*Journal of Organometallic Chemistry*, 248 (1983) 1–15
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# ALKALI METAL DERIVATIVES OF OCTAMETHYLTRISILADIAZANE. UNUSUALLY SHORT Na–C CONTACTS IN THE MOLECULAR STRUCTURE OF THE DISODIUM SALT *

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(Received January 4th, 1983)

## Summary

Alkali metal derivatives $(Me_3SiNM)_2SiMe_2$ of octamethyldisilatriazane (I) have been obtained by the reaction of I with $MNH_2$ (M = Na, K, Cs), or with M in the presence of styrene (M = K, Rb) or with elemental Cs. A monosodium derivative has also been prepared. The dilithium derivative II and the disodium analogue III form stable complexes with ethers. In contrast to the dimeric molecular weights of II and III in benzene solution, an X-ray study of III has revealed trimeric association in the solid state. The crystals belong to the monoclinic space group $C2/c$ with $a$ 21.725(2), $b$ 18.5012(9), $c$ 12.7867(7) Å, $\beta$ 103.347(4)°, $Z = 4$ and $d_c$ 1.11 g/cm$^3$. Refinement yielded a conventional $R$ value of 0.045 for 2909 counter-measured observed reflections. The trimers possess a cluster of six $Na^+$ which are bridged by the N atoms of the anions. If only N–Si and N–Na bonds are considered, the N atoms have coordination numbers of 4 and 5 while coordination numbers of 2, 3 and 4 are found for the cations. The N–Na distances (2.304(3)–2.601(3) Å) reflect the coordination numbers of both N and Na. Surprisingly, the shortest Na–C contact, 2.656(6) Å, is comparable to the longest N–Na bond, and the possible chemical consequences of such metal–alkyl interactions are discussed. The Si–N–Si bond angles vary over a substantial range 122.6(2)–140.0(2)°.

## Introduction

Since the late sixties the alkali metal bis(silyl)amides have become increasingly important in inorganic, organometallic and organic chemistry. Much of the pioneer-

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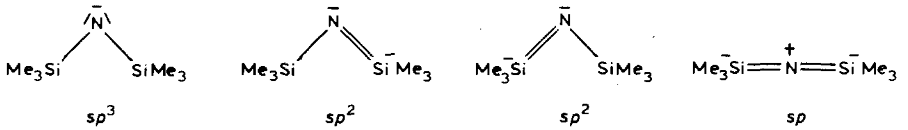
* Dedicated to Prof. U. Wannagat on the occasion of his sixtieth birthday.

0022-328X/83/$03.00

ing work was done by Wannagat and his coworkers who isolated the Li, Na and K derivatives of hexamethyldisilazane, $MN(SiMe_3)_2$* [1]. The applications of these stable amides have been reviewed [2,3].

Numerous properties of these amides, including their volatility and solubility, indicate that their ionic character increases from Li to Cs. The molecular structures in nonpolar solvents of $LiN(SiMe_3)_2$ (**A**) and $NaN(SiMe_3)_2$ (**B**) are oligomeric, at least dimeric [3], and a solvent and concentration dependent equilibrium of oligomers has been established for **A** [4]. Adduct formation with Lewis bases like ether, THF, and dioxane has been observed [1], removal of the donor generally being possible. In the solid state, **A** forms a cyclic trimer [5], while **B** adopts a structure in which $Na^+$ and $N(SiMe_3)_2^-$ ions form an infinite chain [6]. Clearly separate $N(SiMe_3)_2^-$ anions and $K(dioxane)_2^+$ cations make up the structure of $KN(SiMe_3)_2 \cdot 2C_4H_8O_2$, the cation having one N and four O atoms as nearest neighbours [7]. The increase in ionicity from Li to K is reflected in the enlargement of the SiNSi bond angle from 118.6(9) to 136.2(1.2)°, the reduction of the Si–N bond length from 1.729(4) to 1.640(1) Å, and the increase of the $\nu_{as}$(SiNSi) stretching frequency from 973 to 1085 $cm^{-1}$. Even the latter value is exceeded in the Rb and Cs derivatives, 1106 and 1095 $cm^{-1}$, respectively [3,8]. These observations may be rationalized in terms of enhanced importance of multiple bonded canonical forms with increasing polarity (1):



(1)

The lithiation (see eq. 2) of the $Me_3SiNHSiMe_3$ homologue octamethyltrisiladiazane (I) (a compound first described by Brewer and Haber [9], and since synthesized more conveniently [10]) was reported by Fink [11].

$$(Me_3SiNH)_2SiMe_2 + 2LiBu \rightarrow (Me_3SiNLi)_2SiMe_2 + 2C_4H_{10} \qquad (2)$$

(I) (II)

The derivative II is a reactive species from which monocyclic and spirocyclic amides containing four-membered rings may be synthesized by reaction with main group element and transition metal halides as e.g. in eq. 3 [11] and eq. 4 [12].

(3)

(4)

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* $Me = CH_3$, $Et = C_2H_5$, $Bu = n\text{-}C_4H_9$, THF = tetrahydrofuran.

The compound II sublimes in vacuo and is highly soluble in hydrocarbons. Its structure in the gaseous and the solid state is still unknown, but in solution association to a dimer has been reported [11]. The present study, which is related to our efforts to synthesize cyclic transition metal amides, is concerned with the synthesis of the Na, K, Rb and Cs homologues of II, their properties and their structures. For this purpose we undertook a single crystal X-ray investigation of $(Me_3SiNNa)_2SiMe_2$ (III) and the results are described below.

## Synthesis

The dilithium compound II is conveniently prepared by lithiation of I with butyllithium [11] and can either be isolated by sublimation in vacuo or used in solution. If I reacts with butyllithium in a 1/1 ratio, the monolithium derivative IIa is obtained, and attempted distillation of this results in decomposition to I and II (eq. 5) [11].

$$2Me_3SiNHSiMe_2NLiSiMe_3\ (IIa) \xrightarrow{\Delta} I + II \qquad (5)$$

Treatment of $NaNH_2$ suspended in toluene with I at reflux temperature for 24 h affords a product which contains ca. 12.4% Na, corresponding roughly to a 1/1 mixture of the disodio compound III (16.51% Na) and the monosodio compound IIIa (8.96% Na). Separation of III and IIIa is made possible by their very different solubilities. For example, IIIa may be extracted from the mixture with petroleum ether, or III may be crystallized from a solution made by dissolving the mixture in refluxing heptane. Heating equal molar quantities of $NaNH_2$ and I in toluene for one hour yields IIIa quantitatively.

No significant reaction occurred when I was treated with Na in the presence of styrene. However, the analogous reaction (eq. 6) of I with K in refluxing toluene gave a quantitative yield of the dipotassium compound IV. Pure IV is obtained by extraction of the residue with ether and subsequent precipitation with n-hexane. The dirubidium derivative is prepared similarly, the enhanced reactivity of Rb being reflected in the immediate precipitation of V upon gentle heating of the starting material.

$$2K + I + C_6H_5C_2H_3 \rightarrow \underset{(IV)}{(Me_3SiNK)_2SiMe_2} + C_6H_5C_2H_5 \qquad (6)$$

Finally, Cs and I in toluene at room temperature or $CsNH_2$ and I in liquid ammonia react to give a quantitative yield of the dicesium salt VI (eq. 7, 8):

$$2Cs + I \rightarrow H_2 + \underset{(VI)}{(Me_3SiNCs)_2SiMe_2} \qquad (7)$$

$$2CsNH_2 + I \rightarrow 2NH_3 + VI \qquad (8)$$

The monolithium amide IIa may be further metallated with $NaNH_2$, but the reactivity of the mixed lithium/sodium derivative offers no advantages over II and III.

TABLE 1

PROPERTIES OF COMPOUNDS I TO VI

| Compound | M.p. (°C) | B.p. (°C/Torr) | Solubility | | $\delta(^1H)$ (ppm) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Petroleum ether | Toluene | $Si(CH_3)_3$ | $Si(CH_3)_2$ | $CCH$ | $OCH$ |
| I | – | 70/10 | very good | very good | 0.08 | 0.08 | – | – |
| II | 72 | $50/10^{-3}$ | good | very good | 0.15 | 0.25 | – | – |
| IIa | 144 (dec) | – | good | very good | 0.27 | 0.34 | 1.27 | 3.54 |
| IIb | 82 (dec) | – | good | very good | 0.25 | 0.34 | – | 3.52 |
| III | 146–149 | $160/10^{-3}$ (dec) | poor | moderate | 0.18 | 0.22 | – | – |
| IIIa[a] | 130 (dec) | – | moderate | good | 0.17 | 0.27 | – | – |
| IIIb | (25) (dec) | – | good | good | 0.19 | 0.22 | 1.01 | 3.23 |
| IV | 150 (dec) | – | insoluble | poor | 0.20 | 0.22 | – | – |
| V | 120 (dec) | – | insoluble | poor | 0.24 | 0.27 | – | – |
| VI | 180 (dec) | – | insoluble | poor | 0.24 | 0.26 | — | – |

[a] $\delta(^{13}C)$ 2.90, 6.95, 7.21 ppm.

## Properties

The dimetallated octamethyltrisiladiazane derivatives II–VI are colourless solids, and their properties are set out in Table 1. The solubility in nonpolar organic solvents decreases from II to VI, the polar character obviously increasing in the same sequence. Compounds II and III react exothermically with Lewis bases to form the 1/1 adducts $(Me_3SiNLi)_2SiMe_2 \cdot THF$ (IIb), $(Me_3SiNLi)_2SiMe_2 \cdot$ dioxane (IIc) and $(Me_3SiNNa)_2SiMe_2 \cdot Et_2O$ (IIIb). Compound IIIb decomposes at 25°C, while the soluble complex obtained from IV and ether decomposes on removal of the solvent in vacuo at room temperature.

Compound II has been reported to be dimeric in nonpolar solvents [11]. We confirm this observation, and the $M_2^+$ ion is undoubtedly present in the mass spectrum of II. Similarly the cryoscopic molar weight of III in benzene corresponds to a dimer, but the $M^+$ ion is the parent peak in the mass spectrum. In the light of the previous observations on the oligomerization of **A** in solution [4] and in the solid state [5], the degree of aggregation of II and III in solution is likely to depend on the temperature, solvent and concentration, and the particular oligomer favoured in the solid state does not necessarily exist in solution. The crystal structure of III reported below suggests that the cation coordination requirements are sufficiently flexible to allow monomers of III (and probably II) to give various oligomers.

On a whole, the dilithio and disodio derivatives of I appear to be less associated than the corresponding disilylamides **A** and **B**. This is reflected by the greater volatility of II in comparison to **A** and the cluster-like solid-state structure of III.

In addition to the analyses, spectra, and X-ray structure, the chemical properties of II and III confirm the constitution. Hydrolysis with $H_2O$ and $D_2O$ yields I and $(Me_3SiND)_2SiMe_2$ ($\nu$(ND) 2500 $cm^{-1}$), respectively, the sensitivity towards $H_2O$ increasing from II to VI. Compounds II to VI are decomposed to $NH_4^+$ and siloxane by mineral acids.

The disodium compound III reacts more vigorously with halides than II, and details of its reactions with Groups IVa and IVb halides will be published elsewhere. We mention here only that, in an experiment to test the selectivity of such reactions, III and $Me_2SiCl_2$ formed the well-known [11] bis(trimethylsilyl)tetramethylcyclodisilazane in yields exceeding 95%.

The $^1H$ NMR spectra reveal individual signals for the $Me_3Si$ and $Me_2Si$ protons; in I, both signals accidently coincide. In solution the monosodium derivative IIIa is rigid on the NMR time scale, the chemically different $Me_3Si$ groups exhibiting discrete $^{13}C$ resonances while the $^1H$ signals are just resolvable.

The vibrational spectra confirm the presence of MeSi groups and, in carefully prepared samples, prove the absence of NH groups. Some intense features related to the $Si_3N_2$ skeleton may be identified: 585 (II)/555, 575 $cm^{-1}$ (III) in the Raman spectrum, 1069/1075/1145/1155/1125 $cm^{-1}$ (II to VI) in the IR spectrum. The latter frequencies show a variation which is consistent with that of $\nu_{as}$(SiNSi) of the alkali metal bis(trimethylsilyl)amides $MN(SiMe_3)_2$ [3], though vibrational coordinates differ and therefore reservations are advisable when comparing vibrational frequencies.

## X-ray examination

Crystals of III were sealed in a nitrogen-filled glass capillary. The symmetry and systematic absences found on Weissenberg and precession photographs were indicative of the monoclinic space groups *Cc* or *C2/c*, the latter being supported by the refinement. Intensity data were collected by the variable speed $\omega$–$2\Theta$ scan technique with a CAD-4 diffractometer employing Ni filtered Cu-$K_{\bar{\alpha}}$ radiation. The crystal and instrument remained stable during the measurement, the periodically monitored standard reflections drifting less than ± 1.6%. Thereafter 75 reflections were accurately centered, and their Bragg angles were used in the calculation of the cell constants. These and other crystal data are included in Table 2.

Two structural fragments of III were revealed by an *E*-map generated by multisolution direct methods, the remaining nonhydrogen atoms being located in subsequent electron density syntheses. The structure was refined by least-squares techniques, the function minimized was $\Sigma w\Delta^2$, where $w = 1/(\sigma^2(|F_0|) + 0.0004|F_0|^2)$, $\Delta = ||F_0| - |F_c||$ and only reflections with $|F_0| \geq 4\sigma(|F_0|)$ being considered.

Dispersion corrected, isolated atom scattering factors were used for all atoms except H (SDS) [13]. Hydrogen atoms were entered and constrained to remain in calculated positions (C–H 0.95 Å, H–C–H 109.5°, staggered) with an isotropic thermal parameter which was common for each methyl group. A numerical absorption correction was applied. Refinement converged $|\zeta/\sigma|_{\max} = 0.07$ with $R = \Sigma\Delta/\Sigma|F_0| = 0.045$ and $R_w = [\Sigma w\Delta^2/\Sigma w|F_0|^2]^{1/2} = 0.053$ for reflections used in the

*(Continued on p. 9)*

TABLE 2

CRYSTAL DATA FOR $[(Me_3SiNNa)_2SiMe_2]_3$

| | |
|---|---|
| Crystal system | monoclinic |
| *a* | 21.725(2) Å |
| *b* | 18.5012(9) Å |
| *c* | 12.7867(7) Å |
| $\beta$ | 103.347(4)° |
| *Z* | 4 |
| $d_c$ | 1.11 g/cm³ |
| *T* | 20°C |
| Systematic absences | $hkl\ h + k = 2n + 1$ |
| | $h0l\ l(h) = 2n + 1$ |
| Space group | *C2/c* |
| $\lambda$(Cu-$K_{\bar{\alpha}}$) | 1.54178 Å |
| Filter | Ni |
| Octants measured | $hkl$, $\bar{h}kl$ |
| $\Theta$ Range | 1.00–75.00° |
| Scan technique | $\omega$–$2\Theta$ |
| Scan width ($\omega$) | 0.80° + 0.14° tan $\Theta$ |
| Scan speed ($2\Theta$) | 1.25–10.00° min$^{-1}$ |
| Reflections measured | 5701 |
| Unique (minus absences) | 5125 |
| with $|F_0| > 4\sigma(|F_0|)$ | 2909 |
| Crystal size | 0.20 × 0.56 × 0.76 mm |
| $\mu$ (Cu-$K_\alpha$) | 29.93 cm$^{-1}$ |
| Transmission | 0.209–0.583 |

TABLE 3

POSITIONAL [a] AND THERMAL [b,c] PARAMETERS [d] FOR $[(Me_3SiNNa)_2SiMe_2]_3$

| Atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Si(1) | 35969(5) | 41880(5) | 28402(8) | 533(5) | 516(5) | 677(7) | 8(5) | 274(5) | 44(5) |
| Si(2) | 45772(5) | 34672(5) | 45609(8) | 562(6) | 532(6) | 564(6) | −32(5) | 235(5) | −36(5) |
| Si(3) | 39190(6) | 22039(6) | 55636(10) | 960(9) | 780(8) | 761(8) | −95(7) | 353(7) | 213(6) |
| Si(4) | 50000 | 11852(7) | 25000 | 609(8) | 391(7) | 793(11) | 0 | 105(8) | 0 |
| Si(5) | 36809(5) | 13927(6) | 10916(10) | 589(6) | 586(6) | 865(8) | −126(5) | 64(6) | −121(6) |
| Na(1) | 37939(7) | 24459(7) | 30087(11) | 598(8) | 630(8) | 744(10) | −79(7) | 159(8) | −37(7) |
| Na(2) | 50000 | 44912(11) | 25000 | 855(16) | 555(12) | 1315(20) | 0 | 694(15) | 0 |
| Na(3) | 50000 | 28674(9) | 25000 | 616(11) | 458(10) | 711(13) | 0 | 271(10) | 0 |
| Na(4) | 51976(8) | 18951(9) | 48061(13) | 811(11) | 875(11) | 876(12) | 228(9) | 212(10) | 176(9) |
| N(1) | 4288(1) | 3733(1) | 3248(2) | 49(2) | 48(2) | 57(2) | −2(1) | 22(1) | −1(1) |
| N(2) | 4338(1) | 2625(1) | 4801(2) | 66(2) | 55(2) | 65(2) | −1(2) | 26(2) | 10(2) |
| N(3) | 4380(1) | 1707(1) | 1841(2) | 54(2) | 45(2) | 67(2) | −5(1) | 7(2) | −3(1) |
| C(1) | 3636(2) | 5170(2) | 3207(4) | 121(4) | 63(3) | 108(4) | 18(3) | 11(3) | −6(3) |
| C(2) | 2914(2) | 3805(3) | 3345(4) | 72(3) | 127(4) | 144(4) | 22(3) | 61(3) | 56(4) |
| C(3) | 3301(2) | 4207(2) | 1335(3) | 67(3) | 97(3) | 76(3) | 10(2) | 11(2) | −3(2) |
| C(4) | 4453(2) | 4157(2) | 5592(3) | 99(3) | 73(3) | 71(3) | 0(2) | 38(3) | −10(2) |
| C(5) | 5472(2) | 3454(2) | 4816(3) | 64(2) | 77(3) | 66(3) | −7(2) | 11(2) | −8(2) |
| C(6) | 3185(2) | 1785(3) | 4735(4) | 105(4) | 137(4) | 128(4) | −46(4) | 53(4) | 14(4) |
| C(7) | 3680(3) | 2742(3) | 6620(4) | 210(7) | 138(5) | 120(5) | −49(5) | 110(5) | −13(4) |
| C(8) | 4380(3) | 1397(3) | 6262(5) | 204(7) | 126(5) | 148(5) | 24(5) | 45(5) | 85(4) |
| C(9) | 4732(2) | 555(2) | 3486(4) | 92(3) | 68(3) | 118(4) | −7(3) | 18(3) | 27(3) |
| C(10) | 2981(2) | 1938(3) | 1247(4) | 67(3) | 119(4) | 152(5) | 1(3) | −27(3) | −46(4) |
| C(11) | 3433(3) | 454(3) | 1359(6) | 106(4) | 77(3) | 256(8) | −35(3) | −18(5) | 10(4) |
| C(12) | 3620(3) | 1419(4) | −396(4) | 108(4) | 289(9) | 93(4) | −100(5) | 4(4) | −45(5) |

[a] $\times 10^5$ for Si and Na, otherwise $\times 10^4$. [b] $\times 10^4$ for Si and Na, otherwise $\times 10^3$. [c] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(h^2a^*U_{11} + \ldots + 2klb^*c^*U_{23})]$.
[d] Coordinates of the H atoms are not given since they may be readily calculated.

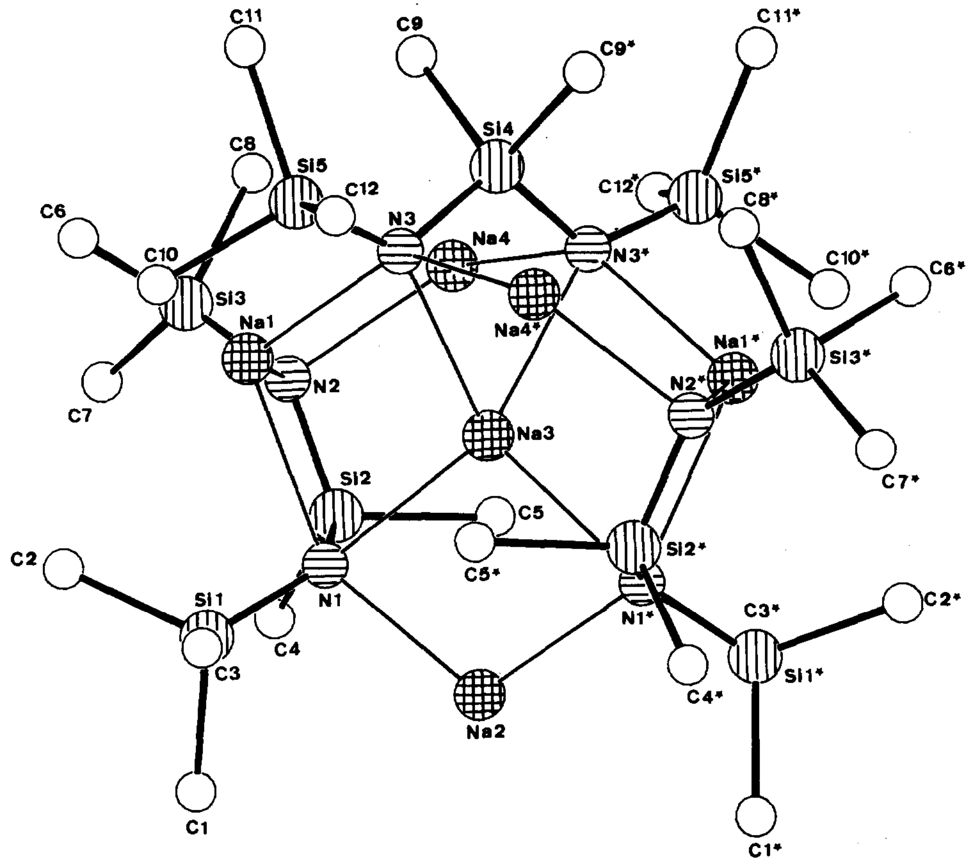

Fig. 1. Projection of the nonhydrogen atoms of $[(Me_3SiNNa)_2SiMe_2]_3$.

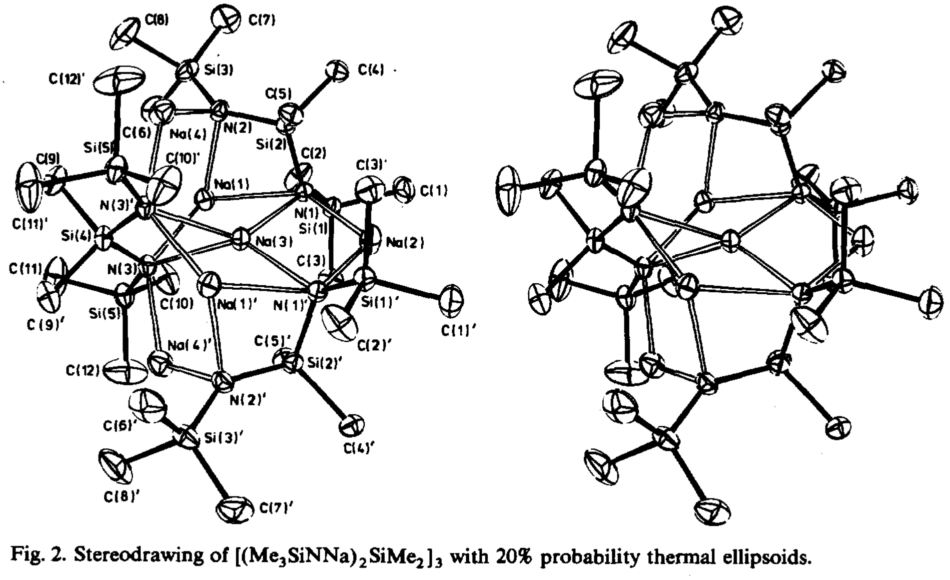

Fig. 2. Stereodrawing of $[(Me_3SiNNa)_2SiMe_2]_3$ with 20% probability thermal ellipsoids.

refinement, the residuals being 0.102 and 0.057 respectively for all reflections. Inspection of an $|F_0|$, $|F_c|$ list * showed that no extinction correction was necessary. The difference Fourier calculated with the final parameters (Table 3) contained densities between 0.34 and −0.24 e/Å$^3$ and thus confirmed the structure. The numbering scheme is shown in Fig. 1 and a stereodrawing is presented in Fig. 2.

### *Description of the crystal structure*

Discrete trimeric molecules of III are found in the solid state, Fig. 3. The trimers possess crystallographic $C_2$ symmetry, Na(2), Na(3) and Si(4) lying on the twofold axis. Bond distances and angles are tabulated in Tables 4 and 5 respectively. Intermolecular contacts are not unusual, the shortest being H(8B)–H(8B) ($1-x$, $y$, $1.5-z$), 2.05(1) Å.

Each trimer contains a cluster of six Na cations. Na(3) is near the center of the cluster, about which the other cations are distributed in a distorted trigonal-bipyramidal fashion. Here Na(1) and Na(1)′ occupy axial sites while Na(2), Na(4) and Na(4)′ are located in equatorial positions. The equatorial cations enter two Na–N bonds with N atoms of two different anions. On the other hand, the axial cations form three Na–N bonds, two of which involve N atoms of one anion. Only the central, four-coordinate cation is bonded to each anion of the trimer.

The cations do not possess the geometries which would be predicted from their coordination numbers. The deviations from tetrahedral geometry at Na(3) are not surprising; that is, the small N(1)–Na(3)–N(1)′, 102.6(1)°, and N(3)–Na(3)–N(3)′, 66.8(1)°, angles are obvious consequences of their being in four-membered rings. Similarly the two-coordinate cations Na(2) and Na(4) exhibit bent (the respective N–Na–N angles being 109.9(1) and 122.2(1)°) rather than linear geometries since they are members of four- and six-membered rings, respectively. The reason for the distinct pyramidality at Na(1), which lies 1.166(2) Å from the plane through its substituents N(1), N(2) and N(3), is less obvious. This distortion greatly relieves the Na(1)–Na(3) repulsions, but the distance found (2.947(2) Å) is still considerably shorter than in the metal (3.72 Å) or in NaF (3.26 Å). We note that of the four unique Na–Na contacts in III which are less than the distance in the metal (Table 4), the shorter contacts Na(1)–Na(3) and Na(2)–Na(3) are bridged by two N atoms while the longer contacts Na(3)–Na(4) and Na(1)–Na(4) are bridged by only one N atom.

The N–Na bond lengths range from 2.304(3) to 2.601(3) Å. The shorter of these are comparable with the average distance in $NaN(SiMe_3)_2$, 2.355(5) Å [6], while the longer linkages resemble those of the cation $[Na(Me_2NCH_2CH_2NMe_2)_2]^+$, 2.511(1)–2.604(1) Å [14]. In III the wide variation of these distances appears to be associated with the different coordination numbers (cn) of the Na and N atoms (Table 6); that is, N(cn4)–Na(cn2) ~ N(cn4)–Na(cn3) < N(cn5)–Na(cn2) < N(cn5)–Na(cn3) ~ N(cn5)–Na(cn4). The fluctuations within categories appear to result from overall structural demands; for example, the relatively short N(2)–Na(4) bond may be compensating for the relatively long N(3)′–Na(4) distance.

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* $F_0$, $F_c$ lists may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen, by quoting the deposit number CSD 50353, the names of the authors, and the literature reference.

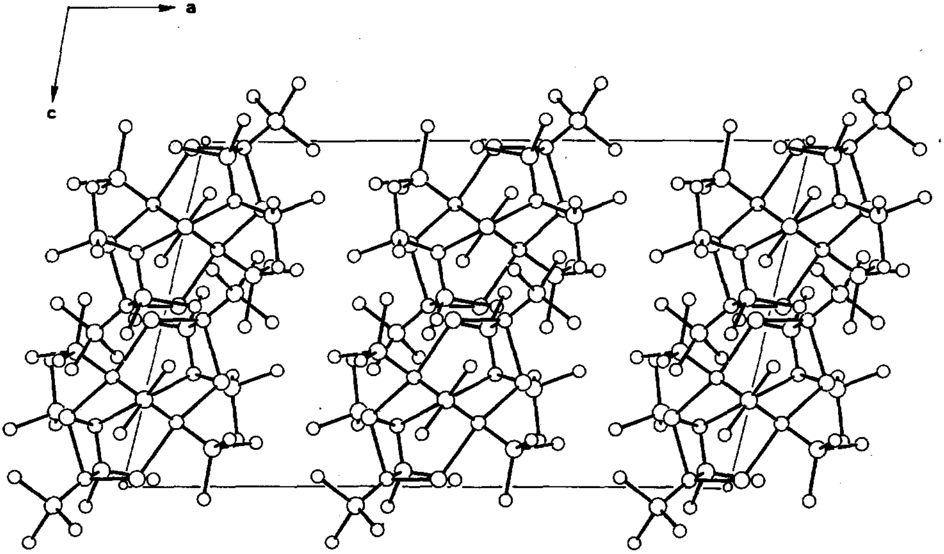


Fig. 3. Projection of the cell contents on the *a*, *c* plane.

TABLE 4

SELECTED INTERATOMIC DISTANCES (Å) IN $[(Me_3SiNNa)_2SiMe_2]_3$

| | | | |
|---|---|---|---|
| ***Bond lengths*** | | | |
| Si(1)–N(1) | 1.695(3) | Si(5)–C(11) | 1.873(5) |
| Si(3)–N(2) | 1.671(3) | Si(5)–C(12) | 1.877(5) |
| Si(5)–N(3) | 1.700(3) | Si(2)–C(4) | 1.899(4) |
| Si(2)–N(1) | 1.723(3) | Si(2)–C(5) | 1.895(4) |
| Si(2)–N(2) | 1.694(3) | Si(4)–C(9) | 1.904(4) |
| Si(4)–N(3) | 1.712(3) | Na(1)–N(1) | 2.601(3) |
| Si(1)–C(1) | 1.873(4) | Na(1)–N(2) | 2.347(3) |
| Si(1)–C(2) | 1.886(4) | Na(1)–N(3) | 2.568(3) |
| Si(1)–C(3) | 1.883(4) | Na(2)–N(1) | 2.441(3) |
| Si(3)–C(6) | 1.867(5) | Na(3)–N(1) | 2.561(3) |
| Si(3)–C(7) | 1.847(5) | Na(3)–N(3) | 2.572(3) |
| Si(3)–C(8) | 1.902(5) | Na(4)–N(2) | 2.304(3) |
| Si(5)–C(10) | 1.872(5) | Na(4)–N(3)′ [a] | 2.509(3) |
| ***Na–C distances*** | | | |
| Na(1)–C(2) | 3.247(5) | Na(3)–C(5) | 3.098(4) |
| Na(1)–C(6) | 3.076(5) | Na(4)–C(5) | 2.944(4) |
| Na(1)–C(10) | 2.691(6) | Na(4)–C(8) | 3.000(7) |
| Na(2)–C(1) | 3.522(5) | Na(4)–C(9) | 3.038(5) |
| Na(2)–C(5) | 3.479(4) | Na(4)–C(12)′ | 2.656(6) |
| ***Na–Na distances*** | | | |
| Na(1)–Na(3) | 2.947(2) | Na(2)–Na(3) | 3.004(3) |
| Na(1)–Na(4) | 3.519(2) | Na(3)–Na(4) | 3.396(2) |

[a] Coordinates of the primed atoms are related to those of Table 3 as follows: $x', y', z' = 1 - x, y, 0.5 - z$.

TABLE 5

BOND ANGLES (°) IN $[(Me_3SiNNa)_2SiMe_2]_3$

| | | | |
|---|---|---|---|
| Si(1)–N(1)–Si(2) | 122.6(2) | N(1)–Si(2)–C(4) | 114.0(2) |
| Si(2)–N(2)–Si(3) | 140.0(2) | N(1)–Si(2)–C(5) | 107.5(1) |
| Si(4)–N(3)–Si(5) | 125.7(2) | N(2)–Si(2)–C(4) | 113.2(2) |
| | | N(2)–Si(2)–C(5) | 107.6(2) |
| N(1)–Na(1)–N(2) | 69.83(9) | N(3)–Si(4)–C(9) | 110.2(2) |
| N(1)–Na(1)–N(3) | 108.0(1) | N(3)–Si(4)–C(9)′ | 110.2(2) |
| N(2)–Na(1)–N(3) | 115.9(1) | | |
| N(1)–Na(2)–N(1)′ [a] | 109.9(1) | C(1)–Si(1)–C(2) | 105.8(2) |
| N(1)–Na(3)–N(1)′ | 102.6(1) | C(1)–Si(1)–C(3) | 102.9(2) |
| N(1)–Na(3)–N(3) | 109.18(9) | C(2)–Si(1)–C(3) | 104.3(2) |
| N(1)–Na(3)–N(3)′ | 135.74(9) | C(4)–Si(2)–C(5) | 101.2(2) |
| N(3)–Na(3)–N(3)′ | 66.8(1) | C(6)–Si(3)–C(7) | 106.9(3) |
| N(2)–Na(4)–N(3)′ | 122.2(1) | C(6)–Si(3)–C(8) | 103.2(3) |
| | | C(7)–Si(3)–C(8) | 106.6(3) |
| Na(1)–N(1)–Na(2) | 139.6(1) | C(9)–Si(4)–C(9)′ | 104.5(2) |
| Na(1)–N(1)–Na(3) | 69.62(8) | C(10)–Si(5)–C(11) | 101.9(2) |
| Na(2)–N(1)–Na(3) | 73.79(9) | C(10)–Si(5)–C(12) | 102.9(3) |
| Na(1)–N(2)–Na(4) | 98.4(1) | C(11)–Si(5)–C(12) | 104.6(3) |
| Na(1)–N(3)–Na(3) | 69.97(8) | | |
| Na(1)–N(3)–Na(4)′ | 137.8(1) | Na(1)–N(1)–Si(1) | 96.1(1) |
| Na(3)–N(3)–Na(4)′ | 83.87(9) | Na(1)–N(1)–Si(2) | 84.3(1) |
| | | Na(2)–N(1)–Si(1) | 101.0(1) |
| N(1)–Si(2)–N(2) | 112.4(1) | Na(2)–N(1)–Si(2) | 115.1(1) |
| N(3)–Si(4)–N(3)′ | 111.4(2) | Na(3)–N(1)–Si(1) | 139.8(1) |
| | | Na(3)–N(1)–Si(2) | 94.0(1) |
| N(1)–Si(1)–C(1) | 114.7(2) | Na(1)–N(2)–Si(2) | 93.4(1) |
| N(1)–Si(1)–C(2) | 114.8(2) | Na(1)–N(2)–Si(3) | 106.6(2) |
| N(1)–Si(1)–C(3) | 113.1(2) | Na(4)–N(2)–Si(2) | 104.9(2) |
| N(2)–Si(3)–C(6) | 111.8(2) | Na(4)–N(2)–Si(3) | 106.0(1) |
| N(2)–Si(3)–C(7) | 117.3(2) | Na(1)–N(3)–Si(4) | 117.0(1) |
| N(2)–Si(3)–C(8) | 110.0(2) | Na(1)–N(3)–Si(5) | 90.7(1) |
| N(3)–Si(5)–C(10) | 113.4(2) | Na(3)–N(3)–Si(4) | 90.9(1) |
| N(3)–Si(5)–C(11) | 118.1(2) | Na(3)–N(3)–Si(5) | 143.4(2) |
| N(3)–Si(5)–C(12) | 114.1(2) | Na(4)′–N(3)–Si(4) | 95.3(1) |
| | | Na(4)′–N(3)–Si(5) | 91.5(1) |

[a] See Table 4.

The positions of the axial and equatorial cations beneath the methyl surface of the trimer may be seen from Fig. 2. Note that Na(1) is surrounded in a nearly trigonal prismatic fashion by three N atoms and three methyl groups while two N atoms and four methyl groups occupy corners of a distorted octahedron about Na(4). While the methyl groups are about 3.50 Å removed from Na(2), they approach Na(1) and Na(4) much more closely (Table 4). Two of the contacts, Na(1)–C(10) (2.691(6) Å) and Na(4)–C(12)′ (2.656(6) Å), are unusually short; indeed, they are comparable with the Na–C distances in $NaC_2H_5$ (2.6(1)–2.7(1) Å) [15]. In III these contacts may be stereochemically active, the orientation of the $SiMe_3$ groups at Si(3)′ and Si(5) obviously favoring these interactions (Fig. 2). Numerous Na–H contacts in the range of 2.3 to 2.6 Å are indicated; however, discussion of their significance is precluded by the fact that the H positions were not experimentally determined.

The two crystallographically unique anions possess distinctly different conformations. The anion on the diad axis has a planar $N_2Si_3$ backbone (rms deviation 0.002 Å) while Si(1) and Si(3) lie 1.426(1) and 0.944(1) Å, respectively, out of the plane through the N(1)–Si(2)–N(3) fragment, the deformation pivoting the $SiMe_3$ groups away from the center of the molecule and simultaneously relaxing Na–Si repulsions. The Si(4)–N(3)–Si(5) angle, 125.7(2)°, is statistically indistinguishable from that in **B**, 125.6(1)° [6]. While the Si(1)–N(1)–Si(2) angle is somewhat smaller, 122.6(2)°, the Si(2)–N(2)–Si(3) angle is much larger, 140.0(2)°. The latter value is the largest on record for a Si–N–Si angle in silylamides, the previous largest being 138.1(4)° in $HN[Si(C_6H_5)_3]_2$ [16].

Several other stereochemical features distinguish N(2) from the other N atoms. First, since it is four rather than five coordinate, N(2) enters the two Na–N bonds which are not only the shortest in III but also shorter than those in **B** (Table 6). Incidentally, the Na(1)–N(2)–Na(4) angle, 98.4(2)°, lies between that found in **B**, 102.0(1)° [6], and the mean Li–N–Li angle found in **A**, 92(2)° [5]. Second, the N(2)–Si(2) and N(2)–Si(3) bonds are nearly eclipsed by the Si(3)–C(7) and Si(2)–C(4) bonds, respectively, the corresponding torsional angles being −8.9 and 12.4°. This constellation of bonds involves only Pitzer strain, since C–C contacts across this and the other Si–N–Si angles exceed the 3.40 Å Van der Waals radii sum. Such strain should be less evident for the other Si–N–Si bond angles because the absolute value of the other C–Si–N–Si torsional angles is 22.8° or larger. Third, the N–Si bonds formed by N(2) are 0.024(8) and 0.027(5) Å shorter than the mean of the other $N{-}SiMe_2$ and $N{-}SiMe_3$ bonds, respectively. Note that the overall mean $N{-}SiMe_3$ bond length, 1.689(9) Å, agrees well with that in **B**, 1.690(5) Å [6].

Inspection of the N–Si–C bond angles reveals that $SiMe_3$ groups of Si(3) and Si(5) are tilted so as to open the N(2)–Si(3)–C(7) and N(3)–Si(5)–C(11) angle. This tilting could be a response to the above mentioned Pitzer strain. It should be noted, however, that the tilting at Si(5) pivots C(10) and C(12) towards Na(1) and Na(4)′ and thus strengthens the strongest Na–C interactions, and an alternative explanation involving direct Na–H interactions cannot be ruled out.

TABLE 6

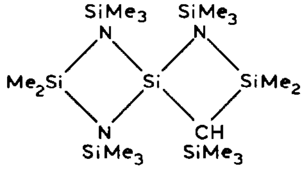
COORDINATION NUMBER DEPENDENCE OF Na-N BOND LENGTHS (Å) IN SILYLAMIDES

| | |
|---|---|
| N(cn4)–Na(cn2) | 2.304(3)<br>2.355(4) [a] |
| N(cn4)–Na(cn3) | 2.347(3) |
| N(cn5)–Na(cn2) | 2.441(3)<br>2.509(3) |
| N(cn5)–Na(cn3) | 2.568(3)<br>2.601(3) |
| N(cn5)–Na(cn4) | 2.561(3)<br>2.572(3) |

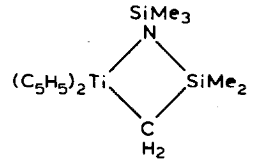
[a] Ref. 6.

## Discussion

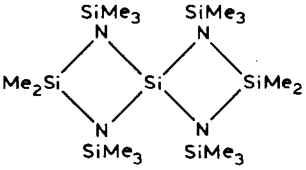
New stereochemical details for alkali metal derivatives of silylamides were revealed by the structural investigation of III. First, the clustering of two, three and four-coordinate cations in III contrasts with the two-coordinate cations found in A [5] and B [6]. Furthermore, the sharply bent two coordination and distinctly pyramidal three coordination encountered in III are not as indicative of covalent Na–N bonding as are the moderately bent geometries (N–M–N ~ 150°) found in A and B. Second, the ability of the N atoms in silylamides to assume five coordination is certainly a prerequisite for the observed cluster formation. This ability was revealed for the first time in this study. Investigations of $N(SiMe_3)_2$ derivatives had disclosed trigonal [7] and distorted tetrahedral geometries [5,6] for the N atoms. Third, the large range of Si–N–Si angles observed in this structure can hardly be explained by the simple electronic arguments presented in the introduction. Presumably these angles are determined by a number of factors, the relative importance of each being difficult to define at present. Fourth, intimate association of cations with the alkyl groups of the silylamide has not been previously detected. Such an interaction is likely to lead to C–H bond activation and thus possibly have consequences for the reactivity of these species. Indeed, such C–H activation may be the cause of several unusual observations in the chemistry of alkali metal silylamides. For example, reaction of **B** with $SiCl_4$ under forcing conditions results in substantial yields of **C** [17].



(C)



(D)



(E)

A related example may be the formation of **D** from $(C_5H_5)_2TiCl_2$ and A [18]. A further observation may be relevant here. While II and III are suitable transfer agents for the doubly charged bidentate ligand $Me_3Si\bar{N}SiMe_2\bar{N}SiMe_3$ [11,12], their reactions with $SiF_4$ or $SiCl_4$ did not yield the desired spirane E even under forcing conditions. Here the difficulties are probably not steric in nature (the spirane can be easily obtained by another route [19]); instead, C–H cleavage may be competing with the expected pathway under these circumstances.

## Experimental

### *Synthesis*

Compound I was prepared according to ref. 10, compound II was made from I and BuLi [11], and purified by sublimation in vacuo, yield 82%.

*Disodiooctamethyltrisiladiazane (III).* A solution of 2.28 g (59 mmol) $NaNH_2$ and 6.0 g (26 mmol) I in 70 ml n-heptane is heated to reflux for 15 h and filtered. The solution is cooled to room temperature and the crystalline material filtered off, yield 40%. For analyses see Table 7.

*Monosodiooctamethyltrisiladiazane (IIIa).* A solution of 1.3 g (33 mmol) $NaNH_2$

TABLE 7

ELEMENTAL ANALYSES

| Sum formula | | Analyses (Found (calcd.)(%)) | | | |
|---|---|---|---|---|---|
| | | C | H | N | Metal |
| IIa | $C_{12}H_{32}Li_2N_2OSi_3$ | | | 8.69<br>(8.79) | 4.33<br>(4.36) |
| IIb | $C_{12}H_{32}Li_2N_2O_2Si_3$ | | | 8.60<br>(8.37) | 4.39<br>(4.15) |
| III | $C_8H_{24}N_2Na_2Si_3$ | 34.37<br>(34.50) | 8.58<br>(8.68) | 10.01<br>(10.06) | 16.22<br>(16.51) |
| IIIa | $C_8H_{25}N_2NaSi_3$ | | | 11.06<br>(10.91) | 9.11<br>(8.96) |
| IIIb | $C_{12}H_{34}N_2Na_2OSi_3$ | | | 7.72<br>(7.94) | 12.66<br>(13.04) |
| IV | $C_8H_{24}N_2K_2Si_3$ | | | 8.78<br>(9.02) | 25.59<br>(25.18) |
| V | $C_8H_{24}N_2Rb_2Si_3$ | | | 6.79<br>(6.94) | 41.74<br>(42.37) |
| VI | $C_8H_{24}Cs_2N_2Si_3$ | | | 5.20<br>(5.62) | 52.53<br>(53.34) |

and 7.7 g (33 mmol) I in 50 ml toluene is refluxed for 1 h and then quickly filtered. The solvent is removed in vacuo and the residue washed with petrol ether, yield 84%.

*Dipotassiooctamethyltrisiladiazane (IV).* (a) 1.12 g (29 mmol) K are dissolved in liquid $NH_3$ in the presence of iron(III) nitrate and the residual $NH_3$ is removed after disappearance of the blue colour. 3.35 g (14 mmol) I in 50 ml toluene are then added and the mixture is heated to reflux for 5 h. The precipitate is extracted with 50 ml ether, 20 ml n-hexane are added to the ethereal solution and the ether removed in vacuo. The precipitate is collected, yield 63%.

(b) A mixture of 1.65 g (42 mmol) K, 5.0 g (21 mmol) I and 2.25 g (22 mmol) styrene in 60 ml toluene is refluxed for 15 h and the precipitate worked up as described in (a), yield 47%.

*Dirubidiooctamethyltrisiladiazane (V).* A mixture of 1.09 g (13 mmol) Rb, 1.5 g (6.4 mmol) I and 1.3 g (13 mmol) styrene in 20 ml toluene is refluxed for 1 h and the precipitate is recrystallized from ether/hexane at −25°C, yield 68%.

*Dicesiooctamethyltrisiladiazane (VI).* (a) 0.5 g (3.8 mmol) Cs is dissolved in liquid $NH_3$, then 0.44 g (1.9 mmol) I is added. The $NH_3$ is removed during 4 h and the residue collected, yield 76%. (b) To 1.48 g (11 mmol) Cs and 20 ml toluene are added 1.29 g (5.5 mmol) I. $H_2$ is evolved in an exothermic reaction, a precipitate of VI being rapidly formed in 70% yield.

*Complexes with Lewis bases.* II and III are dissolved in tetrahydrofuran, dioxane or diethyl ether, the solvent is removed in vacuo and the crystalline residues are collected.

*Analyses.* See Table 7.

*Spectra.* $^1H$ NMR: Varian EM 390, 90 MHz, $\leq 10\%$ in $C_6D_6$, TMS as internal standard. $^{13}C$ NMR: Varian FT 80, 20.0 MHz, $C_6D_6$ as solvent and internal standard, $\delta$ 127.96 ppm. IR: Nujol mulls, 300–4000 $cm^{-1}$, Perkin–Elmer 580 B.

Raman: Crystalline material in 1 mm o.d. capillaries, Cary 82, $Kr^+$ 6471 Å excitation.

## Acknowledgement

Support by the Fonds der Chemie and by Bayer AG through a gift of chemicals is gratefully acknowledged.

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