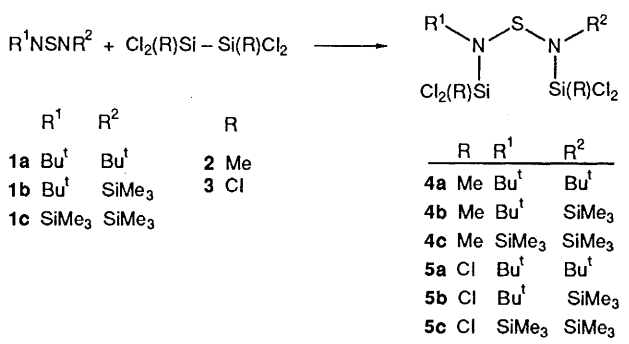
# Reactions of Sulphur Diimides with Di- and Tri-silanes: $^{15}N$ and $^{29}Si$ Nuclear Magnetic Resonance Study and the Crystal Structure of Bis[*tert*-butyl(trichlorosilyl)amino]sulphane†

**Bernd Wrackmeyer,**[*,a] **Stefan M. Frank,**[a] **Max Herberhold,**[a] **Arndt Simon**[b] **and Horst Borrmann**[b]

[a] *Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 101251, D-8580 Bayreuth, FRG*
[b] *Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart, FRG*

Sulphur diimides $R^1NSNR^2$ **1a** ($R^1 = R^2 = Bu^t$), **1b** ($R^1 = Bu^t$, $R^2 = Me_3Si$) and **1c** ($R^1 = R^2 = Me_3Si$) react with tetrachloro-1,2-dimethyldisilane **2**, hexachlorodisilane **3** and octachlorotrisilane **6** by cleavage of the Si–Si bond to give the corresponding diaminosulphanes (**4**, **5**, **7**) in quantitative yield. In the case of **6** only one of the two Si–Si bonds is cleaved. The reaction between **1b** and **6** affords two isomers in a ratio close to 1 : 1 which suggests the intermediacy of a cyclic adduct prior to the intramolecular redox process. The products have been characterized by $^1H$, $^{13}C$, $^{15}N$ and $^{29}Si$ NMR spectroscopy in solution as well as by $^{29}Si$ cross polarization magic angle spinning NMR in the solid state. The crystal structure of $(Cl_3Si)Bu^tNSNBu^t(SiCl_3)$ **5a** (prepared from **1a** and **3**) has been determined: space group *Pbcn* (no. 60), with *a* = 2212.9(6), *b* = 1172.4(3), *c* = 2160.5(8) pm, and *Z* = 12.

Sulphur diimides are attractive reagents owing both to the reactivity of the multifunctional NSN system[1] and the convenient access to sulphur diimides bearing organometallic substituents.[1,2] Much attention has been given to the Lewis-base properties of sulphur diimides which might act as potential ligands for both Lewis acids typical of main-group elements such as $SnCl_4$[3] and various transition-metal fragments.[4] Another aspect is concerned with intramolecular redox reactions once the adducts between sulphur diimides and the Lewis acids are formed. Such redox processes would explain the products obtained from the reaction between certain boranes and sulphur diimides[5] as well as cleavage of the Si–Si bond of polychlorodisilanes when treated with sulphur diimides.[6] A preliminary report[6] on the latter reactions has shown that a large variety of N-silylated diaminosulphanes can be prepared in high yields (Scheme 1).



Scheme 1

One derivative (**4b**) has been characterized by X-ray crystallography,[6] showing that there is disorder of the Me,Cl substituents in the $N(SiMe_3)Si(Me)Cl_2$ group. In continuing this work, we have isolated crystals of **5a** for X-ray crystallographic studies. Furthermore, the synthetic work has been extended to reactions of the trisilane $Si_3Cl_8$ **6** with **1** in order to shed some light on the reaction mechanism. Solid-state $^{29}Si$ cross polarization magic angle spinning (CPMAS) NMR and $^{29}Si$ NMR spectra in liquids have been measured and a systematic $^{15}N$ NMR study carried out.

## Experimental

All experiments and the handling of the compounds were routinely carried out under an inert atmosphere (Ar), excluding traces of oxygen and moisture. The sulphur diimides **1a**,[7] **1b**[8a] [from the potassium salt $KNSNBu^t$ (ref. 8*b*) and $SiMe_3Cl$], **1c**,[9] the disilane **2**[10] and the trisilane **6**[11] were prepared following literature procedures. All other materials were obtained as commercial products and used without further purification.

[tert-*Butyl(pentachlorodisilanyl)amino*][tert-*butyl(trichlorosilyl)amino*]*sulphane* **7a**.—A solution of octachlorotrisilane **6** (0.734 g, 2 mmol) in hexane (30 cm$^3$) was cooled to 0 °C. After addition of compound **1a** (0.348 g, 2 mmol) the reaction solution was allowed to warm to room temperature and kept stirring for 2 h. Hexane was removed *in vacuo*, leaving a white powder which can be recrystallized from hexane or pentane to give **7a** (1.03 g, 95%), m.p. 72–74 °C (Found: C, 17.95; H, 3.55; N, 5.30. Calc. for $C_8H_{18}Cl_8N_2SSi_3$: C, 17.70; H, 3.35; N, 5.15%). Mass spectrum: *m*/*z* 542 ($[M]^+$, 0.2), 486 ($[M - C_4H_8]^+$, 2.6), 450 ($[M - C_4H_9 - Cl]^+$, 3.1); 430 ($[M - C_4H_8 - C_4H_8]^+$, 8.0), and 57 ($[C_4H_9]^+$, 100%). In the same way the 1:1 mixture (as shown by the $^1H$ NMR spectra) of the isomers **7b** and **7b′** was obtained as a colourless oil and the pure compound **7c** as a colourless solid, m.p. 30–35 °C (Found: C, 12.70; H, 3.30; N, 5.15. Calc. for $C_6H_{18}Cl_8N_2SSi_5$: C, 12.55; H, 3.15; N, 4.90%). Mass spectrum: *m*/*z* 574 ($[M]^+$, 8%), 466 ($[M - Me_3SiCl]^+$, 35), 366 ($[M - Me_3SiCl - SiCl_2]^+$, 35), and 73 ($[Me_3Si]^+$, 100%).

NMR spectra for liquid samples were recorded on JEOL FX90Q and Bruker AC300 spectrometers. Routine parameters served for measuring $^1H$, $^{13}C$ and $^{29}Si$ NMR spectra (see Tables 1 and 2 and Fig. 1 for further details). All $^{15}N$ NMR spectra (30.4 MHz) were obtained using the refocused insensi-

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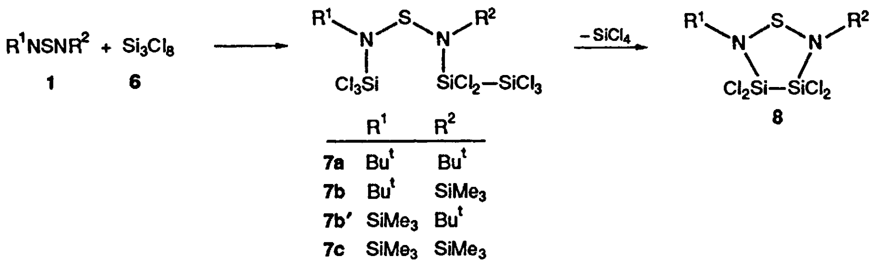
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.



Scheme 2

Table 1 Proton and $^{13}C$ NMR data* for compounds 7

| | $\delta(^{13}C)$ | | $\delta(^{1}H)$ | |
|---|---|---|---|---|
| Compound | $Bu^t$ | $SiMe_3$ | $Bu^t$ | $SiMe_3$ |
| 7a | 30.8, 31.6 | — | 1.37 | — |
| | 63.7, 64.0 | — | 1.41 | — |
| 7b, 7b′ | 30.4, 31.8 | 2.8 (57.8) | 1.33 | 0.30 |
| | 64.0, 64.3 | 3.1 (57.8) | 1.39 | 0.36 |
| 7c | — | 3.1 (57.6) | — | 0.34 |
| | — | 3.4 (58.1) | — | 0.36 |

* In $[^2H_8]$toluene, *ca.* 10–15%, at 26–27 °C. Coupling constants $^1J(^{13}C^{29}Si)$ in Hz are given in parentheses.

tive nuclei enhanced by polarization transfer (INEPT) pulse sequence[12] with optimized delays related to $^3J(^{15}N^1H)$ values for *N-tert*-butyl groups (2.0–2.5 Hz) and *N*-trimethylsilyl groups (1.0–1.5 Hz) (see also Fig. 2). The successful $^{15}N$ NMR experiments depend critically on temperature stability throughout the measurement, on careful adjustment of the shim coils and on a high digital resolution. This is related to the small natural linewidth (< 0.05 Hz) of the $^{15}N$ NMR signals.

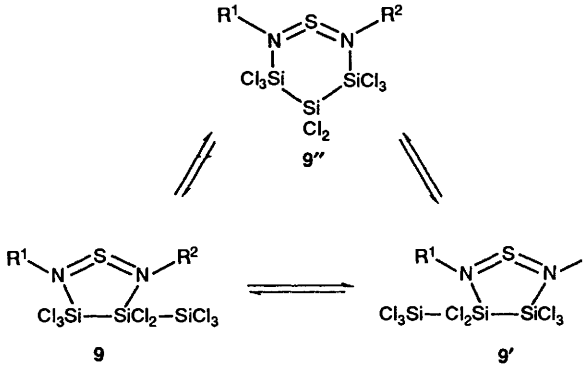
Solid-state $^{29}Si$ CP MAS NMR spectra were obtained with a Bruker MSL 300 spectrometer. The air-sensitive samples **4**, **5** and **7** were measured using inserts[13] for the commercial $ZrO_2$ rotors. A sample of $[\{(Me_3SiO)(SiO_3)\}_8]$ served as an external reference of the $^{29}Si$ chemical shifts[14] which were then converted into the $SiMe_4$ scale. Mass spectra [electron impact (EI), 70 eV (*ca.* 1.12 × $10^{-17}$ J)] were recorded on a Finnigan MAT 8500 spectrometer.

*Crystallographic Data Collection and Structure Refinement.*—Crystal data with other pertinent information on the data collection and structure determination are given in Table 3. Unit-cell parameters were refined from 2θ values (29.7–33.7°) of 25 reflections. Data were collected in ω–θ scan mode with variable scan width and time. A total of 16 048 reflections were measured and averaged to a unique data set after application of the usual data reduction and an empirical absorption correction. The structure was solved *via* direct methods and refined by full-matrix least squares with anisotropic displacement factors for all non-hydrogen atoms. All hydrogen atoms were located in a Fourier difference map and finally refined to a common C–H distance (95.7 pm) and with a common isotropic thermal parameter. For all calculations the program package SHELXTL-PLUS[15] was used and the final bond lengths and angles were calculated with ORFFE.[16]

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

## Results and Discussion

*Reactions of Sulphur Diimides* **1** *with* $Si_3Cl_8$ **6**.—Like the disilanes **2** and **3**, the trisilane $Si_3Cl_8$ **6** reacts smoothly with **1** (Scheme 2) to give quantitatively the diaminosulphanes **7** as colourless powders. Treatment of **7** with an excess of **1** does not induce cleavage of the remaining Si–Si bond. Instead, heating the compounds **7** in toluene in the presence or absence of compound **1** affords both $SiCl_4$ and the five-membered heterocycles **8*** which are also sometimes found as an impurity in reaction solutions of **7** (see Fig. 1). One interesting aspect of the reaction between **1** and **6** concerns the mechanism of the reactions shown in Schemes 1 and 2. According to $^1H$ NMR spectra, the ratio of the products **7b** and **7b′** is close to 1:1. This is consistent with the intermediacy of short-lived cyclic intermediates of the type **9**, **9′** and **9″** (Scheme 3) prior to the intramolecular redox process. One would expect a stronger preference for one of the two isomers if only a single silicon atom were involved in the adduct formation.



Scheme 3

*NMR Spectroscopic Studies.*—Proton, $^{13}C$ and some $^{29}Si$ NMR data for compounds **4** and **5** have been reported previously.[6] Table 1 lists $^1H$ and $^{13}C$ NMR data for compounds **7** and Table 2 contains $^{15}N$ and $^{29}Si$ NMR data for **4**, **5** and **7** and bis[bis(trimethylsilyl)amino]sulphane **10** included for comparison.

All reactions (Schemes 1 and 2) can be monitored by $^{29}Si$ NMR spectroscopy. In the case of **1b**, **1c** and the disilane **2**, the refocused INEPT pulse sequence[12] yields conclusive information on the fate of the $Me_3Si$ (**1b**, **1c**) or the MeSi groups (**2**) within minutes, even for diluted solutions in non-deuteriated solvents. Fortunately, the $^{29}Si$ relaxation rate in the $SiCl_3$ and $SiCl_2$ moieties is sufficiently fast $[T_1(^{29}Si) \approx 10\text{–}20\ s]$ that their $^{29}Si$ NMR signals can be observed by direct single-pulse methods without $^1H$ decoupling for moderately concentrated samples within an hour or less (see Fig. 1).

At first glance, the measurement of natural-abundance $^{15}N$ NMR spectra appeared to constitute the major problem. Only a few diaminosulphanes had been studied previously by this technique. Direct measurement of neat or concentrated samples together with the addition of $[Cr(acac)_3]$ (acac = acetyl-

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* The full characterization and the chemistry of compounds **8** will be described elsewhere. Some relevant NMR data are: **8a**, $\delta(^{15}N)$ −276.0, $\delta(^{29}Si)$ −26.1; **8b**, $\delta(^{15}N)$ −277.4 ($NBu^t$), −305.1 ($NSiMe_3$), $\delta(^{29}Si)$ uncertain; **8c**, $\delta(^{15}N)$ −306.3, $\delta(^{29}Si)$ −25.5 ($SiCl_2$), and +22.3 ($SiMe_3$).

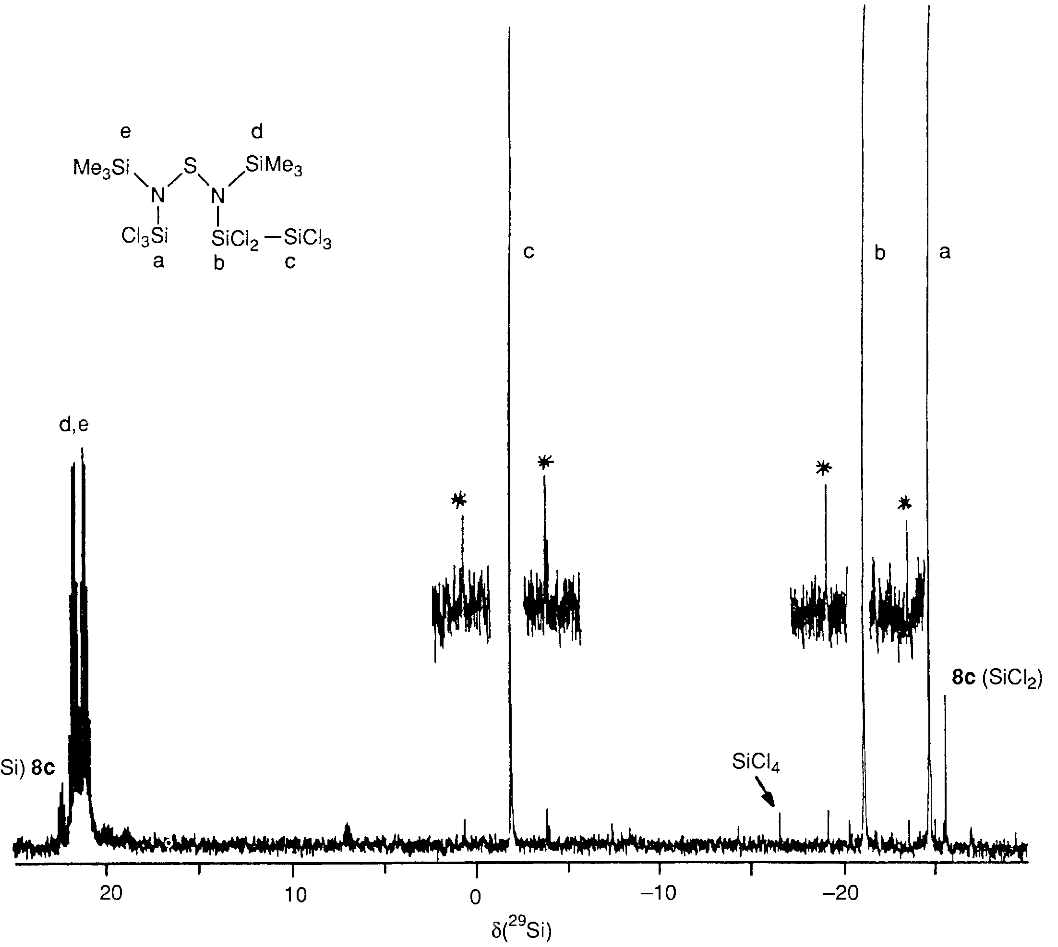

**Fig. 1** 59.6 MHz $^{29}$Si NMR spectrum of a reaction solution, in a 10 mm (outside diameter) tube, containing compounds **7c** and **8c** in toluene. The spectrum was obtained without $^{1}$H decoupling by single-pulse methods (pulse angle $\approx$ 25°, acquisition time 1 s) and required $\approx$ 1 h to reach a signal-to-noise ratio sufficient for the determination of $^{1}J(^{29}Si^{29}Si)$ from the $^{29}$Si satellites (asterisks) with the typical pattern of an AB spin system

acetonate), as a relaxation agent, was employed.[17,18] Furthermore, in the case of $[(Me_3Si)_2N]_2S$ **10** it was stated that the application of distortionless enhancement by polarization transfer (DEPT) had not been successful.[18] However, according to our previous experience with the application of such techniques to a great number of aminosilanes,[19] the presence of $NSiMe_3$ and/or $NBu^t$ groups should allow the use of small scalar $^{3}J(^{15}N^{1}H)$ coupling as a basis for the polarization transfer. In contrast with the literature,[18] the $^{15}$N NMR spectrum of compound **10** can readily be measured using the refocused INEPT or DEPT technique [the $\delta(^{15}N)$ value could be obtained with a single scan for a saturated $CDCl_3$ solution of 133 mg **10** in a 5 mm tube] and, indeed, the same is true for all compounds **4**, **5** and **7** (Table 2). In all cases a signal-to-noise ratio could be achieved within a few hours sufficient to measure not only the $\delta(^{15}N)$ values but also the coupling constants $^{n}J(^{29}Si^{15}N)$ (see Fig. 2). The $\delta(^{15}N)$ value for **10** recorded by us (−325.0) differs from the literature[18] value (−332.0). This may be due to the presence of $[Cr(acac)_3]$.[20]

*Solid-state* $^{29}$Si *CP MAS NMR spectra*. In those cases where the crystal structure had been determined by X-ray crystallography, solid-state $^{29}$Si CP MAS NMR spectra were recorded for comparison with liquid-state $^{29}$Si chemical shifts. If $Me_3Si$ groups are present the CP MAS technique gives slightly broadened or partially split $^{29}$Si NMR signals for crystalline solids as a result of the neighbourhood of the $^{29}$Si to the quadrupolar $^{14}$N nucleus.[21] In the presence of two or three chlorine substituents at the silicon atoms the $^{29}$Si NMR signals are much more broadened, this time as a result of non-averaged quadrupolar interactions between $^{29}$Si and $^{35,37}$Cl nuclei (see Fig. 3). The $^{29}$Si CP MAS NMR spectrum of compound **4b** (Fig. 3) reflects the disorder found by X-ray analysis of single crystals.[6] There are two slightly different molecules in the unit cell of compound **5a** (see below). However, the non-equivalence of the $^{29}$Si nuclei is not resolved in the $^{29}$Si CP MAS NMR spectrum which shows only a single broad signal. Again, the increase in the linewidth must be attributed to the influence of the chlorine atoms. In the case of **10**, there are only $Me_3Si$ groups giving rise to two signals in the $^{29}$Si CP MAS NMR spectrum, each showing a splitting that is attributed to non-averaged quadrupolar and scalar $^{14}N$–$^{29}Si$ interactions. This is in accord with the results of the X-ray analysis[22] showing that there are only two different sites for silicon atoms in the unit cell. It is interesting that the weighted average of the different $^{29}$Si NMR signals observed for the solid samples of **4b** and **10**, respectively, corresponds precisely to the $\delta(^{29}Si)$ values of liquid samples. Therefore, the significant shift differences $\Delta(^{29}Si)$ of $\approx$ 5–7 ppm cannot be ascribed to intermolecular interactions in the solid state but rather to intramolecular conformational effects.

$^{29}$Si *Chemical shifts and coupling constants* $^{1}J(^{29}Si^{19}Si)$. The $\delta(^{29}Si)(Me_3Si)$ values for compounds **4**, **5**, **7** and **10** show a marked dependence on the nature of the second silyl ligand. The substitution of $Me_3Si$ groups in **10** [$\delta(^{29}Si)$ 10.6] by $MeSiCl_2$ or $SiCl_3$ groups causes deshielding of the $^{29}$Si nucleus in the remaining $Me_3Si$ group by $\approx$ 7 and $\approx$ 11 ppm, respectively. The influence of the $SiCl_3SiCl_2$ group is similar to that of $SiCl_3$. The $\delta(^{29}Si)(SiCl_3)$ and $(SiMeCl_2)$ values are found in the range typical of corresponding dialkylaminosilanes.[23] For compounds **7**, the $SiCl_2$ and $SiCl_3$ signals can be unequivocally assigned on the basis of the $\delta(^{29}Si)$ values and the coupling constants $^{1}J(^{29}Si^{29}Si)$ (see Fig. 1). The substitution of one

**Table 2** Nitrogen-15 and $^{29}$Si NMR data[a] for the diaminosulphanes **4**, **5**, **7** and **10**

| | $\delta(^{15}N)$ | | $\delta(^{29}Si)$ | |
|---|---|---|---|---|
| Compound | NR$^1$ | NR$^2$ | SiMe$_3$ | SiCl |
| **4a** | −278.5<br>[23.4] (2.4) | −278.5<br>[23.4] (2.4) | — | −2.1[b] |
| **4b** | −278.7<br>[22.9] (<3) | −308.8<br>[14.6, 6.4] (<3) | +17.1[c] | +1.65, −2.55 |
| **4c** | −308.0<br>[14.8, 6.4] (2.7) | −308.0<br>[14.8, 6.4] (2.7) | +17.7 | +2.35 |
| **5a** | −275.9<br>[32.5] (2.7) | −275.9<br>[32.5] (2.7) | — | −25.9[d] |
| **5b** | −277.2<br>[32.4] (2.3) | −304.9<br>[21.3, 6.5] (2.3) | +20.2 | −25.4, −26.5 |
| **5c** | −306.2<br>[20.6, 5.1] (1.6) | −306.2<br>[20.6, 5.1] (1.6) | +22.6 | −25.5 |
| **7a** | −277.0 (NSi)<br>[31.6] (1.7) | −278.1 (NSiSi)<br>[20.2] (5.5, 1.7) | — | −25.6, −22.0, −3.8<br>{285.3} |
| **7b** | −277.1<br>[31.8] (<1.5) | −309.3<br>[12.0, 6.3] (4.4) | +19.5 | −26.9, −19.0, −2.1<br>{265.7} |
| **7b′** | −279.6<br>[20.8] (6.3) | −308.8<br>[19.4, 8.4] (2.7) | +18.5 | −25.2, −22.6, −5.6<br>{296.5} |
| **7c**[e] | −307.4 (NSi)<br>[20.2, 5.0] (1.8) | −311.7 (NSiSi)<br>[11.4, 6.6] (5.0, 1.8) | +21.7, +21.2 | −24.7, −21.1, −1.6<br>{265.8} |
| **10** | −325.0[f]<br>[8.6] (<3) | −325.0<br>[8.6] (<3) | +10.6[g] | — |

[a] In [$^2$H$_8$]toluene, *ca.* 10–15%, at 26–27 °C; $\delta(^{15}N)$ relative to neat MeNO$_2$ (external) with $\Xi(^{15}N)$ = 10 136 767 Hz, $\delta(^{29}Si)$ relative to SiMe$_4$ (external) with $\Xi(^{29}Si)$ = 19 867 184 Hz. Coupling constants in Hz are given in square brackets, $^1J(^{29}Si^{15}N)$, in parentheses, $^{2,3}J(^{29}Si^{15}N)$, and in braces, $^1J(^{29}Si^{29}Si)$. [b] $^{29}$Si CP MAS NMR spectrum: $\delta(^{29}Si)$ −1.8. [c] $^{29}$Si CP MAS NMR spectrum (see Fig. 3): $\delta(^{29}Si)$ −1.8, 4.9 (SiMeCl$_2$); −13.4, −20.0 (SiMe$_3$). [d] $^{29}$Si CP MAS NMR spectrum: $\delta(^{29}Si)$ −26.8. [e] $^{15}$N NMR spectrum (see Fig. 2), $^{29}$Si NMR spectrum (see Fig. 1). [f] In CDCl$_3$. [g] $^{29}$Si CP MAS NMR spectrum: $\delta(^{29}Si)$ 7.8 and 12.4.

**Table 3** Crystallographic data of orthorhombic compound **5a**

| | |
|---|---|
| Formula, *M* | $C_8H_{18}Cl_6N_2SSi_2$, 443.2 |
| Lattice constants/pm | $a$ = 2212.9(6), $b$ = 1172.4(3), $c$ = 2160.5(8) |
| Space group | *Pbcn* (no. 60) |
| Volume/pm$^3$, *Z* | 5605(3) × 10$^6$, 12 |
| $D_c$/g cm$^{-3}$ | 1.576 |
| Crystal size/mm | 0.82 × 0.62 × 0.50 |
| *F*(000) | 2712 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$, $\lambda$/pm | 11.49, 71.073 |
| Diffractometer | Nonius-CAD4, graphite monochromator, scintillation counter |
| 2$\theta$ range/° | 3.0–60.0 |
| Scan speed | Variable, maximum 80 s per reflection |
| *T*/K | 213 |
| Data collected | 16 048, $R_{int}$ = 0.0182 |
| unique, observed | 8127, 6685 [$F > 3\sigma(F)$] |
| Absorption correction | $\psi$ scans, 18 *khl*, $\Delta\psi$ = 10° |
| Parameters | 342 |
| Weighting scheme | $w = 1/[\sigma^2(F) + GFF^*]$, $G$ = 0.0002 |
| Extinction correction | $F^* = F_c/(1.0 + 0.002xF_c^2/\sin 2\theta)^{0.25}$, $x$ = 0.000 110(10) |
| *R*(aniso) | 0.040, 0.053 for all data |
| *R′* | 0.041, 0.042 for all data |
| Goodness of fit | 1.57 |

chlorine atom in the silanes SiMeCl$_3$, SiCl$_4$ and Si$_2$Cl$_6$ by the amino function as in compounds **4**, **5** and **7** leads to shielding of the $^{29}$Si nuclei by ≈10 to ≈12 ppm. Thus for compounds **7**, the signal at $\delta(^{29}Si)$ −19 to −22 represents the NSiCl$_2$ group and that at $\delta(^{29}Si)$ −1.6 to −3.8 stems from the Cl$_3$*Si*Si group. The $^1J(^{29}Si^{29}Si)$ values for **7** are found in the range 265–297 Hz. These are the largest one-bond $^{29}$Si–$^{29}$Si coupling constants observed so far for di- or poly-silanes.[24–27] A $^1J(^{29}Si^{29}Si)$ value of 221 Hz has been reported for pentachlorodisilane.[27] The further increase in the magnitude of $^1J(^{29}Si^{29}Si)$ found here demonstrates the effect of rehybridization of the silicon atoms as a function of the sum of the electronegativities of all substituents.

$^{15}$N *Chemical shifts and coupling constants* $^nJ(^{29}Si^{15}N)$. The $^{15}$N resonances of compounds **4**, **5** and **7** are readily assigned on the basis of substituent effects (Bu$^t$ against a Me$_3$Si group) and coupling constants $^nJ(^{29}Si^{15}N)$ ($n$ = 1–3) (see Fig. 2 and Table 2). As for other amines,[20] the *tert*-butyl group exerts a stronger deshielding influence on $^{15}$N nuclei than does the Me$_3$Si group. For various chlorosilyl groups linked to the same nitrogen atom the $^{15}$N(Me$_3$SiN) resonances cover a range of only 5.5 ppm [$\delta(^{15}N)$ −306.2 to −311.7] and an even smaller range is observed for the $^{15}$N(Bu$^t$N) resonances [$\delta(^{15}N)$ −275.9 to −279.6]. In both series the $^{15}$N(Cl$_3$SiSiCl$_2$N) NMR signals are found at lowest frequencies. In comparison with **10**, the $^{15}$N(Me$_3$SiN) signals are shifted to higher frequencies by 16.1 ± 2.8 ppm. This indicates increasing delocalization of the nitrogen lone pair in the *N*-chlorosilyl derivatives.[28,29]

The $^1J(^{29}Si^{15}N)$ values range from 5.1 Hz for **5c** over 8.6 Hz for **10** to 32.5 Hz for **5a**. This parameter is very sensitive towards the nature of substituents both on the nitrogen and the silicon atom.[19,30] In both cases more electronegative substituents lead to an increase in the magnitude of $^1J(^{29}Si^{15}N)$. Interestingly, the presence of a Si–Si bond in the NSiCl$_2$SiCl$_3$ units of **7** causes smaller $^1J(^{29}Si^{15}N)$ values than does the SiMe group in the corresponding NSiCl$_2$Me units of **4**.

Values of $^nJ(^{29}Si^{15}N)$ ($n$ = 2 or 3; see Fig. 2) were observed in most cases. It appears that the $^3J(^{29}Si^{15}N)$ couplings across the N–S bond are always connected with the chlorosilyl group. The data set for these coupling constants is still rather limited. However, as shown in Fig. 2, these parameters may help to aid the assignment of $^{15}$N resonances.

*Crystallography*.—In addition to the reported[6] disordered structure of compound **4b**, we have determined the crystal structure of **5a** to confirm the structural model of the diaminosulphane entity. The fractional coordinates of the non-hydrogen atoms are listed in Table 4, selected bond

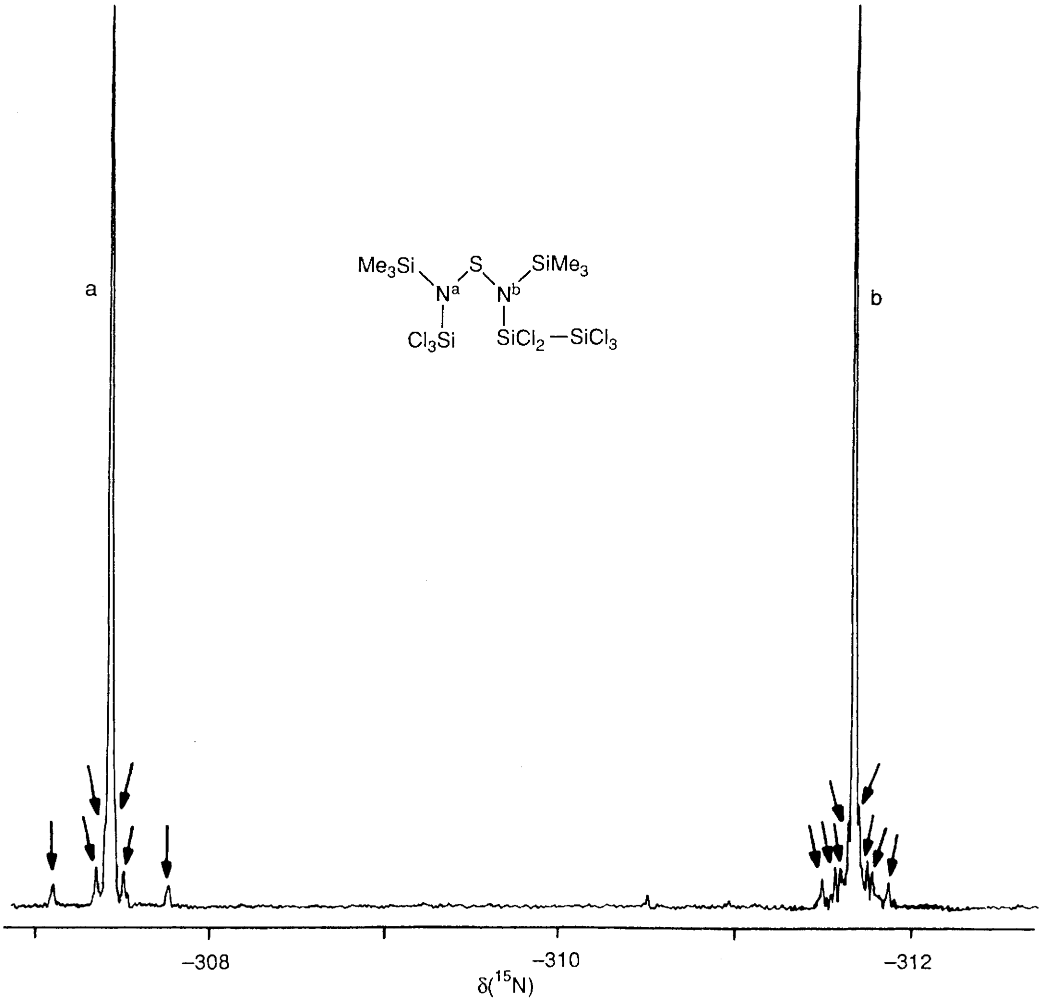

**Fig. 2** 30.4 MHz $^{15}$N NMR spectrum of compound **7c** in toluene–[$^2H_8$]toluene [≈15%, 10 mm (outside diameter) tube], recorded with the refocused INEPT pulse sequence with optimized delays, based on $^3J(^{15}N^1H)$ = 1.3 Hz (recycle delay 5 s, acquisition time 4 s, ≈2400 scans, ≈6 h spectrometer time). The various $^{29}$Si satellite signals corresponding to $^nJ(^{29}Si^{15}N)$ ($n$ = 1–3) are indicated by arrows: N$^a$, $^1J(^{29}Si_{SiCl_3},{}^{15}N)$ = 20.2, $^1J(^{29}Si_{SiMe_3},{}^{15}N)$ = 5.0, $^3J(^{29}Si_{SiCl_2},{}^{15}N)$ = 1.8; N$^b$, $^1J(^{29}Si_{SiCl_2},{}^{15}N)$ = 11.4, $^1J(^{29}Si_{SiMe_3},{}^{15}N)$ = 6.6, $^2J(^{29}Si_{SiCl_3},{}^{15}N)$ = 5.0, $^3J(^{29}Si_{SiCl_3},{}^{15}N)$ = 1.8 Hz

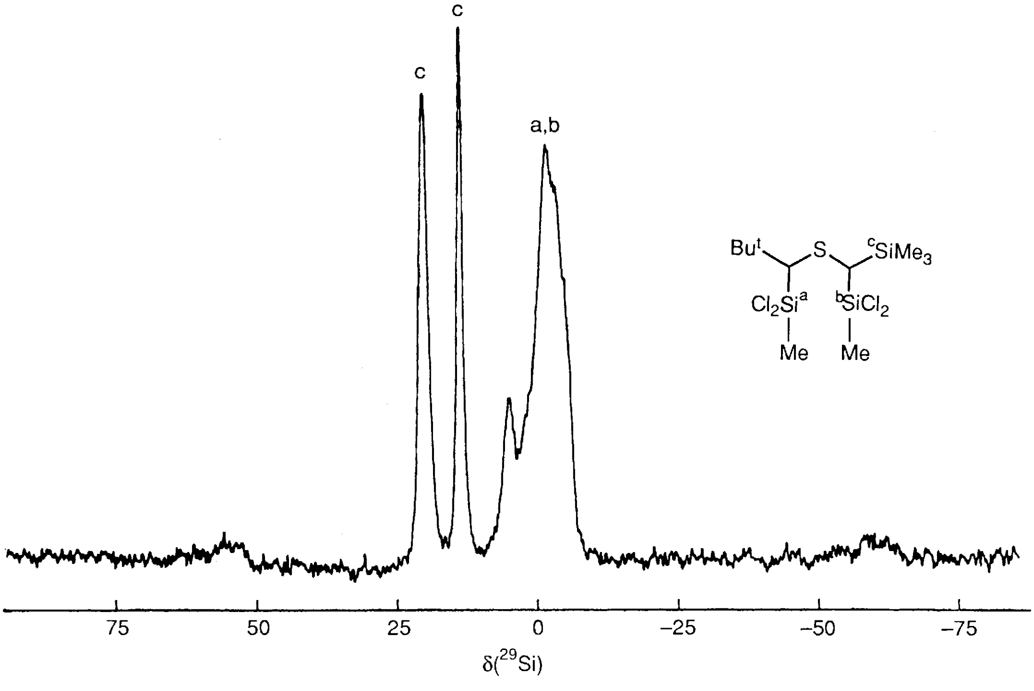

**Fig. 3** 59.6 MHz $^{29}$Si CP MAS NMR spectra of the solid diaminosulphane **4b**. The two regions showing sharp and broad resonances can be assigned to the $Me_3Si$ and the $MeSiCl_2$ groups, respectively. The integral intensities of the sharp signals correspond closely to the various contributions from the disorder as determined by the X-ray analysis[6]

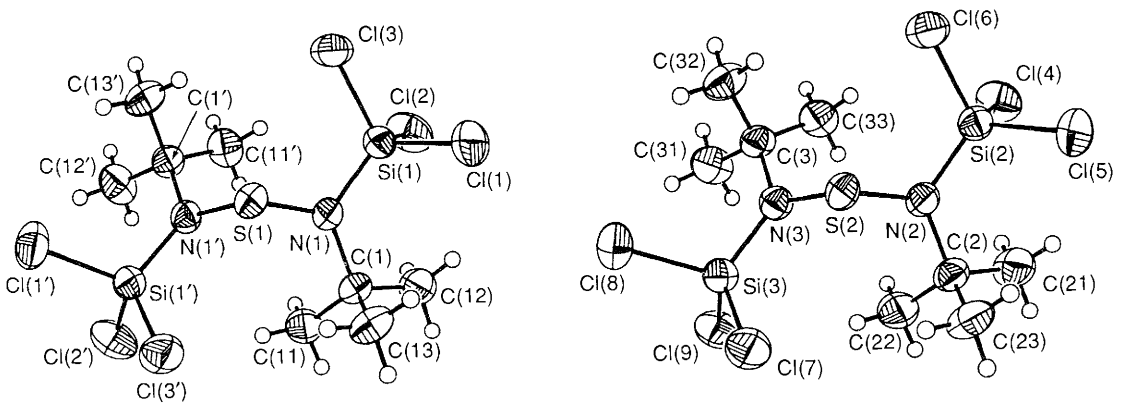

**Fig. 4** Molecular structure and numbering scheme of the two different molecules of compound **5a**. Non-hydrogen atoms are drawn at the 70% probability level, hydrogen atoms with arbitrary size

**Table 4** Atomic coordinates ( × $10^4$)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| S(1) | 0 | 1102(1) | 2500 |
| N(1) | 384(1) | 264(1) | 1981(1) |
| Si(1) | 182(1) | 479(1) | 1223(1) |
| Cl(1) | 796(1) | 1448(1) | 759(1) |
| Cl(2) | 70(1) | −992(1) | 741(1) |
| Cl(3) | −610(1) | 1323(1) | 1117(1) |
| C(1) | 1004(1) | −194(2) | 2172(1) |
| C(11) | 925(1) | −974(2) | 2730(1) |
| C(12) | 1276(1) | −912(2) | 1652(1) |
| C(13) | 1423(1) | 795(2) | 2326(1) |
| S(2) | 1641(1) | 3789(1) | 4160(1) |
| Si(2) | 1484(1) | 4551(1) | 2897(1) |
| Si(3) | 1849(1) | 4353(1) | 5448(1) |
| Cl(4) | 1717(1) | 6043(1) | 2482(1) |
| Cl(5) | 808(1) | 3855(1) | 2384(1) |
| Cl(6) | 2195(1) | 3484(1) | 2762(1) |
| Cl(7) | 1079(1) | 3433(1) | 5538(1) |
| Cl(8) | 2473(1) | 3469(1) | 5949(1) |
| Cl(9) | 1701(1) | 5838(1) | 5906(1) |
| N(2) | 1287(1) | 4709(1) | 3662(1) |
| N(3) | 2060(1) | 4531(1) | 4688(1) |
| C(2) | 693(1) | 5262(2) | 3869(1) |
| C(21) | 463(1) | 6080(2) | 3373(1) |
| C(22) | 805(1) | 5957(2) | 4453(1) |
| C(23) | 226(1) | 4332(2) | 3992(1) |
| C(3) | 2690(1) | 4943(2) | 4500(1) |
| C(31) | 2958(1) | 5691(2) | 5011(1) |
| C(32) | 3094(1) | 3916(2) | 4373(1) |
| C(33) | 2639(1) | 5687(2) | 3919(1) |

**Table 5** Selected bond lengths (pm) for compound **5a**

| | | | |
|---|---|---|---|
| N(1)–S(1) | 171.5(1) | Si(1)–Cl(1) | 203.37(7) |
| N(1)–Si(1) | 171.6(1) | Si(1)–Cl(2) | 203.05(9) |
| N(1)–C(1) | 153.1(2) | Si(1)–Cl(3) | 202.68(8) |
| C(1)–C(11) | 152.5(3) | C(1)–C(12) | 152.6(3) |
| C(1)–C(13) | 152.1(3) | | |
| S(2)–N(2) | 171.3(1) | S(2)–N(3) | 170.9(1) |
| Si(2)–Cl(4) | 203.19(8) | Si(3)–Cl(7) | 202.72(7) |
| Si(2)–Cl(5) | 203.45(7) | Si(3)–Cl(8) | 203.68(7) |
| Si(2)–Cl(6) | 203.01(7) | Si(3)–Cl(9) | 202.83(9) |
| Si(2)–N(2) | 171.9(1) | Si(3)–N(3) | 172.0(1) |
| N(2)–C(2) | 153.3(2) | N(3)–C(3) | 152.9(2) |
| C(2)–C(21) | 152.7(3) | C(3)–C(31) | 153.0(3) |
| C(2)–C(22) | 152.2(3) | C(3)–C(32) | 152.4(3) |
| C(2)–C(23) | 152.7(3) | C(3)–C(33) | 153.3(3) |

**Table 6** Selected bond angles (°) for compound **5a**

| | | | |
|---|---|---|---|
| N(1)–S(1)–N(1A) | 110.2(1) | S(1)–N(1)–Si(1) | 114.33(8) |
| S(1)–N(1)–C(1) | 117.9(1) | Si(1)–N(1)–C(1) | 122.7(1) |
| N(1)–Si(1)–Cl(1) | 112.29(5) | N(1)–C(1)–C(11) | 108.7(1) |
| N(1)–Si(1)–Cl(2) | 113.37(6) | N(1)–C(1)–C(12) | 110.4(1) |
| Cl(1)–Si(1)–Cl(2) | 107.69(4) | C(11)–C(1)–C(12) | 107.2(2) |
| N(1)–Si(1)–Cl(3) | 113.79(5) | N(1)–C(1)–C(13) | 109.8(1) |
| Cl(1)–Si(1)–Cl(3) | 104.46(3) | C(11)–C(1)–C(13) | 110.8(2) |
| Cl(2)–Si(1)–Cl(3) | 104.51(3) | C(12)–C(1)–C(13) | 110.0(2) |
| N(2)–S(2)–N(3) | 110.31(7) | | |
| S(2)–N(2)–Si(2) | 114.79(8) | S(2)–N(3)–Si(3) | 115.41(8) |
| S(2)–N(2)–C(2) | 118.4(1) | S(2)–N(3)–C(3) | 118.5(1) |
| Si(2)–N(2)–C(2) | 123.0(1) | Si(3)–N(3)–C(3) | 122.6(1) |
| Cl(4)–Si(2)–Cl(5) | 106.91(3) | Cl(7)–Si(3)–Cl(8) | 104.34(3) |
| Cl(4)–Si(2)–Cl(6) | 105.73(3) | Cl(7)–Si(3)–Cl(9) | 105.89(3) |
| Cl(5)–Si(2)–Cl(6) | 104.12(3) | Cl(8)–Si(3)–Cl(9) | 106.72(3) |
| Cl(4)–Si(2)–N(2) | 113.30(6) | Cl(7)–Si(3)–N(3) | 112.60(5) |
| Cl(5)–Si(2)–N(2) | 112.40(5) | Cl(8)–Si(3)–N(3) | 112.64(5) |
| Cl(6)–Si(2)–N(2) | 113.65(5) | Cl(9)–Si(3)–N(3) | 113.92(6) |
| N(2)–C(2)–C(21) | 110.3(1) | N(3)–C(3)–C(31) | 110.0(1) |
| N(2)–C(2)–C(22) | 109.2(1) | N(3)–C(3)–C(32) | 109.5(1) |
| C(21)–C(2)–C(22) | 107.5(2) | C(31)–C(3)–C(32) | 110.8(2) |
| N(2)–C(2)–C(23) | 109.3(2) | N(3)–C(3)–C(33) | 109.3(1) |
| C(21)–C(2)–C(23) | 110.1(2) | C(31)–C(3)–C(33) | 107.0(2) |
| C(22)–C(2)–C(23) | 110.4(2) | C(32)–C(3)–C(33) | 110.1(2) |

distances and angles in Tables 5 and 6. The orthorhombic unit cell contains 12 molecules. One molecule in the asymmetric unit exhibits crystallographic $C_2$ symmetry while the second one does not show any symmetry element (Fig. 4). Nevertheless, a careful inspection of the molecular geometry shows that both molecules are almost identical. Chemically equivalent bond lengths and angles are in excellent agreement, both within one particular molecule and between both molecules, respectively. A comparison with corresponding values of the disordered compound **4b** suggests that some values are slightly falsified by the disordered model, but the model itself was correct and even details were well described. For instance, the influence of the bulky groups is reflected by the bond angles at the silicon atom bearing the chlorine substituents, where all N–Si–Cl angles are larger than the ideal tetrahedral angle and the Cl–Si–Cl angles are smaller, respectively. Most important, the geometry of the central N–S–N entity is identical within experimental errors in the three molecules in the two structures studied.

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