaboracyclopentane, ClB(NRCH$_2$-)$_2$

(R = Me, ^{n}Bu, ^{i}Pr, ^{t}Bu) [31], were prepared according to literature procedures.

3.1 Syntheses of boryl-substituted sulfur diimides $R^1R^2B(NSN)R$ (2 – 8, 9a, 10a, 11a,b, 12a,b, 9b), of sulfur diimides bearing diazaborolidinyl substituents (5 - 8, 13a – 16a, 13b, 15c), *and of bis(sulfurdiimido)boron compounds*(17a – 20a, 17b)

General procedure

A suspension of K[(NSN)R] (R = ^{t}Bu, $SiMe_3$, P^tBu_2; 6 mmol) in hexane (30 ml) · was combined with a solution of R^1R^2BCl, $ClB(\text{-}NRCH_2\text{-}CH_2NR\text{-})_2$ (6 mmol) or $R^1R^2NBCl_2$ (3 mmol), respectively, in ether (20 ml) at –78°C. The mixture was stirred for 30 min at –78°C and then warmed to –5°C (**2**, **8**, **9a,b**, **10a**, **16a**), or room temperature, respectively. After filtration the solvent was removed in vacuo. The products **3–7**, **9a**, **11a-20a**, **9b**, **11b-13b** and **17b** are yellow to orange liquids, **15c** is a red oil, **2**, **8** and **10a** are pale yellow powders which decompose at temperatures > 0°C. The yields are in the range of 75–85%.

3.2 Reactions of boryl-substituted sulfur diimides with hexachlorodisilane

General procedure

Hexachlorodisilane (2 mmol) in 20 ml of hexane was added to a solution of $R(NSN)B(NR^1{}_2)_2$ (R^1 = Et, ^{i}Pr) (2 mmol) in 30 ml of hexane at -78°C. The mixture was warmed to room temperature and stirred for additional 5 h. Finally the solvent was removed in a high vacuum. **21b** (70 %) and **22a** (75 %) were obtained as orange oils.

3.3 NMR Spectroscopic studies

NMR instruments (all equipped with multinuclear units and variable-temperature-control units) for liquid state measurements were JEOL FX 90Q (^{11}B NMR), JEOL JNM-EX 270 E (^{1}H, ^{13}C NMR), Bruker ARX 250 and Bruker AC 300 (^{1}H, ^{11}B, ^{13}C, ^{14}N, ^{15}N, ^{29}Si, ^{31}P NMR). Chemical shifts are given with respect to Me_4Si [for δ^1H ; $\delta^{13}C$:$\delta^{13}C(C_6D_5CD_3) = 20.4$,

$\delta^{13}C(C_6D_6) = 128.0$, $\delta^{13}C(CD_2Cl_2) = 53.8$; and $\delta^{29}Si$: $\delta^{29}Si = 0$, for $\Xi(^{29}Si) = 19.867184$ MHz], neat $MeNO_2$ [$\delta^{14}N$, $^{15}N = 0$, for $\Xi(^{14}N) = 7.226455$ MHz and $\Xi(^{15}N) = 10.136767$ MHz], BF_3-OEt_2 [$\delta^{11}B = 0$, $\Xi(^{11}B) = 32.083971$ MHz] and aqueous H_3PO_4, (85%) [$\delta^{31}P = 0$, $\Xi(^{31}P) = 40.480747$ MHz]. A Bruker MSL 300 instrument (equipped with a multinuclear double-bearing probe head) served for the solid state ^{15}N CP/MAS NMR measurement; the sample was packed in an air-tight insert [32] fitting exactly into the commercial ZrO_2 rotor. The spectrum was run at two different spinning speeds for assignment of the isotropic δ values.

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