Solid-state Structure of Sulfur Bis(trimethylsilylimide), $S(NSiMe_3)_2$, and Multinuclear Magnetic Resonance Studies of Some Sulfur Bis(silylimides) in Solution *

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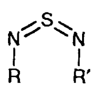
In the solid state sulfur bis(trimethylsilylimide) **1** has been shown to adopt the *E*/*Z* configuration by single-crystal X-ray diffraction (space group $P\bar{1}$, triclinic). In solution sulfur bis(silylimides) R(NSN)R′ [R = R′ = $SiMe_3$ **1** or Si_2Me_5 **2**; R = $SiMe_3$, R′ = Si_2Me_5 **3** or $SiMe_2SiMe_2(NSN)SiMe_3$ **4**] are fluxional at room temperature. Comparison of the ^1H, ^{13}C, ^{29}Si and, in particular, ^{15}N NMR data indicates that **1** and **2** undergo rapid $E/Z \rightleftharpoons Z/E$ isomerization even at 173 K, whereas in the case of **3** and **4** this process is slowed at low temperature and the *E*/*Z* configuration prevails with the $SiMe_3$ group in the *E* position.

Sulfur bis(trimethylsilylimide), $S(NSiMe_3)_2$ **1**, has been extensively used as a versatile reagent in sulfur–nitrogen chemistry.[1] In principle, its structure in solution can be described by any of the three configurations *Z*/*Z*, *E*/*E* and *E*/*Z* (*Z* = *syn*, *E* = *anti*) which are generally possible for sulfur diimides, $S(NR)_2$, bearing identical substituents.[2] However, there appears to be conflicting evidence in the literature concerning the structure of **1**. Analysis of the IR and Raman spectra[3] inferred point group C_2, indicating a distorted *E*/*E* configuration. In contrast a recent electron-diffraction study came to the conclusion that **1** adopts a distorted *Z*/*Z* configuration in the gas phase.[4] Both ^1H and ^{14}N NMR spectra of **1** in solution show a single resonance signal.[5] A single signal was also found in the ^{15}N NMR spectrum,[6] although the reported $\delta(^{15}N)$ value differed considerably from the $\delta(^{14}N)$ value. The conditions for recording the ^{15}N NMR spectrum were probably not correct. All this prompted us to reinvestigate the solution-state NMR spectra of **1** and to compare the data with three other related sulfur diimides **2** (R = R′ = Si_2Me_5),[7] **3** (R = $SiMe_3$, R′ = Si_2Me_5)[7] and **4** [R = $SiMe_3$, R′ = $SiMe_2SiMe_2(NSN)SiMe_3$]. A single-crystal X-ray analysis of **1** was carried out at −160 °C in order to establish its solid-state molecular structure.

Experimental

The sulfur bis(silylimides) **1**,[8] **2**[7] and **3**[7] were prepared as described in the literature. Similar to **2** and **3**, compound **4** was obtained from the reaction between $K(NSNSiMe_3)$ (2 equivalents) and 1,2-dichlorotetramethyldisilane. To a suspension of $K(NSNSiMe_3)$ (0.9 g, 5.4 mmol) in hexane (150 cm^3) was added $ClMe_2SiSiMe_2Cl$ (0.5 g, 2.7 mmol) at room temperature. After stirring for 3 d the mixture was filtered and the solvent removed at high vacuum. The product is a yellow liquid, containing $Me_3Si(NSN)Me_2SiSiMe_2(NSN)SiMe_3$ **4** and $Me_3Si(NSN)SiMe_3$ **1** in a 3:1 ratio.

The NMR spectra (Table 1) were recorded using Bruker AC 300, AM 500 (^{15}N) and a JEOL FX 90Q instrument (^{29}Si), equipped for multinuclear NMR at variable temperature. Conditions for insensitive nuclei enhanced by polarization transfer (INEPT)[9] (^{29}Si, ^{15}N NMR) were optimized according to the coupling constants $^2J(^{29}Si^1H) \approx 7$ Hz and $^3J(^{15}N^1H) \approx 1.3$–1.8 Hz). Careful retuning of the probehead proved to be necessary for the experiments at variable temperature.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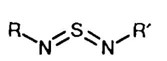
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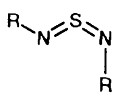
E/*Z*

Crystal Structure Determination of Compound **1**.—Compound **1** was distilled into an X-ray capillary (diameter 0.2 mm) at high vacuum. The capillary was sealed and a needle-like crystal (0.2 × 0.5 × 0.05 mm) grown *in situ* on the diffractometer, maintaining a temperature slightly below its melting point (−52 °C). Preliminary X-ray powder diffraction experiments had shown that **1** is single phase down to −180 °C. Accordingly, the single crystal was cooled to −160 °C at 3 °C h^{-1}.

Crystal data. $C_6H_{18}N_2SSi_2$, $M = 206.46$, triclinic, space group $P\bar{1}$ (no. 2), $a = 6.3647(13)$, $b = 9.9630(18)$, $c = 10.3377(20)$ Å, $\alpha = 73.544(15)$, $\beta = 87.663(16)$, $\gamma = 84.988(15)°$, $U = 626.2(2)$ Å^3 (by least-squares refinement on setting angles for 50 automatically centred reflections; $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 1.095$ g cm^{-3}, $F(000) = 224$, μ(Mo-Kα) = 4.06 cm^{-1}.

Data collection and processing. Synthex $P2_1$ diffractometer; ω–2θ scan mode, scan width 1.28° plus $\alpha_1 - \alpha_2$ separation, scan speed 1.0–29.3° min^{-1}, graphite-monochromated Mo-Kα radiation; 12 207 reflections measured $4.0 \leqslant 2\theta \leqslant 72°$), 5974 unique (merging $R = 0.018$ after absorption correction based on ψ scans).

Structure analysis and refinement. The positions of all non-hydrogen atoms were determined by direct methods.[10] After anisotropic refinement all hydrogen atoms were easily located in a Fourier difference map. Final R and R' values were 0.026 and 0.023, respectively, where $w = 1/[\sigma^2(F) + GFF^*)\{1 - \exp[-B(\sin\theta/\lambda)^2]\}$, $G = 0.000\,02$, and $B = 2.0$. All C–H distances were restrained to a common value.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

NMR Data.—The ^1H, ^{13}C and ^{29}Si NMR spectra of compounds **1** and **2** in $C_6D_5CD_3$ between 173 and 300 K show

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Values of $\delta(^{15}N)$ and $\delta(^{29}Si)$[a] for the sulfur bis(silylimides) **1**–**4**

		$\delta(^{15}N)$		$\delta(^{29}Si)$		
Compound	T/°C	$NSiMe_3$	$NSiMe_2$	$SiMe_3$	$SiMe_2$	$SiMe_2SiMe_3$
1 $Me_3Si(NSN)SiMe_3$[b]	+27	−58.0		+1.6		
	−40	−58.0		+1.9		
	−60	−58.2		+2.0		
	−100	−58.4		+2.4		
2 $Me_5Si_2(NSN)Si_2Me_5$[c]	+27		−56.1		−7.4	−19.5
	−20		−56.2		−7.4	−19.6
	−50		−56.9		−7.3	−19.6
3 $Me_3Si(NSN)Si_2Me_5$[d]	+27	−46.7	−66.4	+1.4	−7.3[e]	−19.4[e]
	−20	−45.2	−71.7	+1.6	−7.1	−19.4
	−50	−38.3	−76.1	+2.0	−6.8	−19.3
4 $Me_3Si(NSN)Me_2Si$[f]	+27	−45.8	−69.1	+1.9	−10.1	
|	−40	−35.6	−76.3	+2.3	−9.8	
$Me_3Si(NSN)Me_2Si$	−50	−33.2	−78.3	+2.4	−9.7	

[a] In $[^2H_8]$toluene. [b] ^{15}N Measurements: INEPT, $^3J(^{15}N^1H)$ = 1.8 Hz assumed. [c] ^{15}N Measurements: INEPT, $^3J(^{15}N^1H)$ = 1.3 Hz assumed. [d] ^{15}N Measurements: +27 °C, INEPT, $^3J(^{15}N^1H)$ = 1.5 Hz assumed; −20 and −50 °C, inverse gated; $\delta(^{29}Si)$ (−80 °C) +2.0 ($SiMe_3$), −6.6 (*Si*Me_2SiMe_3) and −19.2 ($SiMe_2$*Si*Me_3); (+65 °C) +1.1 ($SiMe_3$), −7.4 (*Si*Me_2SiMe_3) and −19.4 ($SiMe_2$*Si*Me_3). [e] $^1J(^{29}Si^{29}Si)$ = 96.4 Hz. [f] ^{15}N Measurements: +27 °C, INEPT, $^3J(^{15}N^1H)$ = 1.3 Hz assumed; −40 and −50 °C, inverse-gated ^1H decoupling.

sharp singlets. No ^{15}N satellites were detected in the ^{29}Si NMR spectra although the signal-to-noise ratio would have been appropriate. The ^{15}N NMR spectra which also show a sharp singlet were readily recorded using the refocused INEPT pulse sequence[9] with ^1H decoupling. Since ^{29}Si satellites were not observed (in spite of the excellent signal-to-noise ratio), the magnitude of $^1J(^{29}Si^{15}N)$ must be very small (< 1 Hz). The successful application of the INEPT technique allows two conclusions: (*i*) there is no rapid exchange at the N–Si bond; and (*ii*) compounds **1** and **2** must either have adopted a fixed configuration (*E*/*E* or *Z*/*Z*, respectively) or the interconversion between the various configurations must be fast as compared to the NMR time-scale, even at 173 K. The latter would lead to the observation of averaged NMR signals, suggesting a rather low energy barrier to inversion at the nitrogen atoms and/or to rotation about the S=N bond.

The sulfur diimide **3** cannot be obtained in pure state since it always contains small amounts of the symmetrical compounds **1** and **2**.[7] Similarly, a small amount of **1** is found in solutions of **4**. This is readily shown by ^1H, ^{13}C, ^{29}Si and, in particular, the ^{15}N NMR spectrum (Fig. 1). The large differences in $\delta(^{15}N)$ observed for **3** and **4**, in comparison with **1** and **2**, strongly indicate that for compounds **3** and **4** the *E*/*Z* configuration prevails in solution. In analogy to Bu^{t}NSNBu^t and other dialkyl or alkyl/aryl sulfur diimides[7] the deshielded ^{15}N nucleus is linked to the substituent in *E* position whereas the shielded ^{15}N nucleus carries the *Z* substituent. This assignment is also supported by ^{15}N NMR data for cyclic sulfur diimides which are necessarily present in the *Z*/*Z* configuration.[11] Two-dimensional ^{15}N–^1H heteronuclear shift correlations (Fig. 2) then show that the Me_3Si group always prefers the *E* position. It clearly follows from the $\delta(^{15}N)$ values of the unsymmetrically substituted sulfur diimides **3** and **4** that the values of **1** and **2** are averaged due to rapid $E/Z \rightleftharpoons Z/E$ interconversion.

Apparently, the energy barrier of the $E/Z \rightleftharpoons Z/E$ isomerization process is much lower in compounds **1** and **2** than in **3** or **4**. Our results show that sulfur bis(silylimides) may be highly fluxional, much more than sulfur bis(organylimides),[12] and that conclusions drawn from NMR spectra must be treated with care, in particular in the case of symmetrically substituted sulfur diimides such as **1** and **2**. Since the ^1H, ^{13}C and ^{29}Si NMR data for **3** and **4** do not reveal significant information on the dynamic behaviour or the preferred configuration, the application of ^{15}N NMR spectroscopy (at natural abundance) at variable temperature in further studies is definitely necessary.

Table 2 Positional parameters for the sulfur diimide **1**

Atom	*x*	*y*	*z*
S	0.283 26(2)	0.513 88(1)	0.387 93(1)
N(1)	0.401 82(7)	0.496 91(4)	0.261 84(4)
N(2)	0.168 00(8)	0.655 36(5)	0.381 03(5)
Si(1)	0.543 33(2)	0.339 67(1)	0.253 62(1)
Si(2)	0.139 33(2)	0.807 90(1)	0.244 50(1)
C(11)	0.493 86(11)	0.192 29(6)	0.406 16(6)
C(12)	0.827 35(10)	0.372 46(7)	0.239 37(7)
C(13)	0.452 32(11)	0.297 90(6)	0.101 84(6)
C(21)	−0.026 66(12)	0.937 64(7)	0.310 77(7)
C(22)	0.400 67(10)	0.875 35(7)	0.187 81(6)
C(23)	0.005 91(10)	0.767 69(7)	0.104 42(6)

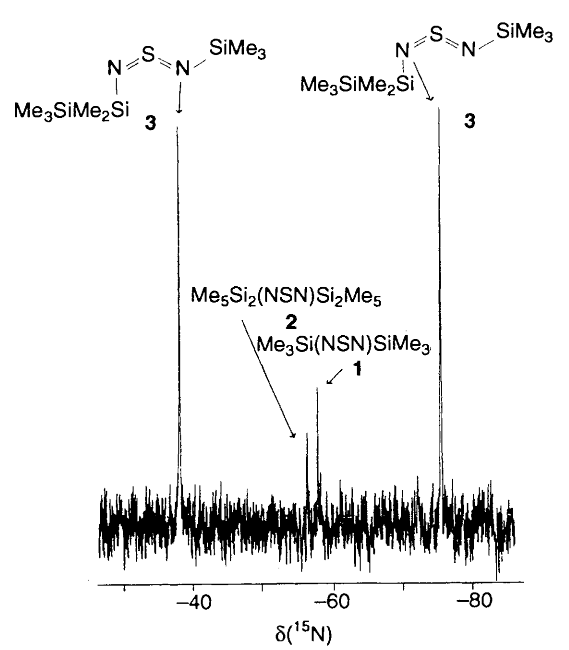
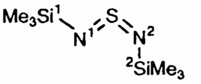
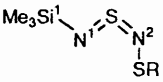
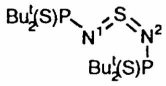


Fig. 1 The 30.5 MHz ^{15}N-{^1H} NMR spectrum of a mixture of compounds **1**–**3** in $[^2H_8]$toluene at −50 °C (inverse-gated ^1H decoupling)

X-Ray Analysis.—Atomic coordinates of compound **1** are given in Table 2 and the molecular structure is shown in Fig. 3 where the legend contains the important distances and bond

Table 3 Selected distances (Å) and angles (°) of sulfur diimides*

	 1	 R = $C_6H_4NO_2$-4	
S–N(1)	1.5230(5)	1.503(5)	1.527(1)
S–N(2)	1.5155(6)	1.558(7)	1.513(1)
N(1)–Si(1) [P(1)]	1.7593(5)	1.749(6)	1.702(1)
N(2)–Si(2) [S(2)/P(2)]	1.7585(6)	1.653(7)	1.697(1)
N(1)–S–N(2)	117.77(3)	114.1(4)	116.9(1)
S–N(1)–Si(1) [P(1)]	123.29(3)	128.8(4)	118.4(1)
S–N(2)–Si(2) [S(2)/P(2)]	129.78(4)	116.1(3)	136.4(1)

*Data for $Me_3Si(NSN)SC_6H_4NO_2$-4 from ref. 12 and for $Bu^t_2(S)P(NSN)P(S)Bu^t_2$ from ref. 13.

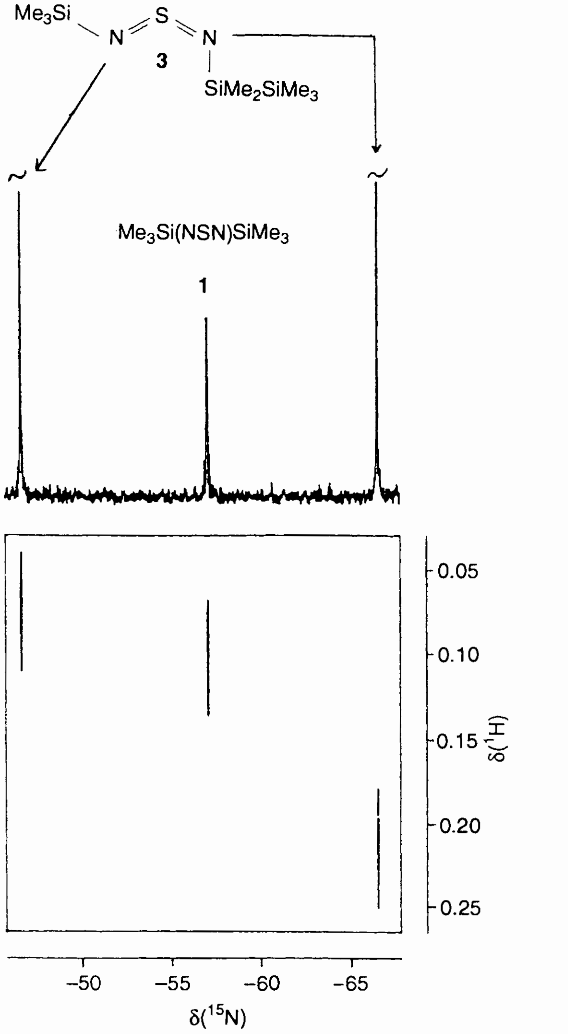


Fig. 2 Two-dimensional $^{15}N-^{1}H$ heteronuclear shift correlation [based on $^3J(^{15}N^1N) \approx 1.5$ Hz] of compound **3** in the presence of a small amount of **1** in [$^2H_8$]toluene at +26 °C. $\delta(^1H)$: **3**, 0.01 ($SiMe_2Si\mathit{Me}_3$), 0.07 ($SiMe_3$) and 0.21 ($Si\mathit{Me}_2SiMe_3$); **1**, 0.10 ($SiMe_3$)

angles. The atoms Si(1), N(1), S, N(2) and Si(2) are coplanar within experimental error (mean deviation from the plane: ± 0.008 Å). Solid-state interactions between discrete molecules of **1** are weak. A comparison between structural data for **1** and those of other sulfur diimides already described, such as $Me_3Si(NSN)SC_6H_4NO_2$-4[13] (*E*/*Z*) and $Bu^t_2(S)P(NSN)P(S)$-Bu^t_2,[14] confirms that the structural parameters of **1** are in the expected range (Table 3). The bond distances S–N (between 1.51 and 1.53 Å) are typical of an S=N double bond and the bond angle N–S–N (117.8°) is characteristic for sulfur diimides with *E*/*Z* configuration. In the case of *Z* substituents, it appears that the bond angle S–N(2)–X (X = C,[3] Si,[13] P[14] or S[3,13]) is mainly determined by steric requirements, with larger bond angles for the more bulky groups. In contrast, with substituents in the *E* position the bond angle S–N(1)–X does not depend on the bulkiness of the substituent. This is apparent from the data in Table 3: (*i*) there is a difference of 5.5° for the same fragments [S–N(1)–Si] and (*ii*) the bond angle S–N(1)–P(1) [in $Bu_2^t(S)P(NSN)P(S)Bu^t_2$] is smaller by 4.9° than S–N(1)–Si(1) in **1**, although the $Bu^t_2(S)P$ group must be considered to be more bulky than the Me_3Si.

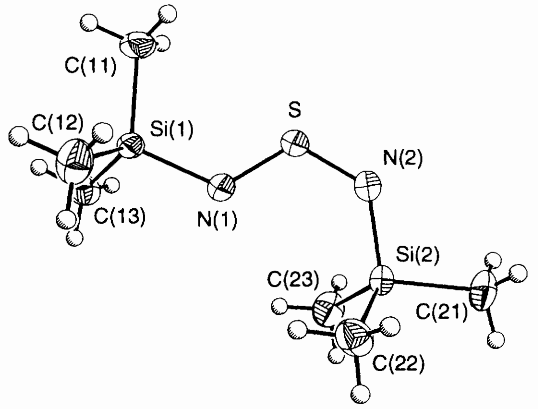


Fig. 3 Molecular structure of $Me_3Si(NSN)SiMe_3$ **1**. Selected bond distances (Å) and angles (°): S–N(1) 1.5230(5), S–N(2) 1.5155(6), Si(1)–N(1) 1.7593(5), Si(2)–N(2) 1.7585(6), Si(1)–C(11) 1.8629(7), Si(1)–C(12) 1.8575(8), Si(1)–C(13) 1.8593(8), Si(2)–C(21) 1.8602(6), Si(2)–C(22) 1.8586(8), Si(2)–C(23) 1.8620(8); N(1)–S–N(2) 117.77(3), S–N(1)–Si(1) 123.29(3), S–N(2)–Si(2) 129.78(4)

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