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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 = ^tBu, SiMe₃, P^tBu₂) and K(NSN)K, with various boron chlorides R¹₂BCl (R¹ = ^tBu, ^cpent, Et₂N, ⁱPr₂N), [CH₂N(R¹)]₂BCl (R¹ = Me, ⁿBu, ⁱPr, ^tBu) and R¹R²NBCl₂ (R¹ = R² = Et, iPr ; R¹ = PhCH₂, R² = ^tBu; R¹ = PhCH₂, R² = Ph) lead to the corresponding boryl-substituted sulfur diimides 2 - 8, 9a - 20a, 9b, 11b - 13b, 17b and 15c.The sulfur diimides (Et₂N)₂B(NSN)SiMe₃ (11b) and (ⁱPr₂N)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 SiCl₃ substituents. A complete NMR spectroscopic study was carried out for the known cyclic sulfur diimide ⁱPr₂B(NSN)₂BNⁱPr₂ (1). All non-cyclic compounds were studied by ¹H, ¹¹B, ¹³C and ¹⁵N NMR at variable temperature aiming for configurational assignment. The ¹⁵N 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.



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 ¹⁵N 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 Si₂Cl₆ was studied for comparison with previous results where cleavage of the Si-Si bond had been observed ¹².



2. RESULTS AND DISCUSSION

2.1 Synthesis of boryl-substituted sulfur diimides

The reaction of the potassium salts K[(NSN)R] (R = ^tBu, SiMe₃, P^tBu₂) 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, SiMe₃) 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(diethyl-amino)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[d₆].



Tris(diethylamino)borane is also formed in the reaction of K(NSN)SiMe₃ with bis(diethylamino)boron chloride, in addition to the desired unsymmetrically substituted sulfur diimide **11b** and the symmetri-

cally 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)SiMe₃] 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)].



2.3 NMR spectroscopic results

The complete sets of NMR data of all compounds are listed in Tables I - VI. ¹⁵N NMR spectra have been measured by using one of the following methods: (i) ¹H inverse-gated decoupling for suppression of the NOE ¹³, (ii) direct measurement with ¹H decoupling and (iii) application of the refocused INEPT pulse sequence ¹⁴ with ¹H decoupling (polarization transfer based on ${}^{3}J({}^{15}N{}^{1}H)$). Application of the latter pulse sequence, based on



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

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

¹⁵N NMR – The δ^{15} N(NSiMe₃) value of ^tBu₂B(NSN)SiMe₃ (9b) (-132.8) is rather close to that of the E/Z isomer of ^tBu(NSN)SiMe₃ (-141.5) where

the SiMe₃ group occupies the Z position ^{9a}. Similarly, the $\delta^{15}N(N^{t}Bu)$ value of tBu₂B(NSN)^tBu (9a) (-101.2) corresponds to the $\delta^{15}N[N^{t}Bu(Z)]$ 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 Me₃Si 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.

Compound	δ	$\delta^{I}H$		$\delta^{I3}C$		δ ¹⁵ N		(-1
	R	R^{I}	R	R ¹	[b]	NB	NR	- [C]
$R = BR_{2}^{1};$		1.05		28.6	51.8	-89.1	•	Α
$R^1 = {}^tBu$				24.4	(400)	(4.0)		
2 [d]								
$R = {}^{t}Bu$	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 = ^t Bu	1.24	1.29	29.7	27.1	50.5	n.m.	n.m.	
$R^1 = C_5 H_9$		1.47	60.1	27.2	(800)			
10a [g]		1.63	•	28.8				
				29.5				

TABLE I NMR data^[a] of R(NSN)BR¹₂ (2, 9a,b, 10a)

[a] Coupling constants ${}^{2}J({}^{29}Si^{1}H)$ 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 ¹⁵N NMR spectra : A: direct measurement, B: refocused INEPT pulse sequence [14]; C: inverse-gated ¹H decoupling [13]. [d] In toluene[d₈], measured at -50° C; δ values at 25° C: δ^{1} H = 1.02; δ^{13} C = 29.1, 24.5; δ^{14} N = -86.0.

[e] In toluene[d₈], measured at -40° C; δ values at 25°C: δ^{1} H = 1.00 (B'Bu), 1.35 ('Bu); δ^{13} C = 29.5, 23.0 (br) (B'Bu), 30.0, 60.3 ('Bu); δ^{14} N = -64.0, -101.0.

[f] In tolucne[d₈], measured at -50° C; δ values at 25° C δ^{1} H= 0.07 (SiMe₃), 0.86 (B'Bu); δ^{13} C = 1.1 (SiMe₃), 29.0, 23.5 (br) (B'Bu); δ^{29} Si = +0.8; δ^{14} N = -39.0, -128.0; $\delta^{15}N(-70^{\circ}C) = -31.8$ (=NB), -132.8 (=NSiMe₃).

[g] In toluene[d₈], measured at +25°C; δ^{14} N = -64.0; δ values at -70°C; δ^{1} H = 0.96, 1.03, 1.25 (¹Bu), 1.20 (²CH), 1.40, 1.69 (²CH₂); δ^{13} C = 29.0, 59.8, 31.1, 61.3, 61.4, 31.6, 59.4 (¹Bu), 32.4 (CH), 26.9, 27.1, 28.7, 29.3 (CH₂).



FIGURE 1: A 30.5 MHz ¹⁵N{¹H} NMR spectrum of ${}^{1}Bu_{2}B(NSN)B{}^{1}Bu_{2}$ (2) in toluene[d₈], recorded at -50°C; B 30.5 MHz ¹⁵N{¹H} NMR spectrum of ${}^{1}Bu(NSN)B{}^{1}Bu_{2}$ (9a) in toluene[d₈], recorded at -40°C; C 30.5 MHz ¹⁵N{¹H} NMR spectrum of Me₃Si(NSN)B{}^{1}Bu_{2} (9b) in toluene[d₈], 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 H₂B(NSN)BH₂ is suggested as a compromise: the H₂B 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.



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 ^tBu or a SiMe₃ group on the $^{15}N(B)$ resonance is similar as in other sulfur diimides (see Table I and Figure 1). ¹¹B NMR -The ¹¹B 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 ¹¹B 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 ¹¹B 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 ¹¹B 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-1 λ^4 ,5 λ^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.



At lower temperature (below -20° C) the ¹H and ¹³C 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 ¹³C(Me) resonances are detected in the ¹³C NMR spectrum. This is in agreement with reported data ¹¹ and indicates hindered rotation about the B-NⁱPr₂ bonds. However, at -90°C the ¹³C NMR spectrum clearly shows the presence of a second conformer for which also two ¹³C(CH) and four ¹³C(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 NⁱPr₂ groups. These features are also reflected in the ¹⁵N NMR spectrum at -50°C. It shows two ¹⁵N(N=S) resonances for each conformer (Figure 3). At -20° C, when the rotation about the N-C bonds is still fast, only one ¹⁵N resonance is detected. The ¹⁵N 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 $BN(pp)\pi$ 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 ¹⁵N CP/MAS NMR spectrum of 1 shows at least two ¹⁵N(N=S) resonances. Unfortunately, the signals are extremely broad, probably as the result of unresolved ¹⁵N-¹¹B scalar and dipolar coupling, and effects exerted by the ¹¹B quadrupolar moment. Therefore, the signal-to-noise ratio is insufficient for a reliable assignment of the actual number of ¹⁵N resonances.

$\delta^{I}H$		δ ¹	³ C	δ ¹⁵	temp.	
Me	СН	Me	СН	=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*				

TABLE II NMR data ^[a] of ${}^{i}Pr_{2}NB(NSN)_{2}BN^{i}Pr_{2}$ (1) at different temperatures and of $1(NEt_{2})$ ^[b]

[a] Measured in CD₂Cl₂ ; $\delta^{11}B(+25^{\circ}C) = 22.8$; $\delta^{14}N(+25^{\circ}C) = -77.0$, -255.0; $h_{1/2}$ in (); (br) = broad; d = doublet; sp = septet; the signals of the minor conformer are marked by *. [b] 1(NEt₂)₁ measured in toluene[d₈]; ¹H, ¹¹B, ¹³C and ¹⁴N NMR spectra recorded at +25°C; $\delta^{1}H= 0.86$, 2.82 (NEt₂); $\delta^{13}C = 15.5$, 42.1 (NEt₂); $\delta^{11}B = 24.5$; $\delta^{14}N = -71.0$ (=NB), -288.0 (NEt); $\delta^{15}N(-40^{\circ}C) = -75.3$ (=NB); $\delta^{15}N(-60^{\circ}C) = -75.5$ (=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 CD₂Cl₂, recorded at –90°C

The ¹¹B nuclear shielding in 1 (δ^{11} B 22.8) is greater than in ⁱPr₂NBCl₂ (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 ¹¹B 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(NR₂)₃ (Tables III and IV), in accordance with



FIGURE 3 NSN part of the 30.5 MHz $^{15}N\{^{1}H\}$ NMR spectrum of $^{i}Pr_{2}NB(NSN)_{2}BNPr_{2}$ (1) in CD₂Cl₂, recorded at $-50^{\circ}C$

BN(pp) π bonding ¹⁸. The δ^{14} N values of 6 correspond to the literature values ^{10 b}

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 ^tBu and the Me₃Si group prefer the Z positions (averaged $\delta^{15}N$ values are -74 for N^tBu and -84 for NSiMe₃ 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.

Compound	$\delta^{I3}C$		sllp		<u> </u>		
	R	R ¹	- 0-8	=NR	=NB	B-N	- [0]
$R = BR^1R^2$		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
$R^1 = N^i Pr_2$	60.1	46.1					
4 [d]							
R = ^t Bu	30.5	15.8	26.2	-76.5	-59.9	-317.3	B, C
$R^1 = NEt_2$	60.2	42.0					
11a [e]							
$R = {}^{t}Bu$	30.9	23.9	29.6	-84.1	-50.9	-289.5	A, B
$R^1 = N^i Pr_2$	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
$R^1 = N^i Pr_2$	(53.8)	46.2					
10L (L)							

TABLE III NMR data^[a] of R(NSN)BR¹₂ (3, 4, 11a,b, 12a,b)

12b [h]

[a] Solutions in C₆D₆, ¹¹B and¹³C NMR spectra recorded at +25°C; coupling constants ${}^{1}J({}^{29}Si^{13}C)$ in Hz in (); d = doublet; t = triplet; q = quadruplet; sp = septet.

[b] See footnote [c] Table I.

[c] ¹⁵N NMR spectrum recorded at -50° C, in toluene[d₈]; δ values at 25°C: δ^{1} H= 0.97 (CH₃ t), 2.90 (CH₂, q); δ^{14} N = -77.6, -316.6. [d] ¹⁵N NMR spectrum recorded at -50°C, in toluene[d₈]; δ values at 25°C: δ^{1} H= 1.19 (CH₃)

d), 3.51 (CH, sp); δ^{14} N = -65.0, -250.0.

d), 5.51 (CH, sp); $\delta^{1*}N = -65.0, -250.0.$ [e] ¹⁵N NMR spectrum recorded at -40°C, in toluene[d₈]; δ values at 25°C: $\delta^{1}H= 1.40$ ('Bu), 0.96 (CH₃, t), 2.89 (CH₂, q); $\delta^{14}N = -63.0, -288.0.$ [f] ¹⁵N NMR spectrum recorded at -60°C, in toluene[d₈]; 6 values at 25°C: $\delta^{1}H= 1.60$ ('Bu), 1.20 (CH₃, d), 3.50 (CH, sp); $\delta^{14}N = -78.0, -308.0; \delta^{13}C(-80°C) = 30.1, 59.7$ ('Bu), 23.2 (CH₃), 45.3 (CH). [g] ¹⁵N NMR spectrum recorded at -60°C, in toluene[d₈]; δ values at 25°C: $\delta^{1}H= 0.17$ (SiMe₃), 0.97 (CH₃, t), 2.85 (CH₂, q); $\delta^{14}N = -58.0$ (=NSiMe₃),-79.0 (=NB), -317.0 (NEt₂); $\delta^{29}S_{1} = 2.0$

 δ^{29} Si = -2.0.

[h] ¹⁵NMR spectrum recorded at -40°C, in toluene[d₈]; δ values at 25°C: δ ¹H= 0.21 (SiMe₃), 1.10 (CH₃, d), 3.39 (CH, sp); δ ¹⁴N = -41.0, -278.0; δ ¹⁵N = -80.5 (=NSiMe₃); δ ²⁹Si = -1.2.

R¹ N N B(NSN) B TABLE IV : NMR data^[a] of (5-8) and B(NSN)R (13a-16a, 13b, 15c) h1 h1 k1

l	$\delta^{I3}C$			sllp		δ ¹⁵ N		
Compouna	CH ₂	R^{I}	R^{I} R		=NB	=NR	NRI	- [0]
$\overline{R^1} = Me$	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	С
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)	
$R^1 = {}^tBu$	51.3	30.6		25.6	-61.0		-294.1	Α
8[f]		44.3		(250)	(7.1)		(5.8)	
$R^1 = Me, R = {}^tBu$	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)	
$R^1 = {}^nBu, R = {}^tBu$	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						
$R^1 = {}^iPr, R = {}^tBu$	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)	
$R^1 = {}^tBu, R = {}^tBu$	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)	
$R^1 = {}^{i}Pr, R = P^{t}Bu_2$	45.0	21.8	28.4	25.4	-80.1	-75.9	-306.0	C
15c [1]		41.6	34.9	(260)	(7.3)	(5.0)	(8.7)	

[a] In toluene[d_s] ¹H, ¹B, ¹³C, ¹⁴N and ²³Si NMR spectra recorded at +25°C, ¹³N NMR spectra recorded at -50°C (other δ values determined at 25°C, if not stated otherwise); coupling constants ¹J(²⁹Si¹³C) in Hz in (); d = doublet; m = multiplet; sp = septet; t = triplet.

Coupling constants 1 (or c) in the in (c), d = 2626.04, in (



FIGURE 4: NSN part of the 30.5 MHz ${}^{15}N{}^{1}H$ NMR spectrum of a mixture of $(Et_2N)_2B(NSN)^{1}Bu$ (11a) and $Et_2NB(NSN^{1}Bu_2)_2$ (17a) in toluene[d₈], recorded at $-50^{\circ}C$

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 ^tBu 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(³¹P,¹⁵N) = 59.8 Hz and the isotope induced chemical shift ¹ Δ ^{15/14}N(³¹P) = -62.4 ppb at natural abundance of ¹⁵N (Figure 5). The δ ³¹P value and the coupling constant ¹J(⁵¹P,¹⁵N), determined at room temperature, point towards Z/E-isomerization of the P^tBu₂ group in 15c. At lower temperature the ³¹P NMR signal is shifted to lower frequencies close to the range which was found typical of the E positions of P^tBu₂ groups ^{8b}. However, the δ ¹⁵N value (-75.9; determined at -50°C) does not support this structural assignment, since δ ¹⁵N around -35 would be expected by comparison with other sulfur diimides bearing the P^tBu₂in Z positions ^{8b}. Therefore, this question cannot be settled without further structural information.

The δ^{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 δ^{15} N(NR) (R = ^tBu, SiMe₃) 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, ¹³C and ¹⁵N NMR spectra of **18a**, **19a** and **20a** show the presence of two different = $N^{t}Bu$ groups, both occupying the Z position (Figure 6). In addition, the ¹⁵N 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 $\Delta G^{\#} = 45.6 \pm 1 \text{ kJ/mol} (\Delta G^{\#} = 46.4^{-11})$, 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 NⁱPr 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 ³¹P NMR spectrum (INEPT-HEED, ¹H decoupled) of tBu₂P(NSN)B[N(¹Pr)CH₂-]₂ (15c) at 25°C in toluene[d₈] (HE delay 0.11 s); 16 scans; ¹J(³¹P¹⁵N) = 59.8 Hz; ¹\Delta^{15/14}N(³¹P) = -62.4 ppb. Asterisks indicate ¹⁵N satellites

ing number of conformations of ⁱPr 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.

A	_	_ 12				. 16		
Compound		διος		SILR		њ		
Compound	R	$\overline{R^{I}}$	R ²	- 0 0	=NR	=NB	NR ¹ R ²	. [0]
$R = {}^{t}Bu$	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	С
$\mathbf{R}^1 = \mathbf{R}^2 = {}^{i}\mathbf{P}\mathbf{r}$	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	В, С,
$R^1 = Bz, R^2 = Ph$	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	С
R ¹ =Bz	61.5	142.6	54.6	(500)	-73.1	-68.5		
$R^2 = {}^tBu$	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 (b)								

TABLE V: NMR data ^[a] of R¹R²NB(NSNR)₂ (17a-20a, 17b)

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[a] ¹H, ¹¹B, ¹³C and ¹⁴N NMR spectra recorded at +25°C (a) in toluene[dg]: 10a,b, 11a, (b) in CD_2Cl_2 : 12a, 13a; ¹³C NMR spectra recorded (a) at -50°C, in CD_2Cl_2 : 12a,b, (b) at -70°C, in toluene[d₈]: 11a, in CD_2Cl_2 : 13a; ¹⁵N 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(²⁹Si¹³C) 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 ¹⁵N/¹H shift correlation (based on ³J(¹⁵N¹H)).

(based on "J(")N'H)). [c] $\delta^1 H = 1.40$ ('Bu), 0.93 (CH₃, t), 2.89 (CH₂, q); $\delta^{14}N = -68.0, -285.0$. [d] $\delta^1H = 1.52$ ('Bu), 1.18 (CH₃, d), 3.53 (CH, sp); $\delta^1H(-70^{\circ}C) = 1.37, 1.44$ ('Bu), 1.00, 1.18 (CH₃, d), 3.16, 3.63 (CH, sp); $\delta^{13}C(+25^{\circ}C) = 30.5, 61.5$ ('Bu), 23.5 (CH₃), 46.4 (CH); $\delta^{14}N = -73.0, -269.0; \delta^{15}N(-70^{\circ}C) = -59.6, -65.1, -72.7, -75.8, -272.6.$ [e] $\delta^1H = 1.52$ ('Bu), 4.79 (CH₂), 7.16, 7.30 (Ph); $\delta^1H(-50^{\circ}C) = 1.41, 1.59$ ('Bu), 4.81 (CH₂), 7.14, 7.27 (Ph); $\delta^{13}C(+25^{\circ}C) = 29.7, 61.7$ ('Bu), 54.7 (CH₂), 140.3, 146.4 (Ci), 124.7, 126.7 (C^P), 127.4, 127.7, 128.2, 128.4 (C^{o·m}); $\delta^{13}N = -69.5, -284.0.$ [f] Other $\delta^{13}C$ data: 139.4 (Ph, Cⁱ), 145.0 (Bz, Cⁱ), 124.3, 126.6 (C^P), 126.8, 127.2, 128.2, 128.3 (C^{om})

128.3 (Corm).

[g] $\delta^1 H$ = 1.24 (B-N¹Bu), 1.35 (^tBu, br), 4.30 (CH₂), 7.02, 7.13 (Ph); $\delta^1 H$ (-70°C) = 1.24 $\begin{bmatrix} B^*N^*Bu \\ 1, 31, 1.50 \\ (Bu), 4.26 \\ (CH_2), 7.18, 7.26 \\ (Ph); \delta^{13}C(+25^\circ C) = 31.6, 55.1 \\ (B^*N^*Bu), 30.4, 61.3 \\ (Bu), 50.4 \\ (CH_2), 143.1 \\ (C), 126.7 \\ (C^\circ), 128.5 \\ (C^m), 126.4 \\ (C^P). \\ [h] \delta^1H = 0.26 \\ (SiMe_3), 0.94 \\ (CH_3, t), 2.90 \\ (CH_2, q); \delta^{14}N = -71.0, -288.0; \delta^{15}N = -77.0 \\ . \\ \end{tabular}$

(NSiMe₃).



FIGURE 6 =N^tBu region of the 2D{¹⁵N¹H} NMR spectrum of Ph(PhCH₂)NB(NSNtBu₂)₂ (19a) in CD₂Cl₂, recorded at -50°C; ³J(¹⁵N¹H) was assumed to be 2.2 Hz

2.3.5 Diaminosulfanes (21b, 22a)

The ²⁹Si NMR spectra of **21b** and **22a** show two signals each, at lower frequencies, in the typical range of N-SiCl₃ 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(²⁹Si¹H), only the latter NMR signal of the Me₃Si group was recorded. The observed δ^{15} N values are in the typical region for aminoboranes.

TABLE VI: NMR data ^[a] of $\begin{array}{c} R \\ R $										
Compound	δ ¹	H	δ ¹	³ C	 sllp	δ ²⁹	Si	δ ¹	5 _N	
Compouna -	R	R ¹	R	R^{I}	0 0	R	SiCl ₃	NR		
R=SiMe3	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	
$R^1 = {}^iPr$		3.18	62.0	47.1			-26.1		-323.0	
22a										

[a] ¹H, ¹³C, ¹¹B and ²⁹ Si NMR spectra recorded at +25°C, ¹⁵N NMR spectra recorded at -50°C in toluene[d₈], assignment of the ¹⁵N 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 = ^tBu, SiMe₃, P^tBu₂) ²⁴, ⁱPr₂NB(NSN)₂BNⁱPr₂ (1) ¹¹, Me₃Si(NSN)SiMe₃ ²⁵, ^tBu₂BCl ²⁶, (cyclo-C₅H₉)₂BCl ²⁷, (R₂N)₂BCl (R = Et, ⁱPr) ²⁸, R₂NBCl₂ (R = Et, ⁱPr) ²⁹, BzRNBCl₂ (R = Ph, ^tBu) ³⁰ and 1, 3-dialkyl-2-chloro-1, 3,2-diazaboracyclopentane, CIB(NRCH₂-)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] ($R = {}^{t}Bu$, SiMe₃, P^tBu₂; 6 mmol) in hexane ml) . was combined with solution of R¹R²BCL (30)a ClB(-NRCH₂-CH₂NR-)₂ (6 mmol) or R¹R²NBCl₂ (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 $R(NSN)B(NR_2^1)_2$ ($R^1 = Et$, ⁱPr) (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 (¹¹B NMR), JEOL JNM-EX 270 E (¹H, ¹³C NMR), Bruker ARX 250 and Bruker AC 300 (¹H, ¹¹B, ¹³C, ¹⁴N, ¹⁵N, ²⁹Si, ³¹P NMR). Chemical shifts are given with respect to Me₄Si [for δ^{1} H; δ^{13} C : δ^{13} C (C₆D₅CD₃) = 20.4

 $δ^{13}C(C_6D_6) = 128.0$, $\delta^{13}C(CD_2Cl_2) = 53.8$; and $\delta^{29}Si$: $\delta^{29}Si = 0$, for $\Xi(^{29}Si) = 19.867184$ MHz], neat MeNO₂ [$\delta^{14}N$, $^{15}N = 0$, for $\Xi(^{14}N) = 7.226455$ MHz and $\Xi(^{15}N) = 10.136767$ MHz], BF₃-OEt₂ [$\delta^{11}B = 0$, $\Xi(^{11}B) = 32.083971$ MHz] and aqueous H₃PO₄, (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 ¹⁵N CP/MAS NMR measurement; the sample was packed in an air-tight insert ³² fitting exactly into the commercial ZrO₂ rotor. The spectrum was run at two different spinning speeds for assignment of the isotropic δ values.

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References

- [1] R. Bussas, G. Kresze, H. Münsterer and A. Schwöbel, Sulfur Rep. 2, 215 (1983).
- [2] a) R. Busetti, Acta Crystallogr., Sect. B 38, 665 (1992); b) G. Leandri, V. Busetti, G. Valle and M. Mammi, J. Chem. Soc., Chem. Commun. 1970, 413.
- [3] a) R. Jones, D.J. Williams, P.T. Wood and J.D. Woollins, Polyhedron 8, 91(1989); b) H. Münsterer, G. Kresze, V. Lamm and A. Gieren, J. Org. Chem. 48, 2833 (1983).
- [4] a) A. Gieren, H. Betz, T. Hübner, V. Lamm, M. Herberhold and K. Guldner, Z. Anorg. Allg. Chem. 513, 160 (1984); b) F.P. Olsen and J.C. Barrick, Inorg. Chem. 2, 1353 (1973).
- [5] A. Gieren, T. Hübner, M. Herberhold, K. Guldner and G. Süss-Fink, Z. Anorg. Allg. Chem. 538, 21 (1986).
- [6] a) M. Herberhold, S. Gerstmann and B. Wrackmeyer, Phosphorus, Sulfur and Silicon 66, 273 (1992); b) M. Herberhold, S. Gerstmann, B. Wrackmeyer and H. Borrmann, J. Chem. Soc. Dalton Trans. 1994, 633; c) M. Herberhold, S. Gerstmann, W. Milius, B. Wrackmeyer and H. Borrmann, Phosphorus, Sulfur and Silicon 107, 257 (1995).
- [7] a) M. Herberhold, S.M. Frank and B. Wrackmeyer, Z. Naturforsch. 43b, 985 (1988); b)
 M. Herberhold, C. Köhler and B. Wrackmeyer, Phosphorus, Sulfur and Silicon 71, 75 (1992); c) M. Herberhold, C. Köhler and B. Wrackmeyer, Phosphorus, Sulfur and Silicon 68, 219 (1992).
- [8] a) B. Wrackmeyer, C. Köhler and M. Herberhold, Magn. Reson. Chem. 31, 987 (1993);
 b) B. Wrackmeyer, S. Gerstmann and M. Herberhold, Magn. Reson. Chem. 31, 499 (1993); c) M. Herberhold, S. Gerstmann and B. Wrackmeyer, Phosphorus, Sulfur and Silicon 113, 89 (1996).
- [9] a) M. Herberhold, S. Gerstmann and B. Wrackmeyer, Phosphorus, Sulfur and Silicon 112, 261 (1996); b) M. Herberhold, S. Gerstmann and B. Wrackmeyer, in preparation.
- [10] a) W. Haubold, H.G. Fehlinger and G. Frey, Z. Naturforsch, 36b, 157 (1981); b) C. Habben, A. Meller, M. Noltemeyer and G.M. Sheldrick, J. Organomet. Chem. 288, 1 (1985).
- [11] G. Schmid, H. Gehrke, H.-U. Kolorz and R. Boese, Chem. Ber. 126, 1781 (1993).
- [12] a) M. Herberhold, S.M. Frank, B. Wrackmeyer, H. Borrmann and A. Simon, Chem. Ber. 123, 75 (1990); b) B. Wrackmeyer, S.M. Frank, M. Herberhold, A. Simon and H.

Borrmann, J. Chem. Soc. Dalton Trans. 1991, 2607; c) M. Herberhold, S. Gerstmann, W. Milius and B. Wrackmeyer, Z. Naturforsch. 48b, 249 (1993).

- [13] R. Freeman, H.D.W. Hill and R. Kaptein, J. Magn. Reson. 7, 327 (1972).
- [14] a) D.P. Burum and R.R. Ernst, J. Magn. Reson. 39, 163 (1980); b) G.A. Morris, J. Magn. Reson. 41, 185 (1980).
- [15] B. Wrackmeyer, S. Gerstmann, M. Herberhold, G.A. Webb and H. Kurosu, Magn. Reson. Chem. 32, 492 (1994).
- [16] W. Sicinska, L. Stefaniak, M. Witanowski and G.A. Webb, Org. Magn. Reson. 15, 241 (1981).
- [17] R. Boese, personal communication; the proposed conformation P is in accordance with ab initio calculations, carried out on various levels (HF/6- 311 + G(3df); QCISD/6-31G* gives bond lengths S-N 151.6, N-B 139.6 pm and bond angles N-S-N 117.1, S-N-B 166.3 °).
- [18] H. Nöth and B. Wrackmeyer, Chem. Ber. 106, 1145 (1973).
- [19] E. Kupce and B. Wrackmeyer, J. Magn. Reson. 97, 568 (1992).
- [20] a) B. Wrackmeyer, E. Kupce, G. Kehr and J. Schiller, Magn. Reson. Chem. 30, 304 (1992); b). B. Wrackmeyer, E. Kupce, S.M. Frank, S. Gerstmann and M. Herberhold, Phosphorus, Sulfur, Silicon, 69, 179 (1992); c) B. Wrackmeyer, C. Köhler and E. Kupce, Magn. Reson. Chem. 31, 769 (1993); d) B. Wrackmeyer, E. Kupce and A. Schmidpeter, Magn. Reson. Chem 29, 1045 (1991); e). B. Wrackmeyer, G. Kehr and H. Zhou, Fresenius, J. Anal. Chem. 357, 489 (1997); (f) B. Wrackmeyer and G. Kehr, J. Magn. Reson. 107A, 106 (1994).
- [21] B. Wrackmeyer, Annu. Rep. NMR Spectr. 20, 61 (1988).
- [22] A. Liden, C. Roussel, T. Liljefors, M. Chanon, R.E. Carter, J. Metzger and J. Sandstrom, J. Am. Chem. Soc. 98, 2853 (1976).
- [23] M. Herberhold and W. Ehrenreich, Angew. Chem. 94, 631 (1982); Angew. Chem. Int. Ed. Engl. 21, 633 (1982); Angew. Chem. Suppl. 1982, 1346.
- [24] a) D. Hänssgen and B. Ross, Z. Anorg. Allg. Chem. 473, 80 (1981); b) M. Herberhold, W. Ehrenreich, W. Bühlmeyer and K. Guldner, Chem. Ber. 119, 1424 (1986).
- [25] U. Wannagat and H. Kuckertz, Angew. Chem. 74, 117 (1962).
- [26] U. Höbel, H. Nöth and H. Prigge, Chem. Ber. 119, 325 (1986).
- [27] H.C. Brown, N. Ravindran and S.U. Kulkarni, J. Org. Chem. 44, 2417 (1979).
- [28] D.W. Aubrey, M.F. Lappert and M.K. Majumdar, J. Chem. Soc. 1962, 4088.
- [29] W. Gerrard, H.R. Hudson and E.F. Mooney, J. Chem. Soc. 1960, 5168.
- [30] P.Y. Chavant, F. Lhermitte and M. Vaultier, Synlett. 7, 519 (1993).
- [31] T. Wang, P.J. Busse and K. Niedenzu, Inorg. Chem. 9, 2150 (1970).
- [32] L.H. Merwin, A. Sebald, I.E. Espidel and R.K. Harris, J. Magn. Reson. 84, 367 (1989).