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Octamethylcyclotetrasilazane, an Ordered Crystal Containing Two Geometrical Isomers

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The crystal structure of octamethylcyclotetrasilazane, $=(Me_2SiNH)_4$, has been determined from zonal X-ray intensity data and has been refined by least-squares on these and partial three-dimensional data. $(Me_2SiNH)_4$ forms monoclinic crystals, space group $P2/c$, with four molecules in the unit cell. The highly unusual feature of the structure is that it consists of a 1:1 mixture of two fundamentally different geometrical isomers packed in an ordered array. These isomers are 'chair' and 'cradle' conformations of the central eight-membered ring.

Introduction

Organo-silicon compounds containing the Si–O–Si linkage, like their counterparts in inorganic chemistry, show a wide variation in the bond angle at oxygen. The following values may be cited to exemplify this variability: 130° in hexamethylcyclotrisiloxane, $(Me_3SiO)_3$ (Peyronel, 1954); 142·5° in octamethylcyclotetrasiloxane, $(Me_2SiO)_4$ (Steinfink, Post & Fankuchen, 1955; hereafter referred to as SPF); and $175\pm5°$ in $(Cl_3Si)_2O$ (Wegener & Post, 1958; Post, 1962). In the cyclic compounds several types of ring have likewise been found: planar six-membered rings in $(Me_2SiO)_3$, puckered rings of $\bar{1}$ symmetry in $(Me_2SiO)_4$ and 'crown-shaped' eight-membered rings in the 'cubic octamer', $(MeSiO_{1\cdot5})_8$ (Larrson, 1960).

Silicon also forms a series of compounds containing the Si–NH–Si linkage, of which octamethylcyclotetrasilazane, $(Me_2SiNH)_4$, contrasts with its isoelectronic analogue, $(Me_2SiO)_4$, in having a somewhat higher melting point, 97 °C *versus* 17·5 °C (Rochow, 1951). A previous gas-phase electron diffraction study by Yokoi & Yamasaki (1953) indicated a puckered ring in $(Me_2SiNH)_4$, although the exact conformation was not established. In anticipation of our results, we report an extraordinary, even singular, behavior for $(Me_2SiNH)_4$, namely, the occurrence of a crystal containing two fundamentally different geometrical isomers. These isomers, present in equal numbers and in an ordered array, are 'chair' and 'cradle' conformations of the central eight-membered ring.

Experimental

Purified samples of $(Me_2SiNH)_4$ were received from two sources — Dr R. L. Merker of Mellon Institute and Prof. E. G. Rochow of Harvard University, and were used without further recrystallization. As a protection against the hydrolyzing effect of atmospheric moisture, crystals used for X-ray examination were quickly sealed in thin-walled (0·01 mm) glass capillaries.

Table 1. *Unit cell data*

	a (Å)	b (Å)	c (Å)	β	Z	Space group
$((H_3C)_2SiNH)_4$	11·65	6·45	22·96	90·4	4	$P2/c$*
$((H_3C)_2SiO)_4$	16·10	16·10	6·47	—	4	$P4_2/n$
(at −50 °C)		($\sqrt{(2)}16\cdot10=22\cdot77$)				

* $0k0$ reflections with k odd are quite weak. Only 030 and 050 were recorded and only as extremely feeble maxima.

Refined values of the lattice constants were measured on a G.E. XRD-5 diffractometer equipped with a single-crystal orienter and are reported in Table 1. With four molecules in the unit cell, the calculated density is 1·13 g.cm^{-3} (compare the measured density of 1·06 g.cm^{-3} for $(Me_2SiO)_4$ cited by SPF). The diffraction symmetry is $2/m$; the systematically absent spectra seemed to be those demanded by $P2_1/c$, namely $h0l$ for l odd and $0k0$ for k odd, and indeed our analysis was begun on this premise. A successful structure determination was possible, however, only in terms of the space group $P2/c$; subsequently, careful diffractometer scans disclosed feeble maxima for the 030 and 050 reflections. The origin of this pseudo-extinction rule is readily seen from our final results: the difference in y parameters of atoms chemically identical but crystallographically distinct is $\sim\frac{1}{2}$.

Because crystals of $(Me_2SiNH)_4$ appear to suffer X-irradiation damage, four different crystals (cubes $\leq 0\cdot3$ mm on an edge) were used on the diffractometer in collecting the intensity data. Peak heights less the average background determined from measurements on both the high- and low-2θ side of a peak were converted to integrated intensities by means of a calibration curve (Alexander & Smith, 1962) experimentally established for each crystal. Intensities from a given crystal were placed on the same relative basis by the daily monitoring of standard reflections.

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Ni-filtered Cu Kα radiation was used for the $h0l$ zone and Nb-filtered Mo $K\alpha$ radiation for the remainder, the intensity measurement being confined to $\sin\theta/\lambda \le 0{\cdot}645$ Å^{-1}. The number of reflections so obtained is apportioned as follows: selected hkl, 296 forms; $h0l$, 302 out of 342 possible; $0kl$, 161 out of 198; $hk0$, 81 out of 98.

The intensities were converted to relative $|F|^2$ by the application of Lorentz and polarization factors. No absorption corrections were applied, the linear absorption coefficient being 30·0 cm^{-1} and 3·4 cm^{-1} for Cu and Mo radiations respectively. A preliminary scaling factor and temperature parameter of 2·9 Å^2 were obtained from a Wilson plot. The form factors used in structure factor calculations were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for N and C; for Si, the values used were those of Freeman (1959) smoothed into the Berghuis curve for Si^{+4} at higher $\sin\theta/\lambda$ values.

Determination of structure

Our expectation that $(Me_2SiNH)_4$ was virtually isostructural with $(Me_2SiO)_4$ was reinforced by a comparison of unit cell data and by *a priori* packing considerations. In Table 1 we see that in both compounds the unique-axis repeat distances are nearly identical; the glide plane translations similarly are nearly identical. At this stage we considered the near halving of the a axis relative to the c axis and the resemblance of symmetry elements (the presumed space group was $P2_1/c$) as further indications of only subtle structural differences. Moreover, the packing arrangement would be analogous in the two materials if the silazane tetramers of point symmetry $\bar{1}$, as in $(Me_2SiO)_4$, were centered at the fourfold positions, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{8})$, *etc.* Such a packing scheme also accounted for the unusual distribution of intensities found in the $h0l$ zone, namely, (i) for h odd and $l=4n$ and for h even and $l=4n+2$ the reflections are rather weak, and (ii) the tendency of $F^2(h0l)$ to be equal to $F^2(l/2,0,2\bar{h})$. Manipulations of the structure factor expression for the plane group $P2$ showed that a centrosymmetric molecule centered at $X=\frac{1}{4}$, $Z=\frac{1}{8}$ would cause the reflections in (i) to be extinguished; for $c=2a$ and $\beta=90°$ an expected fourfold molecular symmetry (in projection) would give rise to condition (ii). Deviations in the observed intensities from these rules were then thought to be a measure of the departure of the actual structure from this 'ideal' model. (Furthermore developments in the structure analysis made it necessary to shift the center of the tetramer from $X=\frac{1}{4}$, $Z=\frac{1}{8}$; inspection, however, of the final electron density projection, $\varrho(X, Z)$ in Fig. 1, reveals a close approach to centrosymmetry about $X=\frac{1}{4}$, $Z=\frac{1}{8}$ and to a fourfold molecular symmetry.

An interpretation of the Patterson projection, $P(U, W)$ along these lines led to trial parameters from which satisfactory electron density maps could be prepared, but without the inclusion of any terms from the class of weak reflections. Although the R value now stood at 19% for the strong class of reflections, we could see no logical way of introducing a distortion into the model which would allow non-zero amplitudes for the weak class of reflections. Thus it was necessary to consider another zone of intensities.

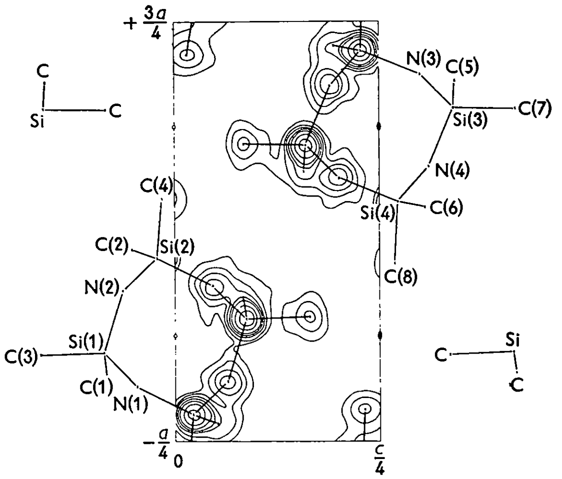

Fig. 1. Electron density projected onto (010). Contours at intervals of 2 e.Å^{-2} starting with 2 e.Å^{-2} contour; after 10 e.Å^{-2} the interval is 5 e.Å^{-2}. The bonding framework is indicated.

Since trial values of the z parameters had already been obtained and reasonable y parameters could be predicted from the parameter data of SPF, the prospects of a ready interpretation of $P(V, W)$ seemed favorable. $P(V, W)$ displayed, however, peaks at the predicted Δy positions, but these did not always occur at W positions corresponding to the predicted Δz values. Conversely, peaks at the predicted Δz positions did not always occur at V positions required by the Δy positions. Moreover, the structure model from the $h0l$ zone required the existence of non-space-group extinctions which, in this instance, were at variance with the observed intensities. In the face of these difficulties and because the establishment of the twofold screw axis had rested on the vanishing of only four $0k0$, k odd reflections, we decided to abandon the space group $P2_1/c$ in favor of either Pc or $P2/c$. $P(V, W)$ was equally inconsistent with the center of the tetramer being situated at a fourfold position of $P2/c$, so that there were two possibilities to consider: two crystallographically independent tetramers situated in the twofold positions of Pc or two independent tetramers situated in the special twofold positions, $\bar{1}$ and 2 of $P2/c$. Since we were prepared for centrosymmetric tetramers, we considered the former as the only genuine possibility (despite the theoretical argument (Kitaigorodskii, 1958) against the occurrence of centrosymmetric molecules in a non-centrosymmetric crystal). In this case, the two independent molecules could be arranged according to a fourfold screw axis (as in $(Me_2SiO)_4$) parallel to b, and it was noted that such a pseudo-axis would account for the near vanishings of the $0k0$, k odd reflections. The Si $\cdots$ Si vectors of this model accounted for the major peaks of $P(V, W)$, and $0kl$ structure factors were calculated using z parameters from the $h0l$ zone and y parameters derived from SPF. The results were quite surprising when sorted out: $R = 26\%$ for l even but $R = 79\%$ for l odd.

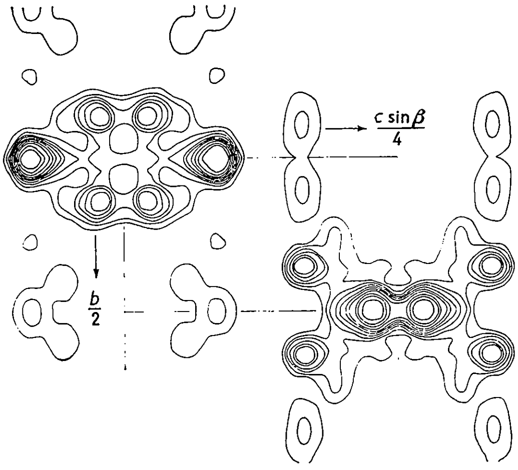

Fig. 2. Electron density projected onto (100) but with only (incomplete) even l terms. Contours at equal but arbitrary intervals except round the 'doubled' silicons where some of higher contours are omitted. At this stage bonding frameworks consistent with the following could be located: (i) two tetramers having $\bar{1}$; (ii) two tetramers having two-fold axes parallel to b; (iii) one tetramer of each from (i) and (ii).

Certain features of the $\varrho(Y, Z)$ synthesis using even l terms (Fig. 2) which had, of course, double the number of atomic peaks and $\varrho(X, Z)$ were reconcilable, it was recognized, not only with molecules of $\bar{1}$ symmetry, but also with those having a twofold axis of symmetry. Structure factor calculations for models having *either* $\bar{1}$ symmetry *or* twofold symmetry failed, however, to reduce the R value of the l odd terms. An $N(z)$ test (Howells, Phillips & Rogers, 1950) showing that the $0kl$ zone is not merely centric, but hypercentric (Lipson & Woolfson, 1952), together with a negative piezoelectric test obtained previously, persuaded us to test the second possibility mentioned earlier: occupancy of the special positions, $\bar{1}$ and 2, of $P2/c$. The reaction of the R value for the l odd terms was immediate; R dropped to 40%. The Si$\cdots$Si vector interactions expected of this model, furthermore, provided a better agreement with $P(V, W)$ in regard to both location and relative heights of the peaks than had any previous model. Refinement then proceeded through successive difference syntheses, which soon removed the distinction in the agreement indices for l odd and l even terms.

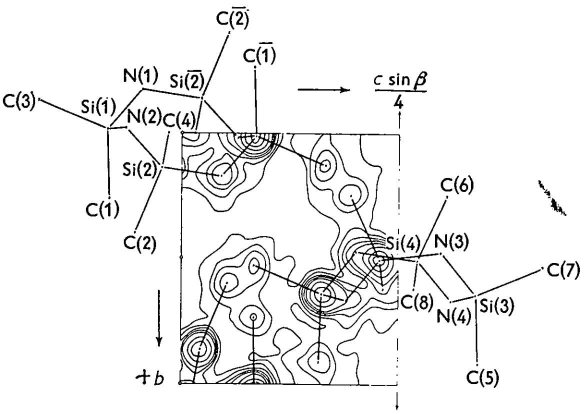

Fig. 3. Electron density projected onto (100). Contours at intervals of 2 e.Å^{-2} starting with 2 e.Å^{-2} contour; after 10 e.Å^{-2} the interval is 5 e.Å^{-2}. The bonding framework is indicated.

Because of the extraordinary nature of the structure model, these difference maps were examined for indications of disorder, particularly of the kind which might cause simulation of the molecular symmetries, $\bar{1}$ or 2. Residual features, however, on our last difference map corresponded at most to $+1{\cdot}6$ e.Å^{-2} and $-1{\cdot}7$ e.Å^{-2}, effects which seemed more ascribable to the inadequacy of but a single thermal parameter for each kind of atom (3·0, 3·4 and 3·4 Å^2 for Si, N and C respectively). Difference maps prepared from the $hk0$ data provided improved x parameters, and these, together with the z parameters from the $0kl$ zone, made it possible to refine the b-axis projection. Of the final electron density projections, shown in Figs. 1 and 3, $\varrho(Y, Z)$ displays quite clearly the fundamental differences in the configurations of the two isomers; $\varrho(X, Z)$ is then all the more remarkable in its absence of detail in support of this effect.

Table 2. *Final parameters*

All atoms in general positions of $P2/c$;
σ values in parenthesis

Atom	10^4x	10^4y	10^4z	B
N($\bar{1}$)	1238 (6)	1748 (22)	453 (3)	3·83 Å^2 (0·18 Å^2)
N(2)	1054 (7)	−223 (23)	−651 (3)	3·81 (0·18)
N(3)	6231 (7)	4748 (24)	2985 (4)	3·28 (0.19)
N(4)	4060 (7)	6658 (23)	3111 (3)	3·07 (0·18)
Si($\bar{1}$)	380 (2)	156 (9)	871 (1)	2·96 (0·07)
Si(2)	1872 (2)	1416 (9)	−218 (1)	3·07 (0·07)
Si(3)	5438 (2)	6406 (8)	3400 (1)	2·80 (0·07)
Si(4)	3212 (2)	5066 (9)	2715 (1)	2·85 (0·07)
C($\bar{1}$)	897 (10)	−2602 (33)	828 (5)	4·41 (0·25)
C(2)	2093 (9)	4026 (32)	−531 (5)	4·99 (0·25)
C($\bar{3}$)	433 (8)	1261 (29)	1622 (4)	4·39 (0·22)
C(4)	3311 (8)	50 (33)	−166 (5)	4·11 (0·23)
C(5)	6080 (9)	9150 (31)	3424 (5)	4·14 (0·24)
C(6)	3126 (10)	2421 (37)	3047 (5)	5·14 (0·28)
C(7)	5401 (8)	5251 (29)	4146 (4)	4·36 (0·22)
C(8)	1747 (9)	6233 (32)	2680 (5)	4·41 (0·25)

Final refinement was carried out on our entire data using the IBM 704 program of Busing & Levy (1959) and employing a weighting scheme appropriate for diffractometric data (Smith & Alexander, 1963). With

Table 3. *Observed and calculated structure factors*

F_c scaled to F_o; $K_1=6{\cdot}25\ (0{\cdot}09)$; $K_2=1{\cdot}77\ (0{\cdot}02)$; $K_3=2{\cdot}65\ (0{\cdot}03)$; $K_4=2{\cdot}37\ (0{\cdot}02)$

h k l	$10\lvert F_o\rvert$	$10\ K_1F_c$
0 0 2	488	287
0 0 4	2728	2529
0 0 6	37	-43
0 0 8	5801	-4475
0 0 10	324	-384
0 0 12	3886	3491
0 0 14	740	795
0 0 16	3872	-3709
0 0 18	602	-567
0 0 20	1053	-1035
0 0 22	179	-243
0 0 24	133	-395
0 0 26	615	631
0 0 28	2355	-2110
1 0 0	491	-345
1 0 4	211	232
1 0 6	269	21
1 0 8	832	-798
1 0 10	4806	5078
1 0 12	692	624
1 0 14	1274	1387
1 0 16	200	-33
1 0 18	1009	1335
1 0 20	630	-634
1 0 22	1827	1929
1 0 24	479	566
1 0 26	1632	-1774
1 0 28	0	128
2 0 0	1843	1854
2 0 2	0	66
2 0 4	9301	-9116
2 0 6	1287	-1181
2 0 8	419	333
2 0 10	0	-113
2 0 12	4382	4080
2 0 14	636	697
2 0 16	269	-426
2 0 18	689	-774
2 0 20	3290	3329
2 0 22	0	70
2 0 24	1269	1052
2 0 26	320	319
2 0 28	1240	-1074
3 0 0	740	617
3 0 4	858	-722
3 0 6	2198	-2896
3 0 8	973	-954
3 0 10	3742	3853
3 0 12	722	793
3 0 14	2610	-2584
3 0 16	301	-310
3 0 18	1400	1351
3 0 20	246	-197
3 0 22	2378	2274
3 0 24	361	317
3 0 26	683	-602
3 0 28	179	-334
4 0 0	4027	-2930
4 0 2	721	629
4 0 4	7360	-7231
4 0 6	912	-862
4 0 8	1353	977
4 0 10	222	299
4 0 12	1332	-1272
4 0 14	0	63
4 0 16	3565	-3200
4 0 18	453	-385
4 0 20	1035	1028
4 0 22	309	329
4 0 24	138	81
4 0 26	151	-222
4 0 28	174	99
5 0 0	876	746
5 0 2	4514	-3995
5 0 4	116	31
5 0 6	2898	2635
5 0 8	507	620
5 0 10	2310	1862
5 0 12	675	642
5 0 14	5786	-6024
5 0 16	403	-480
5 0 18	1444	-1583
5 0 20	170	208
5 0 22	179	-380
5 0 24	182	117
5 0 26	1408	-1257
6 0 0	2543	2298
6 0 2	592	-538
6 0 4	4243	4471
6 0 6	242	-32
6 0 8	6998	6899
6 0 10	1083	1123
6 0 12	199	13
6 0 14	295	170
6 0 16	1880	-1805
6 0 18	0	7
6 0 20	0	-116
6 0 22	475	414
6 0 24	1108	-1147
6 0 26	115	-124
7 0 0	460	-578
7 0 2	3285	-3028
7 0 4	1425	-1270
7 0 6	3985	3882
7 0 8	199	-182
7 0 10	4591	4590
7 0 12	147	271
7 0 14	311	-239
7 0 16	209	-205
7 0 18	1777	1858
7 0 20	224	243
7 0 22	877	854
7 0 24	212	176
7 0 26	329	-316
8 0 0	3923	-3886
8 0 2	137	-62
8 0 4	3512	-3387
8 0 6	865	-848
8 0 8	172	-2
8 0 10	339	-385
8 0 12	925	-974
8 0 14	370	-406
8 0 16	1295	1312
8 0 18	248	-204
8 0 20	1520	1536
8 0 22	100	82
8 0 24	0	138

h k l	$10\lvert F_o\rvert$	$10\ K_1F_c$
9 0 0	925	966
9 0 2	3058	-3250
9 0 4	401	425
9 0 6	2111	-2197
9 0 8	0	-102
9 0 10	1731	-1754
9 0 12	217	-285
9 0 14	1542	-1407
9 0 16	400	-431
9 0 18	1035	1097
9 0 20	0	39
9 0 22	0	-55
10 0 0	199	34
10 0 2	693	780
10 0 4	0	-123
10 0 6	533	510
10 0 8	524	-654
10 0 10	389	355
10 0 12	2389	-2441
10 0 14	188	-273
10 0 16	361	431
10 0 18	187	-110
10 0 20	164	-74
11 0 0	143	-108
11 0 2	431	347
11 0 4	124	38
11 0 6	1514	1641
11 0 8	419	672
11 0 10	495	-460
11 0 12	363	370
11 0 14	621	-581
11 0 16	193	-202
11 0 18	314	282
12 0 0	969	-1229
12 0 2	601	-667
12 0 4	2067	2088
12 0 6	238	-246
12 0 8	1998	1969
12 0 10	471	524
12 0 12	307	-226
12 0 14	0	-30
12 0 16	1107	1106
13 0 0	281	-213
13 0 2	786	-837
13 0 4	851	-911
13 0 6	1323	1344
13 0 8	121	-57
13 0 10	0	88
13 0 12	0	-142
13 0 14	612	728
14 0 0	2301	-2120
14 0 2	190	-256
14 0 4	144	98
14 0 6	0	-112
14 0 8	503	-404
14 0 10	0	-24
-1 0 4	0	-218
-1 0 8	98	12
-1 0 10	4924	-4591
-1 0 12	99	133
-1 0 14	1691	-1580
-1 0 16	223	280
-1 0 18	4217	-4476
-1 0 20	461	-584
-1 0 22	147	-18
-1 0 24	215	204
-1 0 26	226	105
-1 0 28	182	296
-2 0 2	371	-378
-2 0 4	8629	-8737
-2 0 6	562	502
-2 0 8	6484	-6678
-2 0 10	0	187
-2 0 12	4561	4633
-2 0 14	411	434
-2 0 16	2702	-2488
-2 0 18	0	18
-2 0 20	1054	-954
-2 0 22	211	-282
-2 0 24	2871	2865
-2 0 26	309	365
-2 0 28	407	576
-3 0 2	2165	1467
-3 0 4	575	510
-3 0 6	322	-818
-3 0 8	831	794
-3 0 10	2943	2454
-3 0 12	84	-234
-3 0 14	4854	4802
-3 0 16	386	312
-3 0 18	1812	-1742
-3 0 20	0	14
-3 0 22	1028	1214
-3 0 24	104	-216
-3 0 26	2049	1835
-3 0 28	0	36
-4 0 2	1098	1052
-4 0 4	1499	1817
-4 0 6	284	150
-4 0 8	1947	1284
-4 0 10	172	-270
-4 0 12	5699	5452
-4 0 14	239	-277
-4 0 16	566	737
-4 0 18	0	202
-4 0 20	1055	-1114
-4 0 22	163	-193
-4 0 24	1376	1282
-4 0 26	0	-180
-4 0 28	647	-511
-5 0 2	5456	5726
-5 0 4	158	105
-5 0 6	2813	2906
-5 0 8	512	-478
-5 0 10	689	472
-5 0 12	726	-756
-5 0 14	3966	4079
-5 0 16	0	17
-5 0 18	1526	-1380
-5 0 20	0	186
-5 0 22	1133	-1214
-5 0 24	258	-267
-5 0 26	0	63
-6 0 2	88	-93
-6 0 4	3334	3062
-6 0 6	780	-739
-6 0 8	2125	-1796

h k l	$10\lvert F_o\rvert$	$10\ K_1F_c$
-6 0 10	612	-563
-6 0 12	800	-814
-6 0 14	229	-256
-6 0 16	341	-527
-6 0 18	185	195
-6 0 20	2278	-2279
-6 0 22	82	130
-6 0 24	578	-525
-6 0 26	0	4
-7 0 2	533	611
-7 0 4	150	-39
-7 0 6	3061	-3026
-7 0 8	348	-287
-7 0 10	5772	-5791
-7 0 12	0	-49
-7 0 14	161	-287
-7 0 16	288	353
-7 0 18	1120	-1028
-7 0 20	0	294
-7 0 22	463	-463
-7 0 24	0	43
-7 0 26	1021	990
-8 0 2	585	605
-8 0 4	408	363
-8 0 6	170	186
-8 0 8	3011	-2673
-8 0 10	420	414
-8 0 12	1734	-1629
-8 0 14	416	444
-8 0 16	1941	1827
-8 0 18	266	215
-8 0 20	760	870
-8 0 22	0	15
-8 0 24	1202	1140
-9 0 2	2259	2638
-9 0 4	412	337
-9 0 6	1989	1779
-9 0 8	177	77
-9 0 10	896	-1054
-9 0 12	428	584
-9 0 14	1901	2171
-9 0 16	151	109
-9 0 18	1389	1267
-9 0 20	282	-324
-9 0 22	218	185
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-10 0 6	358	-471
-10 0 8	777	679
-10 0 10	140	168
-10 0 12	214	-272
-10 0 14	0	-54
-10 0 16	1568	1441
-10 0 18	503	-418
-10 0 20	590	-603
-11 0 2	1445	1505
-11 0 4	523	-529
-11 0 6	1420	1512
-11 0 8	245	-309
-11 0 10	595	-666
-11 0 12	0	59
-11 0 14	465	486
-11 0 16	281	-275
-11 0 18	384	-412
-12 0 2	385	-309
-12 0 4	577	640
-12 0 6	358	-309
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-12 0 10	0	24
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-12 0 14	0	-84
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-13 0 2	2016	-2086
-13 0 4	72	272
-13 0 6	522	-380
-13 0 8	0	-30
-13 0 10	1045	-1039
-13 0 12	163	170
-13 0 14	360	-301
-14 0 2	586	610
-14 0 4	560	-437
-14 0 6	425	386
-14 0 8	348	387
0 3 0	279	205
0 5 0	148	55
		$10\ K_2F_c$
0 0 2	108	81
0 0 4	709	717
0 0 6	0	-12
0 0 8	1545	-1269
0 0 10	0	-109
0 0 12	1020	990
0 0 14	251	225
0 0 16	1026	-1052
0 0 18	152	-161
0 0 20	275	-293
0 0 22	73	-69
0 0 24	0	-112
0 0 26	191	179
0 0 28	676	-598
0 1 1	918	928
0 1 2	2497	2849
0 1 3	356	304
0 1 4	605	-591
0 1 5	0	-60
0 1 6	605	348
0 1 7	233	359
0 1 8	0	-3
0 1 9	468	448
0 1 10	254	235
0 1 11	131	-172
0 1 12	465	470
0 1 13	669	661
0 1 14	94	-116
0 1 15	499	558
0 1 16	94	-69
0 1 17	93	45
0 1 18	644	-630
0 1 19	242	244
0 1 20	52	-51
0 1 21	102	117
0 1 22	147	-181
0 1 23	73	-73
0 1 24	135	129
0 1 25	82	-113
0 1 26	313	-337

h k l	$10\lvert F_o\rvert$	$10\ K_2F_c$
0 1 27	0	69
0 1 28	0	40
0 1 29	159	-122
0 2 0	1529	1616
0 2 1	1368	-1371
0 2 2	100	-59
0 2 3	217	-165
0 2 4	347	274
0 2 5	123	254
0 2 6	1315	-1269
0 2 7	272	-197
0 2 8	102	101
0 2 9	457	456
0 2 10	288	253
0 2 11	1097	1125
0 2 12	391	430
0 2 13	205	189
0 2 14	522	487
0 2 15	318	268
0 2 16	372	-383
0 2 17	644	594
0 2 18	0	28
0 2 19	74	91
0 2 20	228	-225
0 2 21	59	13
0 2 22	355	302
0 2 23	103	53
0 2 24	0	-46
0 2 25	91	-46
0 2 26	0	53
0 2 27	319	-268
0 2 28	207	-181
0 3 1	459	455
0 3 2	168	156
0 3 3	144	-217
0 3 4	1283	-1221
0 3 5	0	-17
0 3 6	17	-4
0 3 7	551	519
0 3 8	624	-549
0 3 9	579	596
0 3 10	0	27
0 3 11	0	18
0 3 12	813	836
0 3 13	130	125
0 3 14	71	109
0 3 15	62	61
0 3 16	91	66
0 3 17	126	-153
0 3 18	54	-76
0 3 19	121	137
0 3 20	263	288
0 3 21	149	148
0 3 22	0	-51
0 3 23	0	22
0 3 24	297	277
0 3 25	84	-87
0 3 26	0	21
0 3 27	49	54
0 4 1	226	247
0 4 2	256	-181
0 4 3	280	-303
0 4 4	83	82
0 4 5	483	-515
0 4 6	1409	-1464
0 4 7	373	403
0 4 8	191	-165
0 4 9	0	4
0 4 10	706	734
0 4 11	0	-86
0 4 12	26	36
0 4 13	90	-115
0 4 14	377	388
0 4 15	161	-203
0 4 16	86	85
0 4 17	166	-153
0 4 18	281	-220
0 4 19	0	-96
0 4 20	75	-104
0 4 21	148	141
0 4 22	514	474
0 4 23	117	-81
0 4 24	24	33
0 4 25	0	-24
0 4 26	99	79
0 5 1	437	-473
0 5 2	578	615
0 5 3	68	-93
0 5 4	371	-338
0 5 5	188	99
0 5 6	224	-171
0 5 7	452	-458
0 5 8	277	-226
0 5 9	82	-56
0 5 10	0	-11
0 5 11	77	-122
0 5 12	154	176
0 5 13	283	-311
0 5 14	0	-20
0 5 15	255	-248
0 5 16	0	35
0 5 17	93	-117
0 5 18	94	-108
0 5 19	0	-21
0 5 20	144	142
0 5 21	155	-160
0 5 22	0	0
0 5 23	100	80
0 6 1	100	110
0 6 2	0	-7
0 6 3	240	-296
0 6 4	204	219
0 6 5	432	-462
0 6 6	139	-99
0 6 7	124	144
0 6 8	29	9
0 6 9	0	62
0 6 10	0	66
0 6 11	233	-235
0 6 12	164	157
0 6 13	116	-121
0 6 14	25	21
0 6 15	148	-132
0 6 16	250	-233
0 6 17	234	-211
0 6 18	0	-37
0 6 19	0	11

h k l	$10\lvert F_o\rvert$	$10\ K_2F_c$
0 6 20	110	-134
0 7 1	76	-57
0 7 2	575	589
0 7 3	273	-224
0 7 4	55	46
0 7 5	138	-123
0 7 6	133	-82
0 7 7	0	10
0 7 8	0	4
0 7 9	0	-59
0 7 10	186	210
0 7 11	90	68
0 7 12	0	-9
0 7 13	0	13
0 7 14	26	-52
0 7 15	77	-57
0 7 16	51	40
0 8 1	183	-167
0 8 2	43	-41
0 8 3	72	-67
0 8 4	50	72
0 8 5	102	78
0 8 6	68	-43
0 8 7	0	55
0 4 0	234	210
0 6 0	789	864
0 8 0	429	433
1 1 1	1492	-1580
1 1 2	272	-209
1 1 3	1109	-1076
2 0 0	496	526
2 1 2	983	-890
2 1 5	1456	-1416
2 1 6	1218	-1179
3 1 4	1086	-1359
4 1 2	1653	-1634
-1 1 1	125	-89
-1 1 2	277	200
-1 1 3	887	832
-1 1 4	1115	-1050
-2 1 1	1258	1283
-2 1 6	1282	-1551
-3 1 1	1351	-1259
-6 1 2	1622	1732
		$10\ K_3F_c$
0 2 0	2277	2417
0 0 16	1500	-1573
5 0 0	243	316
6 0 0	1009	975
8 0 0	1554	-1648
13 0 0	162	-90
0 4 0	350	315
0 6 0	1181	1292
0 7 0	0	-85
0 8 0	634	648
1 1 0	3787	4228
1 2 0	271	-183
1 3 0	206	144
1 4 0	469	401
1 5 0	778	813
1 6 0	0	-75
1 7 0	792	825
1 8 0	0	8
2 1 0	888	856
2 2 0	395	373
2 3 0	1982	1877
2 4 0	104	59
2 5 0	562	528
2 6 0	235	181
2 7 0	80	-80
2 8 0	59	19
3 1 0	718	443
3 2 0	1861	1942
3 3 0	0	-20
3 4 0	2078	2228
3 5 0	346	-357
3 6 0	183	220
3 7 0	186	-113
3 8 0	121	102
4 1 0	167	-52
4 2 0	0	8
4 3 0	766	649
4 4 0	325	-298
4 5 0	392	361
4 6 0	65	-16
4 7 0	72	81
4 8 0	79	92
5 1 0	515	476
5 2 0	192	-130
5 3 0	125	175
5 4 0	1132	-1209
5 5 0	0	82
5 6 0	0	-50
5 7 0	348	309
6 1 0	288	-269
6 2 0	723	771
6 3 0	916	-939
6 4 0	163	234
6 5 0	118	-159
6 6 0	338	368
6 7 0	0	25
7 1 0	263	-260
7 2 0	339	-354
7 3 0	245	283
7 4 0	108	-148
7 5 0	0	39
7 6 0	77	67
7 7 0	149	-186
8 1 0	273	311
8 2 0	286	-305
8 3 0	165	203
8 4 0	93	144
8 5 0	167	137
8 6 0	320	-562
8 7 0	0	21
9 1 0	704	-785
9 2 0	204	147
9 3 0	0	-16
9 4 0	267	223
9 5 0	0	-5
9 6 0	176	160
10 1 0	110	59
10 2 0	235	-262
10 3 0	572	-566
10 4 0	0	-17
10 5 0	255	-260

h k l	$10\lvert F_o\rvert$	$10\ K_3F_c$
10 6 0	120	-111
11 1 0	123	-187
11 2 0	619	-568
11 3 0	0	25
11 4 0	691	-690
11 5 0	0	40
12 1 0	192	-189
12 2 0	110	-157
12 3 0	284	-287
12 4 0	172	142
12 5 0	231	-226
13 1 0	764	-761
13 2 0	100	-80
13 3 0	41	-30
13 4 0	0	-6
14 1 0	0	-45
14 2 0	405	-370
15 0 0	129	101
15 1 0	186	-219
1 1 6	1116	-1105
1 1 7	1268	-1143
1 1 11	1476	1464
1 1 12	2303	2380
1 1 28	754	-263
2 1 1	647	-668
2 1 6	1763	-1763
2 1 22	930	869
3 1 2	1056	939
4 1 2	2370	-2444
4 1 3	1336	1402
4 1 5	1127	1011
4 1 9	1132	1171
4 1 14	1675	-1725
5 1 1	1369	1296
5 1 7	1254	1357
5 1 16	1608	-1701
6 1 1	1110	-1179
6 1 6	1626	1671
6 1 10	1955	2073
6 1 26	599	-529
7 1 3	1220	-1246
7 1 8	1618	1688
8 1 1	706	-685
8 1 2	1838	-1896
12 1 6	843	802
-1 1 5	2282	2297
-1 1 6	970	-864
-1 1 7	1279	-1066
-1 1 8	2320	-2439
-1 1 16	1847	-1899
-2 1 7	939	891
-2 1 9	1283	-1224
-2 1 11	1180	-1208
-3 1 2	781	834
-3 1 4	1770	-1776
-3 1 7	1160	-1201
-3 1 12	2017	2091
-3 1 13	1397	-1501
-3 1 24	867	770
-4 1 7	1113	1118
-4 1 14	1806	1724
-5 1 12	1484	1617
-6 1 2	2366	2590
-6 1 5	1114	1073
-7 1 8	2017	-2105
-8 1 10	1460	-1533
-8 1 18	745	410
-9 1 16	1038	989
-11 1 4	913	920
-13 1 12	477	-438
-14 1 1	429	-383
-14 1 2	685	-632
		$10\ K_4F_c$
0 1 2	3551	3804
0 0 12	1387	-1404
0 0 16	1395	1322
1 0 2	3231	3239
1 0 10	1743	1923
1 0 22	743	731
1 1 5	556	493
1 1 12	2143	2125
1 2 0	261	-163
1 2 3	1373	-1221
1 2 5	852	-892
1 3 1	1446	-1332
1 3 3	865	-807
1 3 6	2171	-2231
1 3 11	701	723
1 4 4	1788	-1816
1 4 16	816	-722
1 5 1	827	864
1 6 2	504	492
1 7 1	246	-203
2 0 6	458	-447
2 1 6	1648	-1574
2 1 7	569	-600
2 2 1	1666	-1692
2 2 2	1654	1550
2 2 7	1183	-1066
2 2 14	1042	-1077
2 2 18	933	-894
2 3 1	1056	-921
2 3 5	448	-482
2 3 12	775	-916
2 3 16	1618	-1647
2 4 6	1079	-1195
2 4 14	1087	-1125
2 4 18	833	-801
2 5 1	194	239
2 5 4	227	-325
2 6 4	451	-437
2 7 2	293	-312
2 8 1	229	-230
2 8 4	290	-274
3 0 2	4556	-4618
3 0 6	750	-1097
3 0 10	1403	1459
3 1 1	725	-576
3 1 5	593	-412
3 1 9	482	-505
3 1 15	916	-899
3 2 1	295	263
3 2 4	1349	1187
3 2 8	1178	1160
3 2 11	707	-723
3 2 13	997	-997

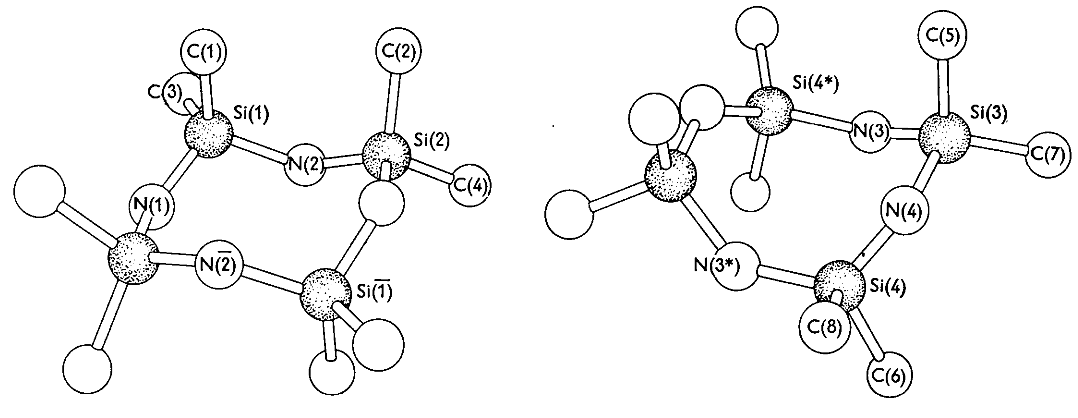
Table 3 (*cont.*)

h k ℓ	10 F_o	10 K_4F_c
3 2 17	679	- 639
3 3 2	2028	2159
3 3 3	459	- 439
3 3 6	929	972
3 3 10	1210	1203
3 3 26	560	- 520
3 4 8	1332	1456
3 4 16	855	- 860
3 5 2	650	670
3 6 1	311	- 267
3 6 2	371	- 429
3 8 2	357	- 296
4 0 2	258	238
4 1 1	499	503
4 1 2	2206	-2182
4 1 13	843	- 826
4 2 5	1128	1139
4 2 10	1180	1116
4 2 21	637	- 656
4 3 3	1029	1005
4 3 8	1851	1975
4 3 20	1004	925
4 4 1	640	- 658
4 4 10	1375	1422
4 5 2	425	- 477
4 7 2	486	- 485
5 1 5	792	757
5 1 7	1159	1212
5 2 3	1614	1735
5 2 9	1145	1107
5 2 14	719	- 754
5 2 15	878	890
5 2 20	816	772
5 3 2	1644	-1631
5 3 4	160	- 206
5 3 5	649	703
5 3 22	734	656
5 4 4	1421	-1493
5 4 8	791	865
5 4 20	889	792
6 0 4	1555	1693
6 1 9	941	945
6 2 2	1299	-1299
6 3 4	1966	-2096
6 3 20	693	597
6 4 2	1515	-1487
7 1 9	596	- 598
7 2 1	1231	-1231
7 2 4	1348	-1379
7 2 7	933	- 990
7 2 10	798	815
7 3 2	1381	-1320
7 3 14	762	- 693
7 4 4	929	- 977
8 2 3	853	- 833
8 2 11	584	- 568
8 3 8	799	786
9 0 6	775	- 832
9 2 8	959	949
9 3 6	1145	1149
9 4 8	951	918
10 1 5	545	514
11 3 12	157	- 138
11 4 0	641	- 616
12 4 10	572	- 524
- 1 0 2	2984	3020
- 1 0 6	4535	-4629
- 1 0 18	1661	-1695
- 1 1 3	1176	1111
- 1 1 11	577	432
- 1 2 1	589	883
- 1 2 3	818	757
- 1 2 4	1856	-1596
- 1 2 7	1451	1443
- 1 2 12	1569	1489
- 1 3 5	948	968
- 1 3 6	1992	-2158
- 1 3 7	503	- 483
- 1 3 9	588	662
- 1 3 10	1599	1547
- 1 3 11	676	672
- 1 3 14	1539	1514
- 1 4 1	1028	-1028
- 1 4 12	1555	1485
- 1 6 1	487	- 502
- 1 6 2	464	409
- 1 8 1	276	238
- 1 8 2	160	126
- 2 2 5	1587	1532
- 2 2 6	1150	- 962
- 2 2 7	843	- 793
- 2 2 10	1616	1635
- 2 2 13	1363	-1397
- 2 2 14	1149	1099
- 2 2 15	666	- 676
- 2 3 3	350	- 270
- 2 3 5	878	- 868
- 2 3 12	1891	2006
- 2 4 2	1800	1828
- 2 4 3	721	- 719
- 2 4 7	515	572
- 2 4 9	478	515
- 2 4 10	1100	1152
- 2 4 14	1049	1057
- 2 5 1	839	- 799
- 2 5 4	312	342
- 2 6 2	154	157
- 2 6 4	548	- 577
- 2 8 4	323	- 312
- 3 0 10	1182	929
- 3 1 5	691	529
- 3 2 1	1112	943
- 3 2 5	796	- 754
- 3 2 9	744	- 768
- 3 2 11	1193	-1184
- 3 2 15	802	- 716
- 3 3 1	561	- 639
- 3 3 2	2060	2109
- 3 3 5	575	- 522
- 3 3 6	933	- 910
- 3 3 7	521	- 519
- 3 3 18	1218	-1203
- 3 4 4	924	1031
- 3 4 8	969	- 904
- 3 5 1	311	343
- 3 5 2	823	892
- 3 6 1	189	- 174
- 3 7 1	261	215
- 4 0 2	415	399
- 4 1 1	1021	- 821
- 4 1 3	563	- 667
- 4 2 1	950	- 935
- 4 2 6	1206	-1298
- 4 2 7	983	-1002
- 4 2 12	802	774
- 4 2 18	860	- 839
- 4 3 3	790	- 755
- 4 3 8	2058	-2129
- 4 3 16	729	- 713
- 4 4 6	1288	-1432
- 4 4 10	904	- 932
- 4 4 18	888	- 849
- 4 5 2	84	- 16
- 4 7 2	358	351
- 5 0 2	2040	2168
- 5 1 9	672	627
- 5 1 11	769	760
- 5 2 3	896	- 858
- 5 2 7	784	751
- 5 2 8	1325	-1312
- 5 2 13	1117	1135
- 5 3 3	611	596
- 5 3 6	1049	-1040
- 5 3 10	714	- 723
- 5 4 8	1183	-1222
- 5 4 24	685	578
- 6 1 1	521	501
- 6 1 2	2172	2313
- 6 1 3	631	- 578
- 6 2 3	1220	1171
- 6 2 9	904	839
- 6 3 1	823	841
- 6 3 4	1016	1137
- 7 1 5	620	- 632
- 7 3 2	863	834
- 7 3 6	1085	1059
- 8 1 3	784	- 806
- 8 1 9	778	- 735
- 8 3 4	1600	1566
- 9 0 2	936	999
- 9 1 5	758	- 753
- 9 3 10	927	- 834
-10 3 8	1026	- 973
-10 4 10	783	- 774
-11 0 14	161	184
-13 3 6	612	575
-13 4 4	370	305

individual isotropic temperature factors for 4Si, 4N and 8C, convergence was achieved in two cycles; no attempt was made to locate the H atoms. Final values of the parameters are listed in Table 2. The overall R value is 8·6% (7·9% for observed reflections only). Residual peaks or troughs on a 3D difference synthesis prepared from the final least-squares parameters were in all cases $\leq 0{\cdot}5$ e.Å^{-3} in absolute value. Bond data and standard deviations were calculated with the aid of the Busing & Levy (1959) Function and Error program and are listed in Table 4.

Description of structure

The highly unusual feature of the structure is that the crystal contains two different geometrical isomers of the tetrameric species, $(Me_2SiNH)_4$, packed in an ordered 1:1 array. One isomer (Fig. 4) has a center of inversion, $\bar{1}$, whereas the other has a twofold axis of symmetry; each shows some approximation to higher symmetry: $2/m$ and $\bar{4}$, respectively. For the purpose of contrasting the isomers, the ring configuration of the $\bar{1}$ isomer is describable as a folding along the parallel lines, Si(1)N($\bar{2}$) and Si($\bar{1}$)N(2) so as to put a Me_2SiNH linkage on either side of a plane defined by Si(1), N(2), Si($\bar{1}$) and N($\bar{2}$); in the isomer of twofold symmetry a reverse folding of one Me_2SiNH segment leaves both linkages on the same side of a mean plane defined by Si(4*), N(3), Si(4) and N(3*). (We use the notation A(n), A($\bar{n}$) to denote a pair of atoms related by $\bar{1}$ and A(n), A(n*) to denote a pair of atoms related by the twofold axis.) In order to sustain dissimilar bond angles at N and Si the 'folded' sections are non-planar; Si(2) deviates by 0·37 Å from the plane defined by N(2), Si($\bar{1}$) and N($\bar{1}$), Si(3) by 0·35 Å from the plane of N(3), Si(4) and N(4). The ring configuration of the $\bar{1}$ isomer by analogy with six-membered rings could be termed a 'chair' form, that of the isomer with a twofold axis a 'cradle' form; and we shall employ this pictorial terminology, although a further assessment of the situation (see below) makes it clear that the four-atom section containing Si(4*), N(3), Si(4) and N(3*) differs significantly in regard to planarity and dimensions from the corresponding section in the $\bar{1}$ isomer, the 'folded' sections being virtually isodimensional.



chair

cradle

Fig. 4. Models of the geometrical isomers of $(Me_2SiNH)_4$.
At left, the centrosymmetric 'chair' form; at right, the 'cradle' form of symmetry 2.

Table 4. *Bond distances and angles*

Standard deviations in parenthesis

'Chair'

Si(1)–N(1)	1·728 Å	(0·011 Å)
Si(1)–N(2)	1·746	(0·008)
Si(2)–N($\underline{2}$)	1·734	(0·011)
Si(2)–N($\bar{1}$)	1·727	(0·008)
Si(1)–C(1)	1·882	(0·020)
Si(1)–C(3)	1·868	(0·012)
Si(2)–C(2)	1·850	(0·020)
Si(2)–C(4)	1·897	(0·014)
Si(1)–N(1)–Si($\bar{2}$)	132·4°	(0·9°)
Si(1)–N(2)–Si(2)	132·3	(0·8)
N(1)–Si(1)–N($\underline{2}$)	112·5	(0·5)
N(2)–Si(2)–N($\bar{1}$)	110·5	(0·5)
N(1)–Si(1)–C(1)	110·3	(0·6)
N(1)–Si(1)–C(3)	105·6	(0·6)
N(2)–Si(1)–C(1)	108·4	(0·7)
N(2)–Si(1)–C(3)	106·4	(0·5)
N(2)–Si(2)–C(2)	114·2	(0·6)
N($\underline{2}$)–Si(2)–C(4)	103·6	(0·7)
N($\bar{1}$)–Si(2)–C(2)	107·2	(0·7)
N($\bar{1}$)–Si(2)–C(4)	112·7	(0·5)
C(1)–Si(1)–C(3)	113·6	(0·7)
C(2)–Si(2)–C(4)	108·8	(0·7)

'Cradle'

Si(3)–N(3)	1·708 Å	(0·012 Å)
Si(3)–N(4)	1·741	(0·008)
Si(4)–N(4)	1·687	(0·011)
Si(3)–N(3*)	1·750	(0·009)
Si(3)–C(5)	1·923	(0·019)
Si(3)–C(7)	1·869	(0·012)
Si(4)–C(6)	1·872	(0·023)
Si(4)–C(8)	1·867	(0·013)
Si(3)–N(3)–Si(4*)	130·1°	(0·9°)
Si(3)–N(4)–Si(4)	133·1	(0·9)
N(3)–Si(3)–N(4)	110·3	(0·5)
N(4)–Si(4)–N(3*)	110·3	(0·5)
N(3)–Si(3)–C(5)	112·4	(0·5)
N(3)–Si(3)–C(7)	106·1	(0·7)
N(4)–Si(3)–C(5)	106·4	(0·6)
N(4)–Si(3)–C(7)	111·0	(0·5)
N(4)–Si(4)–C(6)	111·7	(0·5)
N(4)–Si(4)–C(8)	108·0	(0·7)
N(3*)–Si(4)–C(6)	106·7	(0·7)
N(3*)–Si(4)–C(8)	110·6	(0·5)
C(5)–Si(3)–C(7)	110·6	(0·6)
C(6)–Si(4)–C(8)	109·5	(0·6)

As can be seen from Table 4 the bond data are remarkably similar in the two configurations. Especially noteworthy is the bond angle at nitrogen, which by analogy with the behavior of oxygen in Si–O–Si linkages might have been variable in the two isomers. None of the SiC bond distances is significantly different from a mean value of 1·88 Å. In the case of the 'chair' isomer, the mean SiN distance is 1·734 Å with no significant variation; only in the 'cradle' isomer are the individual deviations of SiN distances large enough to suggest a tendency toward recognizable monomers. The mean SiN distance is then 1·722 Å, and deviations from the mean are 0·014, 0·019, 0·028 and 0·035 Å. Comparison with an average standard deviation of 0·010 Å shows, however, that only the latter two verge on statistical significance. The average of the eight NSiC bond angles in the 'chair' form is 108·6°; in the 'cradle' form, 109·1°, the extreme deviations being about the same in the two cases. It is clear then that the ring systems in both isomers are based on the linking of only slightly irregular tetrahedra.

The SiN bond distances found here are in accord with SiN distances of 1·73 ± 0·02 Å in $(H_3Si)_3N$ (Hedberg, 1955) and 1·72 and 1·75 Å in β-Si_3N_4 (Hardie & Jack, 1957). The average SiC distance is somewhat shorter (but not significantly so) than the value of 1·92 ± 0·02 Å in $(Me_2SiO)_4$ (SPF). Bond distances calculated from the sum of covalent radii with electronegativity corrections are SiN = 1·80 Å and SiC = 1·88 Å (Schomaker & Stevenson, 1941), the latter in excellent agreement with those found here. The experimental SiN distances, on the other hand, are significantly shorter, although the discrepancy is not so marked as in $(Me_2SiO)_4$, where the observed SiO distance of 1·65 Å contrasts with 1·76 Å given by the Schomaker–Stevenson rule. This non-parallel behavior of O and NH is therefore quite different from the situation in the pair, $K_2[(SO_3)_2O]$ and $K_2[(SO_3)_2NH]$, where the structural data (Cruickshank, 1961) give the SN bond distance as only 0·017 Å longer than SO (bridge) and the bond angles at O and N as 124° and 125·5°, respectively.

Table 5. *Comparison of non-bonded distances within the two ring configurations*

σ values in parenthesis

'Chair'			'Cradle'		
Si(1)Si($\bar{1}$)	4·093 Å	(0·005 Å)	Si(4*)Si(4)	4·290 Å	(0·005 Å)
N(2)N($\bar{2}$)	3·89	(0·02)	N(3)N(3*)	3·62	(0·02)
Si(1)N($\bar{2}$)	3·60	(0·01)	Si(4)N(3)	3·57	(0·01)
Si(2)Si($\bar{1}$)	3·161	(0·004)	Si(3)Si(4)	3·145	(0·004)
N(2)N($\bar{1}$)	2·84	(0·01)	N(3)N(4)	2·83	(0·01)
Si(1)Si($\underline{2}$)	3·180	(0·004)	Si(4*)Si(3)	3·136	(0·004)
Si(1)N($\bar{1}$)	3·77	(0·01)	Si(4*)N(4)	3·85	(0·01)
N(2)N($\underline{1}$)	2·89	(0·01)	N(3)N(4*)	2·82	(0·01)
N(2)Si($\bar{2}$)	4·04	(0·01)	N(3)Si(3*)	3·87	(0·01)
Si(2)N($\underline{1}$)	4·19	(0·01)	Si(3)N(4*)	3·53	(0·01)
Si(2)Si($\bar{2}$)	4·842	(0·006)	Si(3)Si(3*)	4·249	(0·005)
N(1)N($\bar{1}$)	4·20	(0·02)	N(4)N(4*)	3·57	(0·02)

In the ideal chair-cradle isomerism, *i.e.* where one four-atom section has undergone an exact reverse folding, the other sections remaining unchanged, it will be appreciated that most of the non-bonded distances between ring atoms should remain the same in the two configurations. In fact, only the interatomic distances between the folded 'flaps' are required to change where shorter distances are expected in the cradle isomer. In addition to these distances, seen in Table 5 to be almost uniformly shorter by 0·6 Å, several other shorter (if only marginally so) non-bonded distances definitely establish the cradle isomer as having a more compact ring structure; concomitantly, perhaps, the thermal parameters of these ring atoms are smaller than those of corresponding atoms in the chair isomer, the behavior of the nitrogens

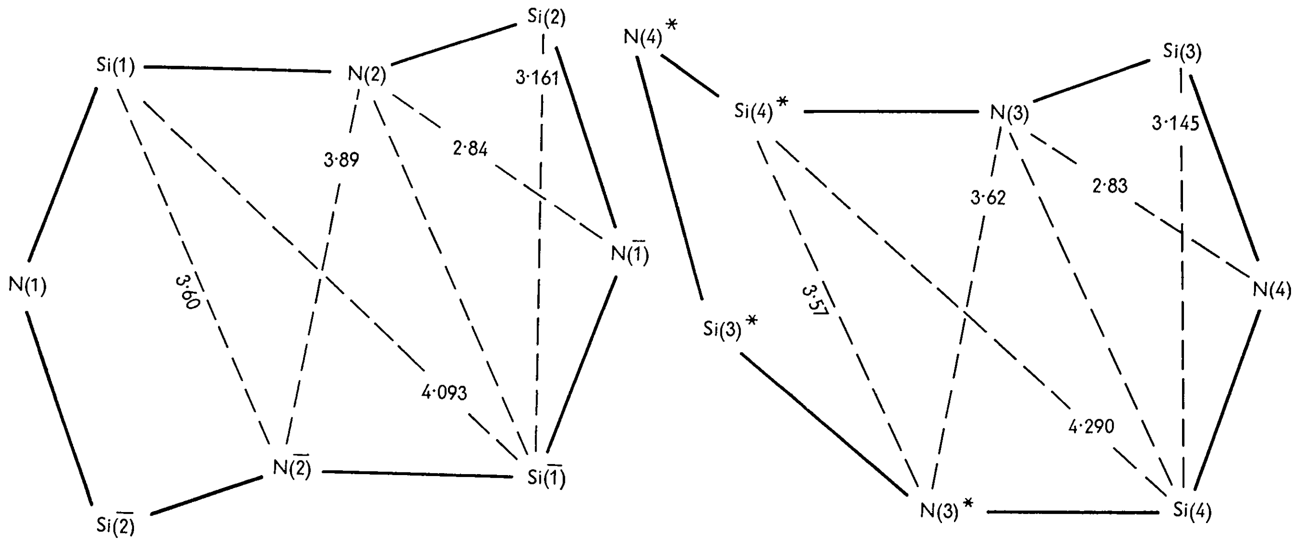


Fig. 5. Schematic drawing showing the ring conformations in the two isomers of (Me$_2$SiNH)$_4$. Non-bonded distances (in Å) within the four-atom sections are also indicated.

being especially marked.† There are, moreover, important differences in the dimensions of the central sections of the two isomers. In the chair form these four atoms are rigorously planar and sheared a bit from a rectangular shape (Fig. 5); in the cradle form, an increased shear places Si(4)Si(4*) about 0·20 Å longer than $\mathrm{Si}(1)\mathrm{Si}(\bar{1})$ and N(3)N(3*) about 0·27 Å shorter than $\mathrm{N}(2)\mathrm{N}(\bar{2})$. The central section is also not required by symmetry to be planar, and indeed as a measure of the non-planarity, the *y* parameters of N(3) and Si(4) differ by 0·20 Å. Because of these differences, concentrated largely in making the central sections structurally non-equivalent, we must conclude that the isomerism displayed here is not strictly of an ideal chair-cradle type, although it suffices for our purposes to continue to use the terminology.

As far as the ring atoms are concerned, it thus appears that the steric repulsive forces are relatively greater in the cradle configuration. On the other hand, the relatively greater freedom afforded the methyl substituents by this configuration must largely offset the energy disadvantage associated with the ring atoms. Relevant to this, the smallest methyl carbon-to-silicon distances in the cradle form are 3·81 and 3·81 Å; to nitrogen, 3·88 and 3·92 Å; to methyl carbon, 4·06 and 4·08 Å (exclusive, of course, of distances within the same tetrahedron). In the chair form the corresponding distances, all involving C(1) (and $\mathrm{C}(\bar{1})$), are 3·59 and 3·72 Å; 3·73 and 3·88 Å; 3·66 and 4·02 Å, respectively. (The values within these pairs would be identical were the symmetry $\bar{4}$ and $2/m$ in each case.) Especially noteworthy is the low value of 3·66 Å, some 0·34 Å shorter than the minimum distance customarily associated with methyl–methyl interactions. A similar situation encountered in (Me$_2$GaOH)$_4$ (Smith & Hoard, 1959) led these authors to believe, in fact, that the difficulties attendant with keying in two methyl groups on either side of the ring require the abandonment of the ideal molecular symmetry $2/m$ in favor of $\bar{1}$.

Thus far, the discussion and comparison of non-bonded distances has not taken into account any difference in the total electrostatic energy which might arise in the two conformations. A crude electrostatic model shows, however, that despite the necessarily shorter interatomic distances in the cradle conformation the net contribution to the coulombic energy need not be unfavorable. For, if we take the extreme case and assume the ring to be made up of NH as -2 ions and Me$_2$Si as $+2$ ions, the four shorter distances (between folded 'flaps') afford two repulsions ($+2\ldots+2$ and $-2\ldots-2$) as well as two $+2\ldots-2$ attractions.

This detailed examination of the bond data and non-bonded distances points strongly to the conclusion that the energy difference between the two isomers cannot be large. Of the (Me$_2$AB)$_4$ compounds studied so far, we note with satisfaction that examples of both types occur: (Me$_2$PN)$_4$ has the cradle configuration (Dougill, 1961) whereas both (Me$_2$GaOH)$_4$ and (Me$_2$SiO)$_4$, as previously mentioned, have the centrosymmetric conformation.† Nevertheless, the small

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† It is important to note that the N(3)N(4*) distance of 2·82 Å may well contribute considerably more repulsion than the corresponding distance of 2·89 Å when considered in terms of a potential energy curve having a minimum at 3·0 Å, *i.e.* 2× the packing radius given by Pauling (1948) for N.

† An alternative description of the $\bar{1}$ configuration makes use of the fact that the 4 A atoms necessarily lie in a plane, likewise those of B. The dihedral angles between planes are 31°, 28° and 17° (incorrectly reported as 30°) in (Me$_2$GaOH)$_4$, (Me$_2$SiNH)$_4$ and (Me$_2$SiO)$_4$, respectively.

energy difference implies an appreciable population of both isomers in the liquid state, and inasmuch as only one crystalline form is (apparently) found, *i.e.* no α and β forms containing exclusively chair isomers in one and cradles in the other, we must presume a ready interconversion during crystallization. The situation realized whether it be a pure solid of one conformation only or a mixed crystal must therefore depend inevitably on the favorableness of the particular molecular grouping within the lattice, assuming, of course, the presence of thermal equilibrium. In $(Me_2SiNH)_4$ we do not require an equal abundance of the two isomers in the liquid, but only that the decrease in free energy accompanying the formation of the 1:1 crystalline mixture more than compensates for the energy expended in interconverting isomers until the proper 1:1 proportion is reached.

One of the truly remarkable features of the lattice arrangement is that three of these compounds, $(Me_2PN)_4$, $(Me_2SiO)_4$ and $(Me_2SiNH)_4$ all have nearly identical unique-axis repeat distances (6·45 Å) despite, as we have just seen, a fundamentally different molecular conformation in each case. In $(Me_2SiNH)_4$ the packing sequence along *b* places 'chair' above 'chair' and 'cradle' above 'cradle'; this arrangement resembles closely, in fact, the one obtainable in $(Me_2SiO)_4$ by replacing every other stack of $\bar{1}$ isomers (parallel to *c*) by a stack of isomers having twofold symmetry, but of the same periodicity. The methyl–methyl and methyl–nitrogen intermolecular distances within either type of column are in the range 4·06–4·20 Å and 3·76–3·91 Å, respectively. From the latter values, each NH proton should doubtless lie in or near a Si–N–Si plane if the *b*-axis repeat distance is to be independent of the attached hydrogens. The packing relations between stacks are characterized (Fig. 1) by a tight arrangement of methyl carbons about those special positions which are unoccupied by molecular centers; these interatomic distances are all satisfactorily 4·0–4·2 Å. The nitrogens are too far apart for a hydrogen-bonding scheme whereby the tetracovalency of N might be satisfied; their principal contacts are, accordingly, with methyl carbons. It is significant that more room is provided for the NH groups than for the (bare) O and N in the other compounds. The shortest methyl $\cdots$ N(O) interatomic distances between stacks are 3·59 Å in $(Me_2PN)_4$ and 3·76 Å in $(Me_2SiO)_4$, whereas in $(Me_2SiNH)_4$ it is 3·91 Å (and of a lower multiplicity because of the monoclinic symmetry).

From the foregoing it may well be that the phenomenon in crystalline $(Me_2SiNH)_4$ of two different isomers, unobserved elsewhere, depends sensitively and critically on the presence of the ring-atom hydrogens. Some factor, related to molecular orientation and shape, is certainly operating to produce an ordered 1:1 crystal in preference to a random structure, and this in spite of an unfavorable entropy of mixing term. It would be exceedingly interesting to establish the binary-phase relationships among these three cyclic tetramers, and especially to see if the equimolar mixture of $(Me_2PN)_4$ and $(Me_2SiO)_4$ forms crystals isomorphous with $(Me_2SiNH)_4$. We note that if such compounds were subjected to crystal structure analyses, it should generally be possible to identify the individual molecules on the basis of their characteristic set of bond distances and angles.

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References

Alexander, L. E. & Smith, G. S. (1962). *Acta Cryst.* **15**, 983.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Busing, W. R. & Levy, H. A. (1959). Oak Ridge National Laboratory Central Files Memorandum 59-4-37, April.

Busing, W. R. & Levy, H. A. (1959). Oak Ridge National Laboratory Central Files Memorandum 59-12-3, December.

Cruickshank, D. W. J. (1961). *J. Chem. Soc.*, p. 5486.

Dougill, M. W. (1961). *J. Chem. Soc.*, p. 5471.

Freeman, A. J. (1959). *Acta Cryst.* **12**, 261.

Hardie, D. & Jack, K. H. (1957). *Nature, Lond.* **180**, 332.

Hedberg, K. (1955). *J. Amer. Chem. Soc.* **77**, 6491.

Howells, E. R., Phillips, D. C. & Rogers, D. (1950). *Acta Cryst.* **3**, 210.

Kitaigorodskii, A. I. (1958). *Soviet Physics, Crystallography*, **3**, 393.

Larrson, K. (1960). *Ark. Kemi*, **16**, 203.

Lipson, H. & Woolfson, M. M. (1952). *Acta Cryst.* **5**, 680.

Pauling, L. (1948). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

Peyronel, G. (1954). *Chim. Industr.* **36**, 441.

Post, B. (1962). Private communication.

Rochow, E. G. (1951). *An Introduction to the Chemistry of the Silicones.* New York: Wiley.

Schomaker, V. & Stevenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

Smith, G. S. & Alexander, L. E. (1963). *Acta Cryst.* **16**, 462.

Smith, G. S. & Hoard, J. L. (1959). *J. Amer. Chem. Soc.* **81**, 3907.

Steinfink, H., Post, B. & Fankuchen, I. (1955). *Acta Cryst.* **8**, 420.

Wegener, R. A. & Post, B. (1958). *Amer. Cryst. Assoc., Program and Abstracts*, Paper A-2. Milwaukee, Wis.

Yokoi, M. & Yamasaki, K. (1953). *J. Amer. Chem. Soc.* **75**, 4139.