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THE CRYSTAL STRUCTURE OF N-SODIOHEXAMETHYLDISILAZANE, $Na[N\{Si(CH_3)_3\}_2]$

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Summary

The crystal structure of $Na[N\{Si(CH_3)_3\}_2]$ has been determined from single-crystal X-ray diffraction data collected by counter methods. N-sodiohexamethyldisilazane crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $\underline{a}$ = 9.426(3), $\underline{b}$ = 6.921(3), c = 17.974(5)Å, β = 93.83(2)°, and ρ_{calc} = 1.04 g cm^{-3} for Z = 4 formula units. Least-squares refinement gave a final conventional R value of 0.034 for 1244 independent observed reflections. In the solid state the compound exists in a polymeric arrangement with an average Na-N distance of 2.355(4)Å. The methyl group are configured such that the angle of rotation of the trimethylsilyl moiety about the Si-N bond is 30° from the eclipsed position. The Si-N bond length is 1.690(5)Å, and the Si-N-Si bond angle is 125.6(1)°.

Introduction

Since the initial preparation of the alkali metal silazanes by Wannagat[1] and coworkers in 1959, there has been a high level of interest in the structure and reactivity of these compounds. The reaction of transition metal chlorides with $M[N\{Si(CH_3)_3\}_2]$ (M = alkali metal) and related compounds has led to a series of low coordination number transition metal complexes.[2] The structural features of the pure three-coordinate species $M'[N\{Si(CH_3)_3\}_2]$ (M' = Fe,[3] Sc,[4], Eu[4]), and the solvated complexes $Cr[N\{Si(CH_3)_3\}_2]_2 \cdot 2C_4H_8O$,[5] $Co[N\{Si(CH_3)_3\}_2]_2 \cdot P(C_6H_5)_3$,[6] and $Ni[N\{Si(CH_3)_3\}_2] \cdot 2P(C_6H_5)_3$[6] have been obtained from single crystal X-ray studies.

The properties of the alkali metal derivatives themselves have also been the subject of numerous investigations. N-lithio- and N-sodiohexamethyldisilazane have properties normally associated with covalent substances: they are readily soluble in hydrocarbon solutions (in which they exist as dimers), and they exhibit no electrical conductivity in solution or in the melt.[1] The potassium, rubidium, and cesium compounds, on the other hand, are insoluble in hydrocarbons, and behave as ionic substances.[1] X-ray crystal structures have been obtained on $Li[N\{Si(CH_3)_3\}_2]$[7] and $K[N\{Si(CH_3)_3\}_2] \cdot 2C_4H_8O_2$,[8] and have revealed surprising results. The former was found to be trimeric in the solid state, while the latter exhibits a much larger Si-N-Si bond angle than expected.

The crystal structure of $Na[N\{Si(CH_3)_3\}_2]$ was of interest to our group for two primary reasons. First, the question of the degree of association in solution versus the solid state raised by the lithium structure was unresolved. Second, the relation of the structure and solution behavior of $M[N\{Si(CH_3)_3\}_2]$ to that of $M[X\{Al(CH_3)_3\}_2]$ (X = halide or pseudohalide)[9] has not been explored.

Experimental

N-sodiohexamethyldisilazane was recrystallized under a nitrogen atmosphere from mesitylene, and the colorless, air-sensitive parallelepipeds were sealed in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of the angular settings of 15 reflections ($2\theta > 20°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table 1.

Table 1. Crystal Data.

Mol. formula: $Na[N\{Si(CH_3)_3\}_2]$

Mol. wt.: 183.38

Linear abs. coeff. μ: 2.84 cm^{-1}

Calc. density: 1.04 g cm^{-3}

Max. crystal dimensions: 0.30 x 0.30 x 0.52 mm

Space group: monoclinic, $P2_1/n$

Molecules/unit cell: 4

Cell constants[a]: a = 9.426(3)Å
b = 6.921(3)
c =17.974(5)
β =93.83(2)°

Cell volume: 1170.0$Å^3$

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[a] MoKα radiation, λ = 0.71069Å. Ambient temperature of 23 ± 1°C.

Data were collected on the diffractometer with graphite crystal monochromated molybdenum radiation. The diffracted intensities were collected by the ω-2θ scan technique with a take-off angle of 3.5°. The scan rate was variable and was determined by a fast 20° min^{-1} prescan. Calculated speeds for the slow scan (based on the net intensity gathered in the prescan) ranged from 7 to 0.4° min^{-1}. Other diffractometer parameters and the method of estimation of standard deviations have been previously described.[10] As a check on the stability of the instrument and crystal, two reflections were measured after every 40 reflections; no significant variation was noted.

One independent quadrant of data was measured out to 2θ = 50°; a slow scan was performed on a total of 1244 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 30 was obtained in the prescan. Based on these considerations, the data set of 1244 reflections (used in the subsequent structure determination and refinement) was considered observed, and consisted in the main of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 2.84\ \mathrm{cm}^{-1}$).

The function $w(|F_o| - |F_c|)^2$ was minimized.[11] No corrections were made for extinction. Neutral atom scattering factors were taken from the compilations of Cromer and Waber[12] for Na, Si, N, and C; those for H were from "International Tables for X-ray Crystallography."[13]

Structure Solution and Refinement

The structure was solved by the straight-forward application of the direct methods program MULTAN.[14] Several cycles of least-squares refinement of the positional and isotropic thermal parameters of the ten nonhydrogen atoms afforded a reliability factor of $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.114$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.068$. The positions of the eighteen hydrogen atoms were determined from a difference Fourier map, and more cycles of refinement led to final values of $R_1 = 0.035$ and $R_2 = [\Sigma w|F_o| - |F_c|)^2/\Sigma|F_o|]$ 0.034. The weighting scheme was based on unit weights, and unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.01 of their estimated standard deviations. The estimated standard deviation of an observation of unit weight was 0.76. The final values of the positional and thermal parameters are given in Table 2.[*]

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[*] The table of structure factors is available and readers can obtain it by applying directly to the authors.

Table 2. Final Fractional Coordinates and Thermal Parameters[a] for $Na[N\{Si(CH_3)_3\}_2]$.

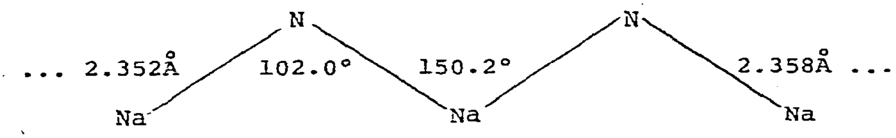
Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	0.3037(2)	0.9698(2)	0.2695(1)	0.0194(2)	0.0372(4)	0.0065(1)	0.0074(3)	-0.0013(1)	-0.0074(1)
Si1	0.0204(1)	0.1849(1)	0.3336(1)	0.0107(1)	0.0237(2)	0.0038(1)	-0.0008(1)	0.0009(1)	0.0005(1)
Si2	0.3132(1)	0.2979(1)	0.3952(1)	0.0122(1)	0.0229(2)	0.0030(1)	0.0008(1)	0.0001(1)	-0.0004(1)
N	0.1944(2)	0.2349(3)	0.3250(1)	0.0108(3)	0.0219(6)	0.0033(1)	0.0001(3)	0.0006(1)	0.0001(2)
C1	-0.0123(4)	-0.0781(6)	0.3472(2)	0.0210(6)	0.0348(12)	0.0069(2)	-0.0100(7)	-0.0003(3)	0.0031(4)
C2	-0.0897(4)	0.2512(7)	0.2473(2)	0.0124(5)	0.0572(16)	0.0074(2)	-0.0020(7)	-0.0006(2)	0.0076(5)
C3	-0.0645(4)	0.3119(8)	0.4109(3)	0.0171(6)	0.0606(18)	0.0080(2)	0.0005(9)	0.0045(3)	-0.0049(6)
C4	0.2866(5)	0.1928(8)	0.4882(2)	0.0244(7)	0.0667(19)	0.0042(2)	-0.0088(10)	-0.0008(3)	0.0038(5)
C5	0.4957(4)	0.2222(7)	0.3730(2)	0.0141(5)	0.0518(14)	0.0050(2)	0.0049(7)	-0.0015(2)	-0.0033(4)
C6	0.3204(4)	0.5655(6)	0.4094(2)	0.0205(6)	0.0293(10)	0.0076(2)	-0.0017(7)	-0.0018(3)	-0.0051(4)
H1(C1)	0.030	-0.120	0.393	b					
H2(C1)	0.007	-0.129	0.304						
H3(C1)	-0.115	-0.110	0.347						
H4(C2)	-0.089	0.382	0.248						
H5(C2)	-0.051	0.219	0.204						
H6(C2)	-0.173	0.213	0.252						
H7(C3)	-0.171	0.302	0.409						
H8(C3)	-0.022	0.248	0.454						
H9(C3)	-0.059	0.434	0.399						
H10(C4)	0.270	0.082	0.485						
H11(C4)	0.192	0.209	0.508						
H12(C4)	0.362	0.216	0.521						
H13(C5)	0.556	0.266	0.404						
H14(C5)	0.516	0.263	0.324						
H15(C5)	0.499	0.091	0.379						
H16(C6)	0.391	0.605	0.445						
H17(C6)	0.358	0.621	0.363						
H18(C6)	0.234	0.615	0.421						

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell)]$.

[b] Hydrogen atom coordinates were located on a difference Fourier map and were not refined. The temperature factors were not refined, but were taken as 5.0Å^2.

Discussion

The structure of the N-sodiohexamethyldisilazane anion and the atom numbering scheme are presented in Figure 1. The compound exists as an infinite chain of cations and anions in the solid state with the parameter given in **I**. This is in contrast to the reported dimeric behavior in solution.[1]



I

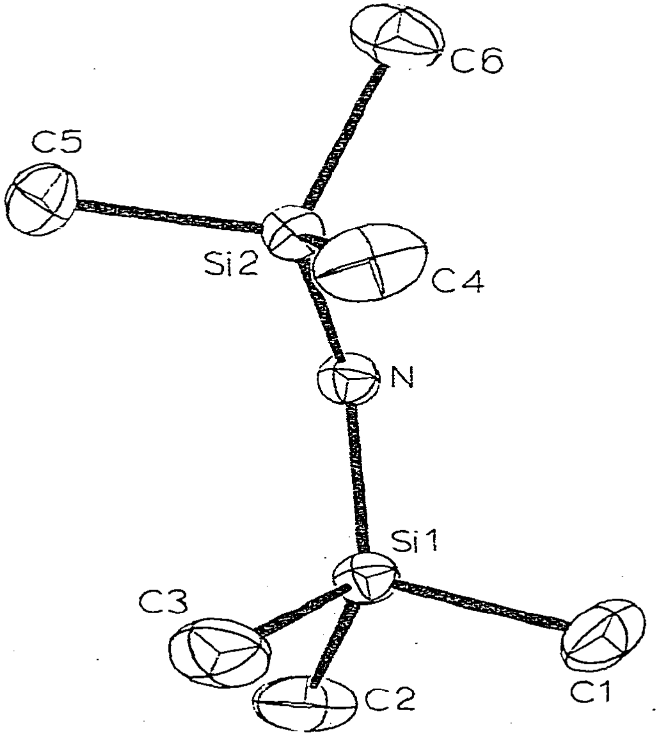
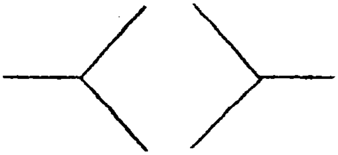
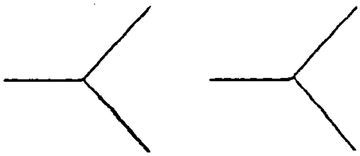


Figure 1. Structure and Atom Numbering Scheme of the Anion in N-sodiohexamethyldisilazane

An important structural aspect of ions or molecules of this type concerns the configuration of the methyl groups. One can envision two possible extremes: eclipsed (C_{2v}) as in II or staggered (C_s) as in III. The crystal structure of $K[Al_2(CH_3)_6N_3]$

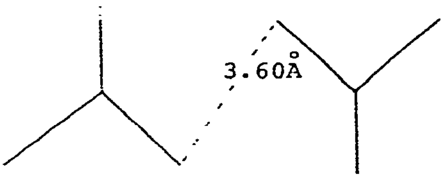


II



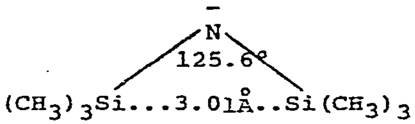
III

revealed that there are two different anions in the asymmetric unit, one eclipsed *and* one staggered.[15] Even though many hexamethyldisilazane structures have been reported,[3-6] data on the configuration of the $N\{Si(CH_3)_3\}_2^-$ ion has not been routinely included. The question was considered by Clark and Haaland[16] in connection with $Be[N\{Si(CH_3)_3\}_2]$. On the basis of electron diffraction data they obtained a value of 7.2(3.5)° for the angle of rotation of the trimethylsilyl group (from the position when one Si-C bond is eclipsed with the Be-N bond; an equivalent frame of reference would be the other Si-N bond). In the present study, an angle of rotation of 30° is observed. This presumably results from the need to minimize the nonbonded methyl-methyl repulsion. With the 30° rotation, the closest C(methyl)-C(methyl) approach is 3.60Å (IV).

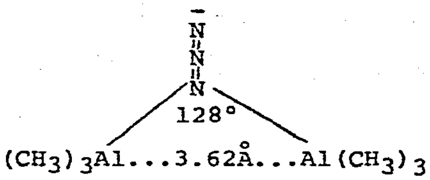


IV

The anions, $N\{Si(CH_3)_3\}_2^-$ (V) and $[N_3\{Al(CH_3)_3\}_2]^-$ (VI), possess an overall structural similarity, but differ in one



V



VI

aspect. The Al-N bond length[15] of 2.02Å compares reasonably well with the 1.90Å value estimated from a sum of covalent radii.[17] However, the Si-N length, 1.690(5)Å (Table 3), is much shorter than the 1.87Å prediction. Steric factors could reasonably be invoked to explain the elongation of the Al-N bond length, but the Si-N bond length is in fact contracted. As has been pointed out previously,[1] this is a manifestation of the presence of d_π-p_π bonding between the silicon and nitrogen atoms. The result of the shortened metal-nitrogen bond length is a Si...Si separation of 3.01Å versus an Al...Al distance of 3.62Å.[15]

Within the hexamethyldisilazane ion there are two parameters of importance: the Si-N bond length and the Si-N-Si bond angle. A tabulation of these values is presented as Table 4. Although the Si-N bond lengths mostly fall within the range 1.69 → 1.73Å, the 1.64(1)Å value found in $K[N\{Si(CH_3)_3\}_2]\cdot 2C_4H_8O_2$ is significantly shortened,[18] and may reflect the fact that the cation and anion interact in a predominantly ionic fashion. The greater degree of covalency in the $Na^+\cdots{}^-N\{Si(CH_3)_3\}_2$ bond is reflected in the 1.690(5)Å N-Si bond length. This criterion has been used to ascribe a greater degree of ionicity in $Eu[N\{Si(CH_3)_3\}_2]_3$ as compared to $Sc[N\{Si(CH_3)_3\}_2]_3$.[4]

The interpretation of the Si-N-Si bond angle is not so straightforward. It may be argued that an increase in the electronegativity of the M group in $MN\{Si(CH_3)_3\}_2$ demands an increase in the p-character of the M-N bond. This in turn must

Table 3. Interatomic Distances (Å) and Angles (°) for $Na[N\{Si(CH_3)_3\}_2]$.

	Bond Distances		
N -Si1	1.694(2)	N -Si2	1.687(2)
Si1-C1	1.865(4)	Si2-C4	1.856(4)
Si1-C2	1.865(4)	Si2-C5	1.868(4)
Si1-C3	1.869(4)	Si2-C6	1.870(4)
Na^{1a}-N	2.352(2)	Na^{11}-N	2.358(3)
	Bond Angles		
N -Si1-C1	112.4(2)	N -Si2-C4	116.7(2)
N -Si1-C2	111.2(1)	N -Si2-C5	110.0(1)
N -Si1-C3	115.9(2)	N -Si2-C6	112.0(2)
C1-Si1-C2	105.1(2)	C4-Si2-C5	105.4(2)
C1-Si1-C3	106.2(2)	C4-Si2-C6	105.7(2)
C2-Si1-C3	105.1(2)	C5-Si2-C6	106.4(2)
Si1-N-Si2	125.6(1)	N -Na -N^{111}	150.2(1)
		Na^{1}-N-Na^{11}	102.0(1)

[a] Na^{1} is related to Na by (x, y - 1, z); Na^{11} is related to Na by (½ - x, y - ½, ½ - z); N^{111} is related to N by (x, 1 + y, z).

Table 4. Comparison of Selected Structural Parameters for the $[N\{Si(CH_3)_3\}_2]^-$ Ion.

Compound	Si-N Distance (Å)	Si-C Distance (Å)	Si-N-Si Angle (°)	Reference
$K[N\{Si(CH_3)_3\}_2]\cdot 2C_4H_8O_2$	1.64(1)	1.90(3)	136.2(1.2)	8
$Eu[N\{Si(CH_3)_3\}_2]_3$	1.68	–	129.4	4
$Na[N\{Si(CH_3)_3\}_2]$	1.690(5)	1.866(5)	125.6(1)	–
$Cr[N\{Si(CH_3)_3\}_2]_2\cdot 2C_4H_8O$	1.69(2)	–	–	5
$Ni[N\{Si(CH_3)_3\}_2]\cdot 2\ P(C_6H_5)_3$	1.70(1)	–	126(1)	6
$Co[N\{Si(CH_3)_3\}_2]_2\cdot P(C_6H_5)_3$	1.706(9)	–	125(1)	6
$Cr[N\{Si(CH_3)_3\}_2]_3\cdot NO$	1.72(3)	–	–	5
$Be[N\{Si(CH_3)_3\}_2]_2$	1.722(7)	1.876(4)	129.2(7)	16
$Sc[N\{Si(CH_3)_3\}_2]_3$	1.73	–	121	4
$Fe[N\{Si(CH_3)_3\}_2]_3$	1.73(3)	1.886(12)	121.2(4)	3
$H[N\{Si(CH_3)_3\}_2]$	1.735(12)	1.867(4)	125.5(1.8)	a
$Al[N\{Si(CH_3)_3\}_2]_3$	1.75(2)	1.90(2)	118.0(1.5)	b

[a] A. G. Robietle, G. M. Sheldrick, and W. S. Sheldrick, Chem. Comm. (1968) 909.

[b] G. M. Sheldrick and W. S. Sheldrick, J. Chem. Soc. A, (1969) 2279.

increase the s-character in the N-Si bonds, and thus, increase the Si-N-Si bond angles. Such is not the case for the compounds given in Table 4: for M = K, the largest Si-N-Si angle is found.[8] The effect may well be of only minor significance, since the range of electronegativities of the M groups is not great. The explanation of the large angle for the potassium salt could well lie in a steric effect. A decrease in the Si-N bond length will force the nonbonded methyl groups of the $-Si(CH_3)_3$ units closer together. This unfavorable effect could be offset by a change in configuration, an opening of the Si-N-Si bond angle, or a combination of both.

All bond lengths and angles involving the methyl carbon atoms are normal. The C-H bond lengths range from 0.78 to 1.01Å, and average 0.92Å. A stereoscopic view of the unit cell packing is given in Figure 2.

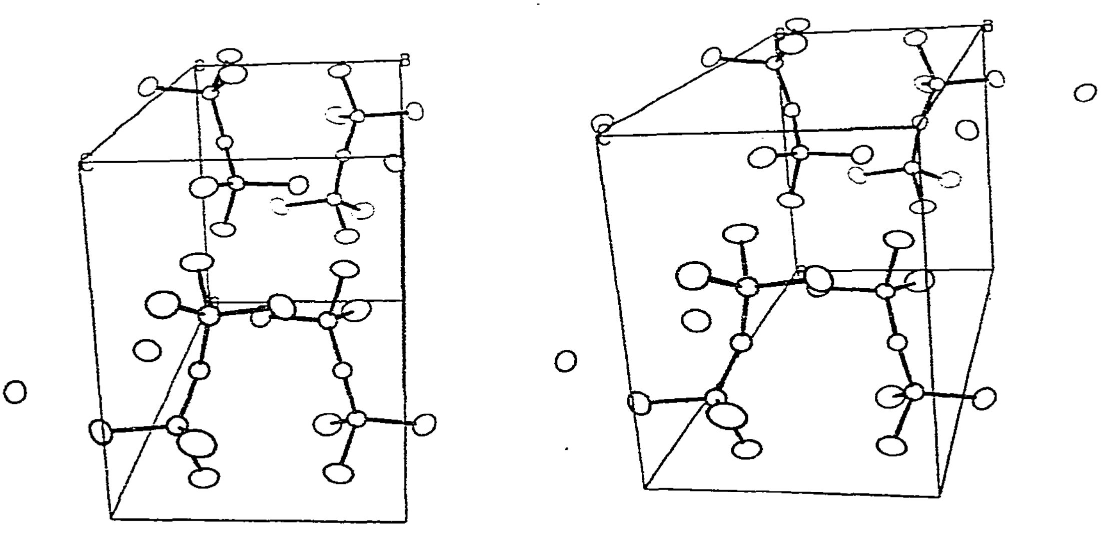


Figure 2. Stereoscopic View of the Unit Cell Contents with the Atoms Represented by Their 40% Probability Ellipsoids for Thermal Motion

Acknowledgment

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