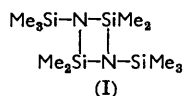


328. *An X-Ray Diffraction Determination of the Crystal and Molecular Structure of Tetramethyl-*NN'*-bistrimethylsilylcyclodisilazane.*

By P. J. WHEATLEY.

A two-dimensional X-ray diffraction analysis of tetramethyl-*NN'*-bistrimethylsilylcyclodisilazane has been carried out. There are two molecules in the unit cell (space group $P2_1/n$). The molecules are, therefore, centrosymmetric, and the four-membered ring of alternate silicon and nitrogen atoms must be planar. The crystal structure is remarkable because of the large number of atoms that happen to lie on, or close to, special positions. The analysis provides values for bond lengths and angles, and shows that the three valencies to the nitrogen atom are co-planar with the limits of the experimental error.

THE first compound containing a four-membered ring of alternate silicon and nitrogen atoms, tetramethyl-*NN'*-bistrimethylsilylcyclodisilazane (I), has recently been prepared by Fink.¹ The present analysis was undertaken to confirm the molecular formula and to determine the molecular geometry.



Experimental.— $\text{C}_{10}\text{H}_{30}\text{N}_2\text{Si}_4$. $M = 290.7$. Monoclinic. $a = 6.75_9 \pm 0.02$, $b = 13.18_1 \pm 0.04$, $c = 11.22_5 \pm 0.03$ Å, $\beta = 104^\circ 23' \pm 0.5^\circ$. $U = 968.7$ Å³. $D_m = 0.998$ (by flotation in diethylene glycol-methanol), $Z = 2$, $D_c = 1.003$, $F(000) = 320$. Space group $P2_1/n$ (C_{2h}^5 , No. 14). Cu- K_α radiation ($\lambda 1.542$ Å), single-crystal rotation and Weissenberg photographs.

The crystals are colourless and melt at 39° . Multiple-film Weissenberg photographs were taken round $[a]$ and $[c]$ with the crystals enclosed in Lindemann glass capillaries. No correction was made for absorption ($\mu = 26.5$ cm.⁻¹). 102 $0kl$ and 93 $hk0$ reflexions were observed to be non-zero, and the analysis is based on these planes. The distribution of intensities in both projections was similar in that those reflexions, the sum of the indices of which was even, were much stronger than those for which the sum of the indices was odd. This suggested that there was a considerable amount of scattering material on the origin. Sharpened Patterson syntheses were calculated for each projection, and these merely confirmed that one of the silicon atoms should be placed on the origin and the other at co-ordinates $y_{\text{Si}}, z_{\text{Si}}$ and $x_{\text{Si}}, y_{\text{Si}}$.

¹ Fink, *Angew. Chem.*, 1961, **73**, 736.

in the $0kl$ and $hk0$ projection, respectively. It was difficult to see how two silicon atoms, one from each half of the centrosymmetric molecule, could appear to lie on the origin in both of these projections, but phases were calculated on this assumption, and attempts were made to refine the structure by including carbon and nitrogen atoms. Although the R factor was reduced to 25% for the $0kl$ projection and 21% for the $hk0$ projection, it was soon apparent that at least one of the projections must be wrong, since further refinement proved impossible. Further, the projections were mutually inconsistent, and no recognizable molecule could be discerned in either projection.

Professor J. D. Dunitz, of the Eidgenössische Technische Hochschule, Zürich, then pointed out that it was possible to consider another trial structure in which the $hk0$ projection was

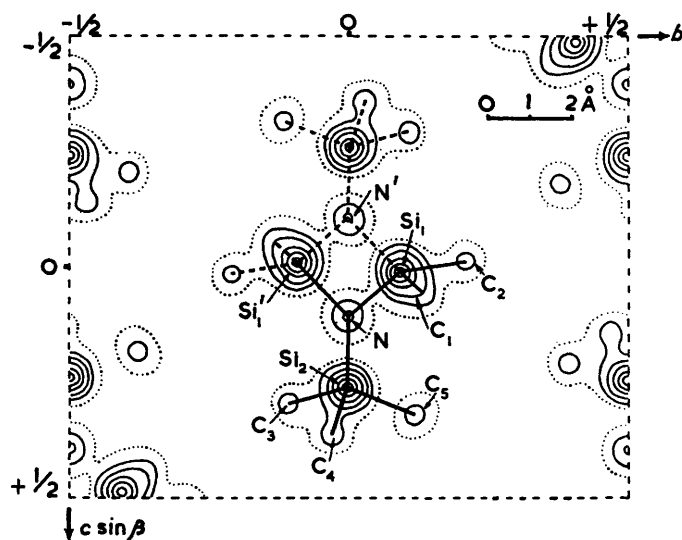


FIG. 1a.

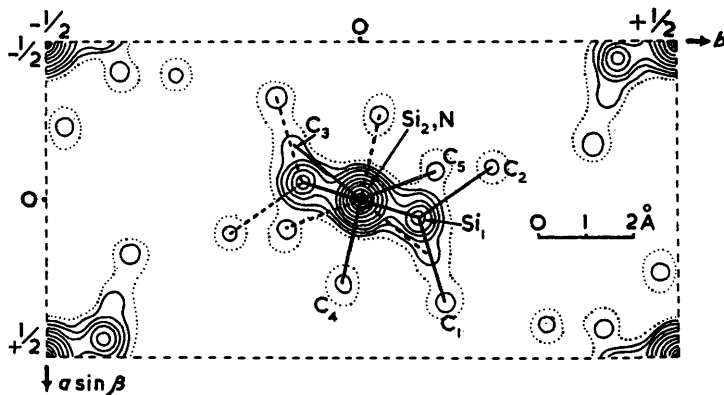


FIG. 1b.

FIG. 1. (a) Projection of the contents of the unit cell down $[a]$. (b) Projection of the contents of the unit cell down $[c]$. (The contours are drawn at equal arbitrary intervals.)

assumed to be basically correct, but in the $0kl$ projection one silicon atom should be placed at $y_{\text{Si}}, 0$ and the other at $0, z_{\text{Si}}$. It was some time before this second trial structure gave better agreement with the observed intensities, but it was soon apparent that the two projections were mutually consistent, and I am grateful to Professor Dunitz for solving the structure.

After the initial difficulty had been overcome, refinement proceeded normally, first by successive Fourier syntheses and then by difference syntheses until the *R* factor for the *0kl* and the *hk0* projection had fallen to 11.6 and 11.3%, respectively. These figures include only the observed reflexions. Table 1 shows how many of the atomic co-ordinates are zero or close to zero. Attempts were made to move the various atoms, particularly the nitrogen atom, away from special positions, but it was finally concluded that the co-ordinates given in Table 1 represent the best that can be obtained from this two-dimensional analysis. The scattering factors used

TABLE 1.
Fractional atomic co-ordinates.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Si ₁	0.054	0.090	0.008	C ₂	-0.108	0.206	-0.017
Si ₂	0.000	-0.003	0.259	C ₃	-0.173	-0.106	0.291
N	0.000	0.000	0.107	C ₄	0.263	-0.030	0.362
C ₁	0.326	0.130	0.052	C ₅	-0.090	0.118	0.317

were those of Berghuis *et al.*² for the carbon and nitrogen atoms, and that of Tomiie and Stam³ for the silicon atoms. Hydrogen atoms were ignored. An isotropic temperature factor *B* = 4.85 Å² was used for the *0kl* projection, and *B* = 5.80 Å² for the *hk0* projection.

Results.—The co-ordinates of the atoms are given in Table 1, and the observed and calculated structure factors in Table 2. Figs. 1(*a* and *b*) show the final Fourier maps for

TABLE 2.

Observed and calculated structure factors for one asymmetric unit.

<i>0kl</i>	<i>F_o</i>	<i>F_c</i>	<i>0kl</i>	<i>F_o</i>	<i>F_c</i>	<i>0kl</i>	<i>F_o</i>	<i>F_c</i>	<i>hk0</i>	<i>F_o</i>	<i>F_c</i>	<i>hk0</i>	<i>F_o</i>	<i>F_c</i>
0.2,0	23.03	25.84	0.0,4	13.85	14.81	0.0,8	7.20	7.17	3	9.05	9.70	4.0,0	5.66	4.87
4	0.88	1.68	1	1.60	2.07	2	6.22	5.80	4	2.51	2.52	1	1.71	1.26
6	3.70	2.91	2	3.79	3.05	3	1.92	1.61	5	4.21	3.93	2	7.50	8.49
8	7.89	9.46	3	3.60	3.28	4	3.67	4.63	6	6.47	-6.40	3	3.75	3.28
10	9.92	9.75	4	2.48	-2.43	6	0.90	1.17	7	3.15	2.88	4	6.49	7.23
12	4.59	3.09	5	3.08	-2.78	8	1.28	0.61	8	2.30	-2.64	5	0.81	0.60
14	2.02	1.41	6	2.88	-2.87	10	2.67	2.83	9	7.90	8.10	6	3.97	4.87
			7	2.09	-2.29	12	2.15	2.20	10	0.99	-1.05	7	1.66	-1.54
			8	0.81	1.82				11	6.56	5.90	8	3.02	2.85
			9	0.96	0.63	0.1,9	1.54	1.26	13	3.09	2.13	9	1.94	-1.43
0.1,1	12.45	14.21	10	5.03	5.72	4	1.12	0.90	14	0.86	0.28	10	2.05	1.44
2	0.85	-0.16	12	2.75	2.88	5	2.58	-1.75	15	0.64	0.62	11	0.89	-0.77
3	5.44	-5.09				7	2.19	-2.22				12	2.02	1.70
4	3.27	-3.14				8	1.27	-1.14	2.0,0	16.56	14.02	13	0.49	0.44
5	2.11	-3.18	0.1,5	1.38	-1.31				1	3.07	-2.81	14	0.69	0.64
6	3.73	-4.00	2	2.16	1.97	0.1,10	1.14	0.73	2	10.28	11.54			
7	4.41	-3.47	3	4.17	-3.88	2	0.91	-0.95	3	5.19	5.72	5.1,0	2.46	2.15
8	0.81	-1.18	4	2.14	2.15	3	2.53	2.39	4	7.95	7.36	2	1.52	1.15
9	3.25	3.27	5	4.74	-3.98	4	3.21	-2.71	5	3.13	3.30	3	3.94	5.02
11	3.35	3.15	6	1.11	-0.75	6	2.84	-3.09	6	3.02	3.54	4	1.73	1.26
13	1.46	1.48	7	6.88	-6.89	7	0.94	-0.82	7	2.44	-1.88	5	2.96	3.76
			9	1.53	-1.84	8	1.02	-1.14	8	4.40	4.16	7	2.38	2.89
			11	1.39	0.63				9	2.52	-2.31	8	1.89	-1.88
			15	0.79	-0.76	0.1,11	3.24	2.64	10	6.00	5.50	9	1.40	1.19
0.1,2	1.48	1.76				3	1.86	1.83	11	1.09	-0.88	10	1.28	-1.27
2	10.78	-10.79							12	3.89	3.65	11	1.13	1.22
3	4.31	-4.65	0.2,6	4.69	-4.75	0.0,12	2.03	1.51	13	1.74	1.64	13	0.37	0.86
4	9.23	-9.85	3	3.03	3.30	2	1.60	1.07	14	1.41	1.55			
5	2.04	1.94	4	8.91	-8.61	7	1.01	-0.42	15	0.69	0.44			
6	11.82	-10.50	6	9.23	-8.73							6.0,0	0.90	0.98
8	7.29	-6.87	7	2.24	-2.71	0.3,13	1.17	-1.07	3.1,0	10.88	11.87	1	0.92	1.49
16	1.48	-1.52	8	4.51	-4.33	6	0.58	-0.33	2	2.97	2.04	2	1.33	1.86
			9	0.82	-0.68				3	8.35	8.92	3	1.46	1.61
						<i>hk0</i>			4	5.83	5.87	4	1.89	2.19
0.1,3	17.78	18.75	0.1,7	5.80	5.30	0.2,0	24.12	25.70	5	4.58	5.39	6	2.28	2.53
2	4.98	4.87	2	3.09	3.32	4	0.61	1.64	7	5.15	5.55	7	0.87	-0.66
3	6.10	-5.70	4	2.24	2.26	6	2.91	2.77	8	1.23	-0.89	8	1.66	1.73
4	1.89	1.78	5	2.94	-2.61	8	8.12	8.66	3.9,0	3.90	3.34	9	0.79	-0.82
5	8.11	-7.75	6	1.66	-1.82	10	8.84	8.50	10	1.94	-1.42	10	0.47	0.51
6	3.58	-3.24	7	1.53	-2.03	12	3.49	2.54	11	3.16	2.33			
7	4.48	-3.33	8	0.88	0.13	14	1.37	1.09	12	0.70	0.60	7.2,0	1.85	1.77
8	0.96	-0.71	9	2.39	2.53				13	2.00	1.74	3	1.23	1.78
9	3.75	4.05	11	2.24	2.76	1.1,0	33.14	31.83	14	1.27	1.15	5	1.93	2.16
11	2.31	2.13	13	0.86	0.81	2	6.14	5.78	15	0.51	0.84	7	1.23	1.30

the *0kl* and the *hk0* projection, respectively. Fig. 2 shows the bond lengths and the numbering of the atoms. Table 3 lists the bond angles. The bond lengths are estimated

² Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

³ Tomiie and Stam, *Acta Cryst.*, 1958, **11**, 126.

1724 *Structure of Tetramethyl-NN'-bistrimethylsilylcyclodisilazane.*

to be accurate to ± 0.04 Å and the bond angles to $\pm 2^\circ$. The mean length of the Si-N bonds within the ring is slightly longer than that of the external Si-N bond, but there is no significant difference between them. The mean of all three Si-N bonds (1.719 Å) agrees with the value (1.738 \pm 0.020 Å) found in trisilylamine by electron diffraction,⁴

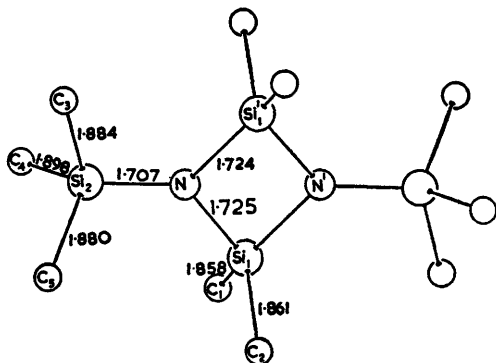


FIG. 2. The numbering of the atoms and the bond lengths.

but appears to be a little less than that found in hexamethylcyclotrisilazane (1.78 \pm 0.03 Å).⁵ The mean Si-C bond length (1.876 Å) agrees well with the standard value.⁶ The four-membered ring of alternate silicon and nitrogen atoms must, by symmetry, be planar. The deviations of the internal angles from 90° cannot be considered significant, but they are in such a sense as to make the distance between the opposing silicon atoms (2.476 Å) rather greater than that between the opposing nitrogen atoms (2.402 Å). The three valencies to the nitrogen atom are exactly coplanar with the co-ordinates listed in Table 1.

TABLE 3.

Bond angles.					
Si ₁ NSi ₁ '	91.7°	C ₃ Si ₂ C ₄	106.3°	NSi ₁ C ₁	112.2°
N'SiN	88.3	C ₃ Si ₂ C ₅	106.0	NSi ₁ C ₂	116.8
Si ₁ NSi ₂	135.4	C ₄ Si ₂ C ₅	106.4	N'Si ₁ C ₁	113.9
Si ₁ 'NSi ₂	132.8	C ₁ Si ₁ C ₂	108.4	N'Si ₁ C ₂	116.4
				NSi ₂ C ₃	111.2°
				NSi ₂ C ₄	112.4
				NSi ₂ C ₅	114.0

Such departure from coplanarity as might exist can only be slight, in agreement with the results found for trisilylamine.⁴ The CSiC and NSiC angles do not differ greatly from the tetrahedral value, but it is noticeable that all the CSiC angles are less than the tetrahedral value (mean value 106.8°), whereas all the NSiC angles are greater than the tetrahedral value (mean value 114.9°).

All intermolecular contacts are between methyl groups, and none of these is less than 4.3 Å.

Apart from Professor J. D. Dunitz, I thank Dr. W. Fink of these laboratories for supplying the sample and for helpful discussions during the attempts to obtain a trial structure.

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[Received, October 23rd, 1961.]

⁴ Hedberg, *J. Amer. Chem. Soc.*, 1955, **77**, 6491.

⁵ Yokoi and Yamasaki, *J. Amer. Chem. Soc.*, 1953, **75**, 4139.

⁶ Sutton *et al.*, "Tables of Interatomic Distances," *Chem. Soc. Special Publ.*, 1958, No. 11.