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THE MOLECULAR STRUCTURE OF HEXAMETHYLCYCLODISILAZANE; AN ELECTRON DIFFRACTION STUDY

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Summary

The molecular geometry of gaseous hexamethylcyclodisilazane has been determined by electron diffraction. The four-membered ring and the nitrogen bond configuration are planar or nearly planar. The main parameters with estimated total error are: bond lengths (r_g) Si–N 1.736 ± 0.004, Si–C 1.864 ± 0.004, and N–C 1.460 ± 0.005 Å; bond angles N–Si–N 86.4 ± 0.3 and Ni–Si–C 115.4 ± 0.5°.

Introduction

The structures of free (vapor-phase) four-membered ring molecules with one or more silicon atoms in the ring have recently attracted considerable interest [1–3]. The structures of several derivatives have been determined by X-ray diffraction in the solid state [3–11]. However, one of the simplest compounds, hexamethylcyclodisilazane, $(CH_3)_2\overline{SiN(CH_3)Si(CH_3)_2N}CH_3$, has not previously been studied. This compound is a liquid at room temperature and so it is not a good subject for an X-ray diffraction study. Its liquid vibrational spectra indicated D_{2h} point group for this molecule, which is consistent with a planar four-membered ring and planar nitrogen bond configurations [12]. We present below the results of an electron

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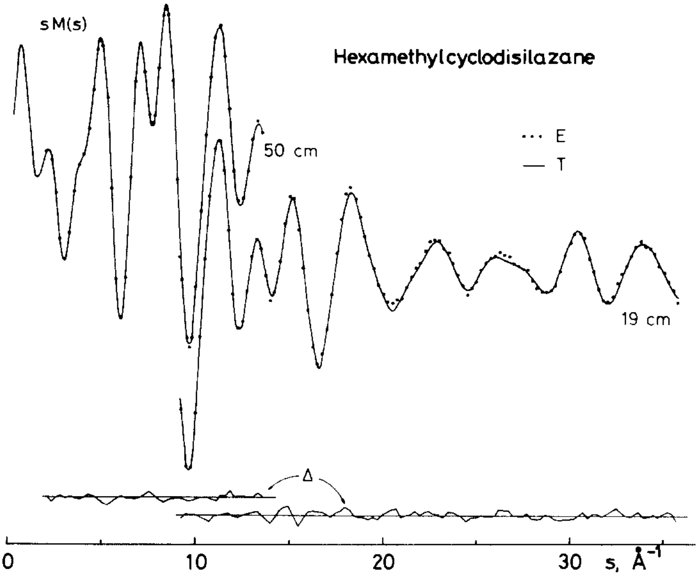

Fig. 1. Molecular intensity curves for the two camera ranges (· · · · · ·) experimental; (———) theoretical obtained for model (a). Also shown are the difference curves (experimental-theoretical).

diffraction investigation of the molecular structure of hexamethylcyclodisilazane in the vapor phase.

Experimental

The sample of hexamethylcyclodisilazane was prepared by Dr. L. Bihátsi using a published procedure [13]. The electron diffraction patterns were taken with a modified EG-100A unit [14] at a nozzle temperature of 18°C. Four plates were selected for analysis from each of the 50 cm and 19 cm camera distances. The experimental data treatment was the same as described before [15]. The ranges of intensity data were $2.00 \leqslant s \leqslant 13.50$ and $9.25 \leqslant s \leqslant 35.75$ with data steps $\Delta s = 0.125$ and 0.25 $Å^{-1}$, respectively. The experimental intensities are available from the authors on request. The molecular intensities and radial distributions are presented in Figs. 1 and 2.

Structure analysis

The numbering of the heavy-atom skeleton is given in Fig. 3. The molecular geometry was characterized by the following parameters: bond lengths Si–N, Si–C, N–C, $(C-H)_{mean}$, bond angles N–Si–N, N–Si–C, Si–C–H, N–C–H, puckering angle between the planes N2N4Si3 and N2N4Si1, and angles φ_1 (and φ_2) between the bisector of the angle Si3–N2–Si1 (Si3–N4–Si1) and the respective adjacent N–C bond, φ_1 and φ_2 confined to have the same absolute values. The silicon and carbon bond configurations were assumed to have local C_{2v} and C_{3v} symmetry, respectively. The C–H bonds of the methyl groups adjacent to a silicon atom were assumed to be staggered with respect to the other Si–C bond of the same silicon atom, and the two *N*-methyl groups were assumed to eclipse each other with one NCH plane being perpendicular to the SiNSi plane for each methyl group.

Three models were constructed in accordance with the above constraints: (a) Planar ring with coplanar N–C bonds ($\varrho = \varphi_1 = \varphi_2 = 0°$) (b) Puckered ring with

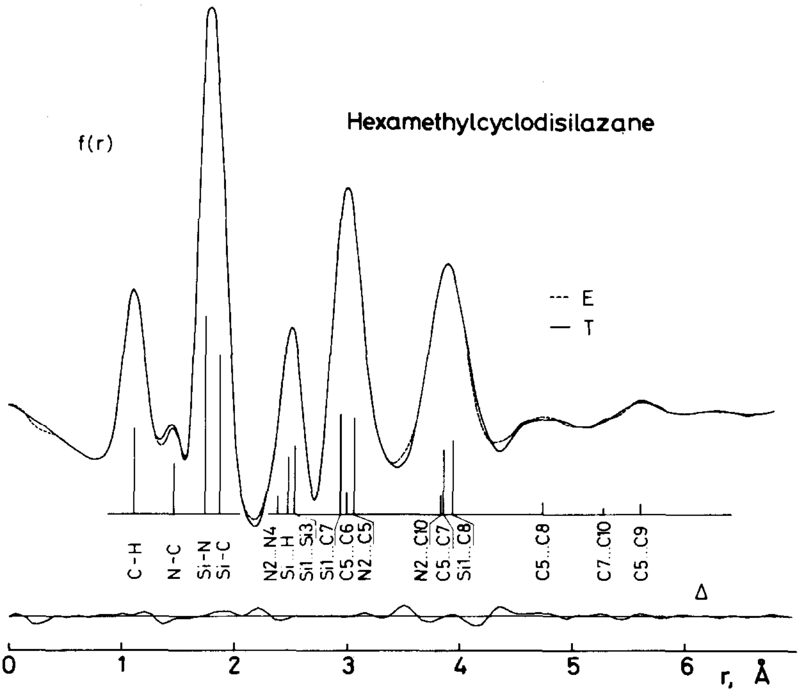

Fig. 2. Radial distribution curves (— — — —) experimental; (———) theoretical obtained for model (a). The positions of more important distances are marked with vertical bars, the height of which is proportional to the weight of these distances. Also shown is the difference curve (experimental-theoretical).

anti N-C bonds ($\varrho \neq 0°$; $\varphi_1 = -\varphi_2$). (c) Puckered ring with *syn* N-C bonds ($\varrho \neq 0°$; $\varphi_1 = \varphi_2$). Model (c) allowed diaxial as well as diequatorial arrangements for the N-C bonds.

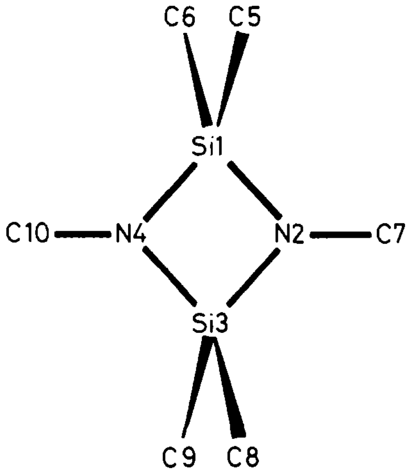

Fig. 3. The numbering of heavy atom skeleton of hexamethylcyclodisilazane.

TABLE 1

INDEPENDENT GEOMETRICAL PARAMETERS, Si...Si AND N...N DISTANCES[a], *R*-FACTORS AS OBTAINED FROM REFINEMENTS OF THE MODELS (a), (b) AND (c). MODEL (a) CORRESPONDS TO A PLANAR RING WITH N–C BONDS IN THE PLANE OF THE RING, MODEL (b) TO A PUCKERED RING WITH *TRANS* CONFORMATION OF N–C BONDS AND MODEL (c), TO A PUCKERED RING WITH *CIS* CONFORMATION OF N–C BONDS. THE RESULTS OF THE REFINEMENT OF MODEL (c) ARE CONSISTENT WITH DIEQUATORIAL CONFORMATION OF THE N–C BONDS.

Parameter	Refinement of model (a)	Refinement of model (b)	Refinement of model (c)
r(Si–N)	1.7348(4)	1.7354(4)	1.7351(4)
r(Si–C)	1.8625(6)	1.8639(7)	1.8630(6)
r(N–C)	1.454(2)	1.458(2)	1.457(2)
r(C–H)$_{\mathrm{mean}}$	1.106(1)	1.107(1)	1.107(1)
∡ N–Si–N	85.52(8)	86.4(2)	86.4(1)
∡ N–Si–C	115.5(1)	115.1(4)	115.4(3)
∡ Si–C–H	109.8(2)	109.7(4)	109.9(4)
∡ N–C–H	99.8(5)	100.6(6)	100.0(6)
φ[b]	0.0[c]	8.0(10)	6.6(12)
ϱ[b]	0.0[c]	4.0(14)	4.7(9)
r(Si...Si)[d]	2.526(2)	2.529(2)	2.527(2)
r(N...N)[d]	2.378(2)	2.376(2)	2.376(2)
R	4.67%	4.54%	4.49%

[a] Distances (r_a) are given in Å, angles in degrees, least squares standard deviations are given in parantheses as units in the last digits. [b] For the definition of φ and ϱ angles see text. [c] Fixed value. [d] Dependent parameter.

The molecular parameters, including mean amplitudes of vibration, l values, were refined by a least squares method based on the molecular intensities [16]. The results for all three models, including some dependent parameters, are presented in Tables 1 and 2. A statistical test [17] indicates that the models with a puckered ring are preferable to the model with planar ring even at a significance level of 99%. On the other hand, the removal of the constraint on planarity has only a limited influence on the results obtained for the bond lengths and bond angles (cf. Table 1). The very small value obtained for the N–C–H bond angle in the various refinements prompted us to constrain this angle to 109° in some calculations. However, such a constraint led to a considerable increase of the R-factor, from 4.5 to 6.3%.

The electron diffraction analysis thus reveals a slightly puckered ring. However, this puckering may be the consequence of the presence of puckering vibrations of a planar ring. In the absence of additional spectroscopic evidence this question cannot be resolved unambiguously on the basis of the electron diffraction data alone. However, since the amount of puckering in the vibrationally averaged electron diffraction model is relatively small, we tend to take this as indicating that the equilibrium structure does indeed have a planar ring. The final results are taken from model (c) of Table 1 and are presented in the summary. The estimated total errors correspond to the following expressions [18], $\sigma_t = [(0.002\ r)^2 + 2\sigma^2 + (\Delta/2)^2]^{1/2}$ where r is the value of the parameters, σ is the standard deviation from the least squares refinement and Δ is the maximum difference between the parameters referring to the three models in Table 1.

TABLE 2

MOLECULAR PARAMETERS [a] OF HEXAMETHYLCYCLODISILAZANE AS OBTAINED FROM REFINEMENT OF MODEL (c)

(a) More important distances [b] and mean amplitudes of vibrations (Å)

Atomic pair	Multiplicity	r_a	l	Key to the coupling scheme
Si-N ^{c}	4	1.7351(4)	0.0386(8)	i
Si-C ^{c}	4	1.8630(6)	0.0413(9)	ii
N-C ^{c}	2	1.457(2)	0.071(2)	iii
$(C-H)_{mean}$ ^{c}	18	1.107(1)	0.070(1)	iv
Si1...Si3	1	2.527(2)	0.054(1)	v
Si1...C7	4	2.929(2)	0.082(1)	vi
Si1...C8	2	3.882(14)	0.129(15)	vii
Si1...C9	2	3.962(14)	0.129	vii
N2...N4	1	2.376(2)	0.0549	v
N2...C5	8	3.041(2)	0.0925	vi
N2...C10	2	3.822(4)	0.1136	vii
C5...C6	2	3.014(8)	0.0929	vi
C5...C7	4	3.941(11)	0.127	vii
C6...C7	4	3.761(12)	0.127	vii
C5...C8	1	4.591(44)	0.232(10)	viii
C6...C9	1	4.839(47)	0.232	viii
C5...C9	2	5.595(4)	0.241(17)	ix
C7...C10	1	5.255(9)	0.242	ix

(b) Angles (°)

Parameter	Value
N-Si-N ^{c}	86.4(2)
N-Si-C ^{c}	115.4(3)
Si-C-H ^{c}	109.9(4)
N-C-H ^{c}	100.0(6)
φ^c	6.6(12)
ϱ^c	4.7(9)
C-Si-C	107.9(4)
Si-N-Si	93.5(3)

[a] Least squares standard deviations are given in parentheses as units in the last digit. [b] The X...H non-bonded interactions are not presented, where X = Si, N, C, H. [c] Independent geometrical parameters.

Discussion

The length of the Si-N bond in hexamethylcyclodisilazane $r_g = 1.736 \pm 0.004$ Å, is in good agreement with the analogous bond lengths in other cyclodisilazanes and other molecules containing the Si-N$<$ linkage [8-11, 18-20]. As a rule, the lengths of these bonds are somewhat less than that estimated for a single bond. Silicon displays the largest relative shortening for X-N$<$ bonds with X = Si, P, S, or Cl [21]. In the discussion of such bond shortenings possible pN-dSi π-interactions are often invoked. The planarity of the nitrogen configuration in silicon-nitrogen derivatives is also often interpreted in terms of these interactions. An alternative interpretation relies on the importance of intramolecular 1,3-nonbonded interactions

[21]. These nonbonded interactions may, in turn, facilitate the geometrical conditions for the *p*–*d* π-interactions. The Si...Si nonbonded distance in hexamethylcyclodisilazane is, however, much shorter, $r_g = 2.528 \pm 0.006$ Å, than twice the intramolecular 1,3-nonbonded radius of silicon, 1.55 Å [22,23]. The four-membered ring, of course, imposes severe constraints on this distance. It is noteworthy, on the other hand, that the 1,3-nonbonded N...N distance in hexamethylcyclodisilazane, $r_g = 2.377 \pm 0.006$ Å, is comfortably larger than twice the intramolecular 1,3-nonbonded radius of nitrogen, 1.14 Å [22,23]. A 2.28 Å N...N distance would correspond to a 82° bond angle N–Si–N and, accordingly, to a 98° bond angle Si–N–Si with a 2.62 Å Si...Si nonbonded distance, which is still very short. There is clearly very little room for maneuver, and electronic effects must also play some role in the structural compromise. The bond angles and, accordingly, the non-bonded distances observed in the four-membered ring of hexamethylcyclodisilazane are also similar to those in the other cyclodisilazanes studied to date.

The planar or nearly planar four-membered ring of hexamethylcyclodisilazane is similar to the nearly planar four-membered ring of octamethylcyclotetrasilane [24].

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