

Dodecamethylcyclotetrasilazane

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Abstract. $[(\text{CH}_3)_2\text{SiNCH}_3]_4$, rhombohedral, $R\bar{3}$, $a = 21.46 \text{ \AA}$, $\alpha = 117.9^\circ$, $D_m = 1.1$, $Z = 28$ monomers, $D_x = 1.108$ (hexagonal cell, $a = 36.78$ (3), $c = 9.37$ (1) \AA , $Z = 84$ monomers). Six tetramers are arranged around the $\bar{3}$ position; these molecules contain an eight-membered Si_4N_4 ring with a tub conformation, $\text{Si-N} = 1.735$, $\text{Si-C} = 1.88$, $\text{N-C} = 1.51 \text{ \AA}$, $\text{N-Si-N} = 110.7$, $\text{C-Si-C} = 107.4$, $\text{Si-N-Si} = 122.8$, $\text{Si-N-C} = 118.0^\circ$. Residual electron-density indicates that a hole around the $\bar{3}$ position probably accommodates a disordered centrosymmetric tetramer.

Introduction. Unit-cell and intensity data were measured with a crystal (Wannagat, Braun, Gerschler & Wismar, 1971) in a sealed capillary, on a Datex-automated G.E.XRD 6 diffractometer with $\text{Cu K}\alpha$ radiation and the usual $\theta-2\theta$ scan. Two sets of data were measured; during collection of the first set the intensity of a check reflexion decreased by 50% as a result of volatilization, and a second set was collected with new crystals being used after 10% intensity decrease. The second set, which was used in the final refinement, consisted of about 3500 independent reflexions with $2\theta \leq 120^\circ$, of which 2700 with intensity greater than 3σ above background [$\sigma^2(I) = S + B + (0.05S)^2$, where $S = \text{scan}$ and $B = \text{background count}$] were used in the re-

finement. Various attempts to determine the structure were unsuccessful, partly as a result of uncertainty in the number of monomer units in the cell, since the rhombohedral cell could not accommodate seven tetramers in an ordered fashion. Finally the positions of four Si atoms were determined from the Patterson function, and all the C and N atoms in six symmetry-related tetramers from electron-density maps. Least-squares refinement converged at $R = 0.26$. A difference map then revealed electron-density in a large hole around the $\bar{3}$ position; some of the peaks were too close together to represent an ordered arrangement of atoms. The structure was further refined with inclusion of atom types on the difference map peaks, appropriate to peak height (Table 1); positional, isotropic thermal, and occupancy parameters were refined for these atoms, while the remainder of the structure was refined anisotropically. R converged at 0.14 for 2700 observed data (0.18 for all data); these high values probably result from the disorder. The function minimized was $\sum w(F_o - F_c)^2$, with $w = 1$. Final positional parameters for the ordered tetramer are in Table 2.†

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† Thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31411 (32 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Interpretation of difference synthesis (hexagonal axes)

| Peak height ($e \text{ \AA}^{-3}$) | Difference synthesis | | | | | Interpretation | | | | |
|---|----------------------|-------|-------|-------------|-----|----------------|--------|--------|--------|-------|
| | x | y | z | $f\ddagger$ | B | Occupancy | Atom | x | y | z |
| 1.7 | 0.05 | 0 | 0.11 | Si | 6 | 0.8 | Si(5) | 0.046 | 0.002 | 0.12 |
| 1.7 | 0.03 | 0.06 | -0.02 | Si | 6 | 0.7 | Si(6) | 0.034 | 0.061 | -0.02 |
| 0.6 | 0.05 | 0.05 | 0.08 | C | 4 | 0.6 | N(5) | 0.054 | 0.052 | 0.12 |
| 1.4 | 0.04 | -0.02 | 0.29 | C | 7 | 2.0 | C(13) | 0.042 | -0.016 | 0.29 |
| —* | 0.02 | 0.03 | -0.19 | C | 4 | 1.5 | C(17) | 0.054 | 0.062 | -0.18 |
| | | | | | | | C(14) | 0.098 | 0.009 | 0.02 |
| 1.7 | 0.09 | 0.01 | 0.02 | C | 7 | 2.2 | C(15)† | 0.095 | 0.004 | -0.08 |
| | | | | | | | C(18)§ | 0.097 | 0.012 | -0.04 |
| | | | | | | | N(6) | -0.017 | 0.043 | -0.02 |
| | | | | | | | C(16) | 0.046 | 0.107 | 0.02 |
| Hidden by Si peaks | | | | | | | | | | |
| No peak in difference map | | | | | | | | | | |

* Tail of Si(5) peak.

† One-third multiplicity for all atoms.

‡ C(15) 0.091, 0.095, 0.08

§ C(18) -0.012, 0.085, -0.04

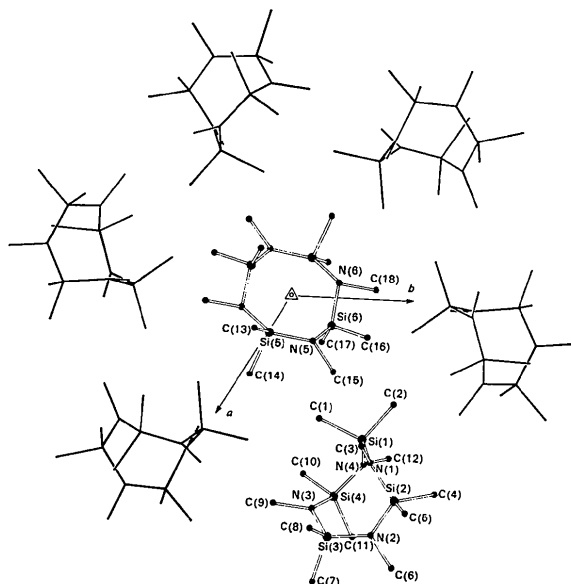


Fig. 1. Structure of dodecamethylcyclotetrasilazane viewed down *c*; the molecule around the $\bar{3}$ position is disordered, and one possible interpretation is shown.

Table 2. Positional parameters of the ordered tetramer (hexagonal axes; $\sigma=0.007, 0.017, 0.022 \text{ \AA}$ for Si, N, C parameters, respectively)

| | <i>x</i> | <i>y</i> | <i>z</i> |
|-------|----------|----------|----------|
| Si(1) | 0.1708 | 0.1683 | 0.3444 |
| Si(2) | 0.2434 | 0.2424 | 0.4953 |
| Si(3) | 0.2901 | 0.1957 | 0.4217 |
| Si(4) | 0.2401 | 0.1750 | 0.1473 |
| N(1) | 0.1993 | 0.1921 | 0.4963 |
| N(2) | 0.2867 | 0.2408 | 0.4196 |
| N(3) | 0.2569 | 0.1601 | 0.2954 |
| N(4) | 0.2011 | 0.1869 | 0.1940 |
| C(1) | 0.1485 | 0.1100 | 0.3576 |
| C(2) | 0.1271 | 0.1782 | 0.3298 |
| C(3) | 0.1791 | 0.1726 | 0.6370 |
| C(4) | 0.2323 | 0.2795 | 0.3911 |
| C(5) | 0.2558 | 0.2603 | 0.6839 |
| C(6) | 0.3234 | 0.2827 | 0.3771 |
| C(7) | 0.3453 | 0.2093 | 0.3748 |
| C(8) | 0.2803 | 0.1720 | 0.6079 |
| C(9) | 0.2521 | 0.1171 | 0.3070 |
| C(10) | 0.2164 | 0.1299 | 0.0129 |
| C(11) | 0.2874 | 0.2210 | 0.0539 |
| C(12) | 0.1918 | 0.2081 | 0.0716 |

Discussion. The interpretation of the disordered part of the structure is uncertain. A threefold-disordered

Table 3. Summary of bond lengths ($\sigma=0.02\text{--}0.03 \text{ \AA}$) and angles ($\sigma=1\text{--}2^\circ$) in the ordered tetramer

| | Range | Mean |
|------|--------------------------------------|-----------------------|
| Si-N | 1.71–1.75(Å) | 1.73 ₅ (Å) |
| Si-C | 1.82–1.93 | 1.88 |
| N-C | 1.50 ₅ –1.51 ₉ | 1.51 |

| | Range | Mean |
|--------------------|--------------|--------|
| N-Si-N | 109.9–111.6° | 110.7° |
| C-Si-C | 105.5–109.9 | 107.4 |
| N-Si-C | 107.5–112.8 | 109.7 |
| Si-N-Si | 121.8–123.8 | 122.8 |
| Si-N-C | 111.3–123.9 | 118.0 |
| Sum of angles at N | 358.4–359.2 | 358.8 |

centrosymmetric tetramer (chair conformation) can be fitted to the peaks moderately well (Fig. 1 and Table 1). The well resolved tetramers (six of seven in the cell) have a slightly twisted tub (cradle) conformation (Fig. 1); Si(2), N(2), Si(4), and N(4) are coplanar to within about 0.1 Å, with the other four atoms displaced by about 1.2 Å on the same side of the plane (and *vice versa*). An ordered arrangement of these two conformers has been found in the octamethyl compound (Smith & Alexander, 1963). Bond lengths and angles (Table 3) are close to those in the octamethyl compound. One reason for examining the structure was interest in the geometry at the N atoms, since the H positions in the NH groups of the octamethyl compound were not located directly. The sums of the angles at N in the present compound (358.4–359.2°, Table 3) indicate that these atoms have close to trigonal planar geometry. Finally, we can suggest no reason for these tetrameric molecules crystallizing in the rhombohedral system.

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