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Crystal and Molecular Structure of Dodecamethylcyclohexasilane

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Crystals of dodecamethylcyclohexasilane are monoclinic, space group $A2/a$, with four molecules per unit cell having lattice parameters $a=14\cdot026$, $b=10\cdot158$, $c=18\cdot168$ Å and $\beta=109\cdot0°$. The data were collected on a four-circle automatic diffractometer with Cu $K\alpha$ radiation. The structure was solved by the symbolic-addition procedure and was refined by full-matrix least-squares methods. The least-squares refinement of the positional and anisotropic thermal parameters of the silicon and carbon atoms, using 1440 observed reflections, yielded a final R of 0·053. The molecules of $[Si(CH_3)_2]_6$ have site symmetry $\bar{1}$ and have the flattened chair conformation of cyclohexane. The Si–C bond lengths have been corrected for riding motion, and a slight difference between equatorial and axial carbon to silicon bond distances is noted: $1\cdot935\pm0\cdot006$ and $1\cdot913\pm0\cdot004$ Å, respectively.

Introduction

The family of permethylated silicon ring compounds, $[Si(CH_3)_2]_n$ where $n=5,6,7$, and 8, has recently been synthesized by Carberry & West (1966, 1969). These compounds are of special interest, because they undergo reduction to anion radicals at low temperatures in the same way that aromatic hydrocarbons do (Carberry, West & Glass, 1969). Electron spin resonance (e.s.r.) measurements indicate that the unpaired electron is fully delocalized over the ring atoms, just as in aromatic anion radicals.

The six-membered ring compound dodecamethylcyclohexasilane $[Si(CH_3)_2]_6$ was known much earlier than the other members of the series, having first been prepared by Burkhard (1949). One can construct strain-free nonplanar models of $[Si(CH_3)_2]_6$ having the chair or boat cyclohexane conformation. However, both models require two nonequivalent kinds of methyl groups in the molecule, and evidence for such nonequivalence has not yet been forthcoming. The nuclear magnetic resonance (n.m.r.) spectrum of $[Si(CH_3)_2]_6$ from $-95°$ to $+30°$ and the e.s.r. spectrum of its anion radical at low temperatures (Carberry, West & Glass, 1969) indicate equivalence of the methyl protons, at least on a time-average basis. Thus, in solution, $[Si(CH_3)_2]_6$ and its anion radical must either be planar, or else undergo surprisingly rapid conformational flips between nonplanar structures.

In the present paper, we describe the results of an X-ray crystallographic study of $[Si(CH_3)_2]_6$ in the solid state.

Experimental

A sample of $[Si(CH_3)_2]_6$ was furnished by Professor R. West of the University of Wisconsin. Crystals suitable for X-ray analysis were obtained from a methyl ethyl ketone solution. It was found that although the crystals were stable in the air, it was necessary to coat them with glue in order to inhibit decomposition during X-ray exposure. The crystals are monoclinic, with cell dimensions $a=14\cdot026\pm0\cdot002$, $b=10\cdot158\pm0\cdot002$, $c=18\cdot168\pm0\cdot003$ Å, and $\beta=109\cdot0\pm0\cdot1°$. The systematic absences, (h,k,l), $k+l$ odd and $(h0l)$, l odd, lead to either the Aa (C_s^4) space group or the $A2/a$ (C_{2h}^6) space group. The density was measured quite roughly and found to be less than 1 g.cm^{-3}; thus, there are four molecules per unit cell. The calculated density for $Z=4$ is 0·906 g.cm^{-3}.

A crystal in the shape of a rhomb that was approximately equidimensional and 0·15 mm on an edge was chosen for collecting intensity data. All the data out to 2θ of 125° were collected on a Picker four-circle automatic diffractometer, using Cu $K\alpha$ radiation. In all, 1836 independent reflections were measured with the stationary-crystal, stationary-counter technique. The peak intensities were converted to integrated intensities empirically from the curve of I(integrated)/I(peak). The integrated intensity values were obtained from several reflections measured by the θ–2θ technique. The Lorentz and polarization factors were applied to the intensities, but no absorption corrections were made ($\mu=28\cdot5$ cm^{-1}). Of those reflections measured, 1440 had an intensity significantly above background $[I_o/\sigma(I)>3]$.

After the data had been placed on an absolute scale (Wilson, 1942), the normalized structure magnitudes, E, and the appropriate statistics were computed. For this data, the averages of $|E|$, E^2, and $|E^2-1|$ are 0·800, 0·984, and 0·938 respectively. The theoretical values for a centrosymmetric distribution are 0·798, 1·000, and 0·968 for $\langle|E|\rangle$, $\langle E^2\rangle$, and $\langle|E^2-1|\rangle$, respectively; the space group is therefore $A2/a$, and the four molecules of $[Si(CH_3)_2]_6$ in the unit cell must lie at points having symmetry 2 or $\bar{1}$. All subsequent calculations were made with space group $A2/a$.

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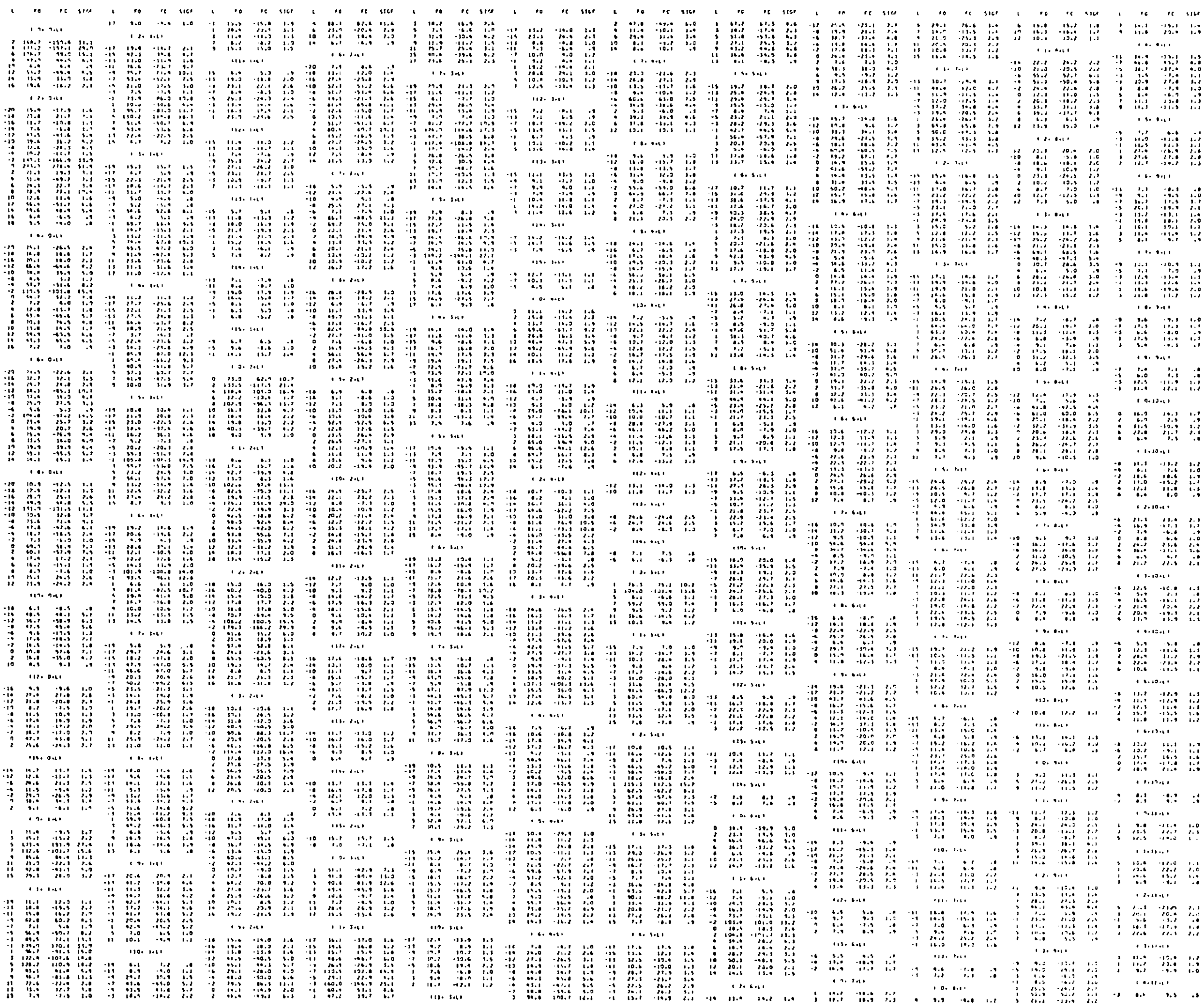
Structure determination

In order to obtain a trial structure, the symbolic-addition procedure (Karle & Karle, 1966) was applied. For space group $A2/a$, the signs of only two reflections may be arbitrarily assigned to specify the origin. In addition to these two signs, two other reflections were assigned the symbols a and b; these four reflections comprised the starting set for the symbolic-addition procedure. From this set, the signs of the 153 reflections for which $|E| \geq 1{\cdot}75$ were determined. The procedure was then extended to all reflections with $|E| \geq 1{\cdot}5$, so that eventually the signs of 237 reflections had been determined. At no time during the sign determination procedure was it necessary to accept the sign of a reflection with a probability of less than 99%. By the time the determination was complete, it was obvious that a was positive and b negative. The E map calculated with these 237 reflections gave the positions of the three independent silicon atoms and six carbon atoms, although there were some spurious peaks which were as high as the peaks representing the correct positions of the carbon atoms. The molecules lie at positions of site symmetry $\bar{1}$ and have the chair conformation.

The trial structure was refined by full-matrix least-squares methods, first with isotropic temperature factors for the silicon and carbon atoms, then with anisotropic thermal parameters for these same atoms. A difference map was then calculated in an attempt to locate the hydrogen atoms. However, this map was characterized by smears of density near the carbon atoms from which no hydrogen atom positions could be distinguished. To determine the effect of hydrogen atoms on the refinement, the hydrogen atom positions were calculated assuming tetrahedral geometry about

Table 1. *Observed and calculated structure factors*



the carbon atoms and C–H distances of 1·05 Å. Two sets of hydrogen coordinates were calculated, the first set assuming the expected staggered conformation, and the second set assuming a combination of the staggered and eclipsed conformations. In the second set, the occupancy factor for the H atoms was $\frac{1}{2}$. The hydrogen atoms were assigned an isotropic temperature factor of 9 Å^2, or about the average of the isotropic temperature factors of the carbon atoms. The refinement was then carried out on both models, one cycle at a time, with only the parameters of the Si and C atoms being allowed to vary. After each cycle, hydrogen coordinates were recalculated to give the ideal geometry. For the first model (hydrogen atoms in the staggered conformation), the R value fell to 0·061. For the second model (six $\frac{1}{2}$H atoms per C atom), the R value fell to 0·053. Throughout the refinement, the weight, w, was taken as $1/\sigma^2(F)$ where $\sigma_F=[\frac{1}{4}\sigma^2(F^2)+0{\cdot}02F^2]^{1/2}$. $\sigma(F^2)$ was derived from counting statistics and instrumental uncertainties.

It is surprising that the inclusion of the hydrogen atoms in the structure factor calculations causes such a large improvement in the agreement index, especially since the thermal motion of the hydrogen atoms is apparently so large in this case. The fact that the model refined with $\frac{1}{2}$H atoms gives somewhat better agreement than the model of staggered H atoms is quite reasonable, in view of the high thermal motion of the methyl carbon atoms and since this model more closely approximates a smearing of the electron density, as seen in the difference map.

All of the least-squares calculations were carried out using *UCLALS*4 (Gantzel, Sparks, Trueblood & Long, 1964) on the IBM 360/65 at the University of Pennsylvania.

Table 1 lists the observed and calculated structure factors; the calculated structure factors are those for the model, assuming six $\frac{1}{2}$H atoms on each C atom. The atomic scattering factors for silicon and carbon are those found in *International Tables for X-ray Crystallography* (1962), while the scattering curve for the hydrogen is that of Stewart, Davidson & Simpson (1965). The scattering factors for silicon were corrected for the real component of anomalous dispersion ($\Delta f' = +0{\cdot}2$).

Results

The coordinates of the Si and C atoms for the disordered hydrogen model are given in Table 2. These coordinates do not differ significantly from those for the model refined assuming the staggered hydrogen atom conformation. Table 3 contains the anisotropic thermal parameters for this model. The calculated positions of the hydrogen atoms are presented in Table 4.

As previously pointed out, molecules of $[Si(CH_3)_2]_6$ are in the chair conformation. A diagram of the molecule is shown in Fig. 1, and the packing of the molecules in the crystal is shown in Fig. 2. The closest approach between methyl groups of neighbouring molecules is 3·98 Å and occurs between C(1) and C(3) and also between C(2) andC(4). In general, the packing is rather loose, a finding which is in agreement with the observation of rather soft crystals with large thermal motion. As expected, the crystals seem to be held together only by weak van der Waals interactions.

Table 2. *Coordinates of the silicon and carbon atoms and the corresponding e.s.d.* (*in parentheses*)

	x	y	z
Si(1)	−0·00374 (8)	0·21103 (10)	0·12630 (5)
Si(2)	0·00094 (7)	0·03852 (9)	0·21289 (6)
Si(3)	0·07768 (8)	0·09984 (10)	0·34249 (6)
C(1)	−0·0817 (5)	0·1575 (6)	0·0253 (3)
C(2)	0·1264 (4)	0·2490 (6)	0·1249 (4)
C(3)	0·0754 (4)	−0·1037 (4)	0·1904 (3)
C(4)	−0·1322 (4)	−0·0180 (5)	0·1953 (4)
C(5)	0·0647 (5)	−0·0407 (5)	0·4074 (3)
C(6)	0·2162 (3)	0·1293 (5)	0·3600 (3)

Table 3. *Anisotropic thermal parameters for the silicon atoms*, (*values* × 10^5), *and carbon atoms*, (*values* × 10^4)

The temperature factor is of the form:

$$\exp\,(-h^2\beta_{11}-k^2\beta_{22}-l^2\beta_{33}-hk\beta_{12}-hl\beta_{13}-kl\beta_{23}).$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	877 (9)	1132 (14)	338 (4)	570 (14)	422 (9)	161 (10)
Si(2)	701 (8)	776 (12)	406 (5)	−6 (11)	324 (9)	−21 (8)
Si(3)	832 (9)	921 (13)	348 (5)	373 (13)	300 (9)	167 (9)
C(1)	185 (6)	245 (9)	38 (2)	201 (12)	2 (5)	−53 (6)
C(2)	133 (5)	191 (7)	102 (3)	80 (9)	152 (7)	100 (8)
C(3)	137 (4)	121 (5)	66 (2)	43 (7)	76 (5)	−5 (5)
C(4)	93 (3)	171 (7)	84 (3)	−64 (8)	50 (5)	−2 (7)
C(5)	209 (3)	151 (6)	53 (2)	74 (7)	79 (4)	80 (6)
C(6)	79 (6)	182 (6)	70 (2)	50 (10)	10 (6)	−36 (5)

Discussion

The bond lengths and angles are given in Table 5. This table also includes Si–C lengths corrected for thermal motion, assuming that the riding-motion correction (Busing & Levy, 1964) is valid. The thermal ellipsoid parameters are presented in Table 6.

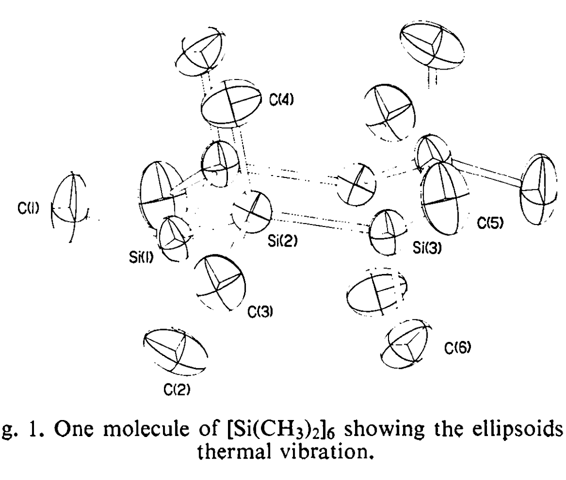


Fig. 1. One molecule of $[Si(CH_3)_2]_6$ showing the ellipsoids of thermal vibration.

Table 4. *Coordinates of the* 36 *half-weight hydrogen atoms* ($\times 10^3$) *for* $[Si(CH_3)_2]_6$

The methyl carbon atoms to which the hydrogen atoms are bonded are also given. Atoms marked with an asterisk are for staggered hydrogen.

	x	y	z		x	y	z
C(1)-H(1)*	−48	74	10	C(4)-H(19)*	−163	−48	137
H(2)*	−82	235	−14	H(20)*	−131	−99	232
H(3)*	−155	136	25	H(21)*	−174	61	207
H(4)	−35	161	−11	H(22)	−138	−117	177
H(5)	−142	224	4	H(23)	−148	−11	248
H(6)	−107	61	28	H(24)	−181	−40	150
C(2)-H(7)*	156	164	108	C(3)-H(25)*	102	−14	466
H(8)*	121	324	84	H(26)*	100	−125	394
H(9)*	170	280	181	H(27)*	−12	−58	397
H(10)	128	233	68	H(28)	138	−74	440
H(11)	141	350	139	H(29)	26	−118	372
H(12)	177	185	164	H(30)	27	−6	445
C(3)-H(13)*	40	133	132	C(6)-H(31)*	251	152	419
H(14)*	75	183	228	H(32)*	248	41	347
H(15)*	150	71	198	H(33)*	224	206	324
H(16)	27	185	173	H(34)	258	61	402
H(17)	136	126	241	H(35)	231	111	308
H(18)	100	76	143	H(36)	234	226	381

Table 5. *Bond lengths and valence angles for* $[Si(CH_3)_2]_6$ *and their standard deviations (in parentheses)*

The values for the Si–C bond lengths corrected for riding motion are also given.

	d(uncorr)	d(riding)
Si(1)-C(1)	1·885 (5) Å	1·935 Å
Si(1)-C(2)	1·874 (4)	1·912
Si(2)-C(3)	1·907 (4)	1·930
Si(2)-C(4)	1·879 (3)	1·912
Si(3)-C(5)	1·898 (5)	1·940
Si(3)-C(6)	1·888 (3)	1·915
Si(1)-Si(2)	2·342 (1)	
Si(1)-Si(3)	2·339 (1)	
Si(2)-Si(3)	2·332 (1)	
Si(1)-Si(2)-Si(3)	112·40 (5)°	
Si(2)-Si(3)-Si(1)	111·64 (5)	
Si(2)-Si(1)-Si(3)	111·68 (5)	
C(1)-Si(1)-Si(2)	108·59 (18)	
C(1)-Si(1)-Si(3)	108·11 (17)	
C(2)-Si(1)-Si(2)	110·42 (19)	
C(2)-Si(1)-Si(3)	110·20 (19)	
C(3)-Si(2)-Si(1)	108·70 (15)	
C(3)-Si(2)-Si(3)	108·35 (16)	
C(4)-Si(2)-Si(1)	107·78 (18)	
C(4)-Si(2)-Si(3)	111·09 (18)	
C(5)-Si(3)-Si(1)	109·12 (16)	
C(5)-Si(3)-Si(2)	108·69 (17)	
C(6)-Si(3)-Si(1)	110·03 (16)	
C(6)-Si(3)-Si(2)	108·90 (16)	
C(1)-Si(1)-C(2)	107·71 (24)	
C(3)-Si(2)-C(4)	108·42 (20)	
C(5)-Si(3)-C(6)	108·43 (23)	

Table 6. *Parameters for the thermal ellipsoids* ($\times 10^3$)

The first column contains the r.m.s. displacements of the principal axes of the ellipsoids, and the next three columns are the direction cosines relative to the orthogonal system *a*, *b*, and *c**.

	i	$(\overline{u_i^2})^{1/2}$ (Å)	Va	Vb	Vc*
Si(1)	1	300	−807	−527	−267
	2	221	−552	515	655
	3	215	−208	674	−709
Si(2)	1	253	939	12	−345
	2	246	343	−42	938
	3	201	2	−999	−47
Si(3)	1	284	−935	−339	−102
	2	237	−257	453	854
	3	201	−243	825	−511
C(1)	1	499	811	566	−146
	2	276	578	−737	351
	3	223	91	−368	−925
C(2)	1	440	366	439	820
	2	283	547	−815	192
	3	253	753	378	−539
C(3)	1	354	−890	−219	−401
	2	308	−348	−242	906
	3	241	−295	945	139
C(4)	1	361	−361	177	915
	2	328	−572	733	−369
	3	253	−737	−656	−163
C(5)	1	439	952	194	237
	2	326	304	−689	−658
	3	208	35	698	−715
C(6)	1	377	564	501	−656
	2	288	34	779	626
	3	246	825	−373	424

The cyclohexasilane ring is in a regular chair conformation, with an average bond length of 2·338 ± 0·004 Å, a value which compares quite favorably with the value of 2·34 Å predicted by the single-bond covalent radius (Pauling, 1960). This distance is slightly shorter than that reported for the Si–Si bond length of 2·352 Å in elemental silicon (Straumanis & Aka, 1952). The average value of the Si–Si–Si valence angle is 111·9 ± 0·4°, a value which is the same as that of 111·55 ± 0·15° found for the C–C–C angle in cyclohexane (Davis & Hassel, 1963), and the value of 111·5 ± 0·5° reported for the cyclohexyl ring in $(PC_6H_{11})_4$ by Bart (1969). The torsion angles Si(1)–Si(2)–Si(3)–Si($\overline{1}$), Si(2)–Si(3)–Si($\overline{1}$)–Si($\overline{2}$), and Si($\overline{3}$)–Si(1)–Si(2)–Si(3) have the absolute values of 53·6, 53·2, and 53·7°, respectively, the average being 53·5 ± 0·3°. For the cyclohexyl ring (Bart, 1969), the value for the C–C–C–C torsion angle was found to be 54·5 ± 0·8°. The Si–C bond lengths, corrected for the riding motion, range from 1·910 to 1·943 Å. On the basis of the nature of the thermal motions, the correction for riding motion seems reasonable. If it is assumed that the estimated standard deviations of the individual corrected Si–C bond lengths are twice those for the uncorrected bond lengths, the smallest difference between corrected and uncorrected bond lengths is $3 \cdot 5\sigma$, so that the corrections are significant. It is interesting to note that there is an appreciable difference in the Si–C bond lengths depending on the steric nature of the methyl carbon, *i.e.* the bond lengths for the equatorial substituents are not the same as those for the axial substituents. The equatorial carbon atoms, C(1), C(3), and C(5), are equivalent, having an average Si–C distance of 1·935 ± 0·006 Å, while the axial carbon atoms, C(2), C(4), and C(6) have an equivalent Si–C distance of 1·913 ± 0·004 Å. The difference of 0·022 Å in the bond lengths of the axial and equatorial atoms is possibly significant. A similar difference in bond lengths of axial and equatorial substituents was recently reported for 2-2′-dichlorotrimethylene sulphite (van Oyen, Hasekamp, Verschoor & Romers, 1968), where the ring is in the chair conformation. In this case, the equatorial C–Cl bond length is 1·800 Å, while the axial C–Cl distance is 0·025 Å shorter, at 1·775 Å. The reported e.s.d.'s for these bond lengths are 0·008 Å, so that the apparent difference in these distances is possibly significant. In the present structure, the difference in the axial and equatorial bond lengths, while possibly significant, cannot be readily explained so that no rationale for this phenomenon is offered here. The possibility that the data may contain systematic errors cannot be discounted so that, indeed, the difference that is observed may not be real.

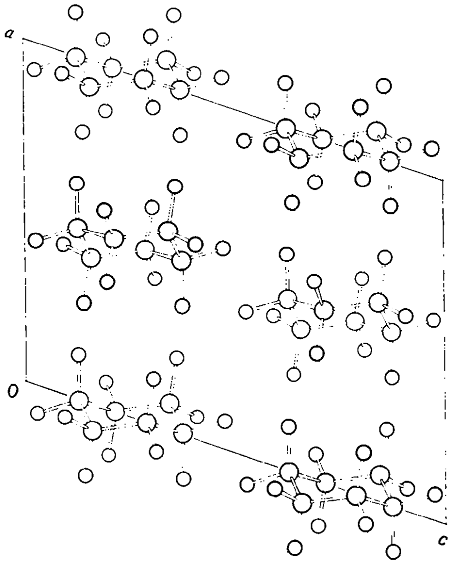


Fig. 2. The structure of $[Si(CH_3)_2]_6$ in projection down the *b* axis.

The C–Si–C valence angles are very nearly the same, with an average value of 108·1 ± 0·5°. The C–Si–Si valence angles range from 107·8 to 111·1°, with an average value of 109·2 ± 1·2°. Within experimental error, there are no differences in these valence angles for the axial and equatorial substituents. The absolute values for all of the torsion angles are tabulated in Table 7. The average C–Si–Si–Si torsion angle, where the carbon atom is axial, is 68·2 ± 1·2°, and where the carbon atom is equatorial the angle is 173·5 ± 0·3°. The C–Si–Si–C torsion angles are of three different classifications, two of these involving carbon atoms of the same type, *i.e.* both carbon atoms are either axial or equatorial. The third class involves one axial carbon atom and one equatorial carbon atom. In the case where the two carbon atoms are axial, the torsion angle has an average value of 169·3 ± 1·5°, and in the case where the two carbon atoms are equatorial, the torsion angle is 66·7 ± 0·8°. The torsion angle for the case involving a carbon atom of each type has a value of 51·3 ± 1·3°. These values are quite different from the values of 180 and 60°, which are the expected values for the classical cyclohexane ring with tetrahedral geometry about each carbon atom.

Table 7. *Torsion angles for* $[Si(CH_3)_2]_6$

	1–2–3/2–3–4
Si(1)–Si(2)–Si(3)–Si(1)	53·6°
Si(2)–Si(3)–Si(1)–Si(2)	53·2
Si(3)–Si(1)–Si(2)–Si(3)	53·7
C(1)–Si(1)–Si(2)–Si(3)	172·7
C(1)–Si(1)–Si(3)–Si(2)	172·6
C(3)–Si(2)–Si(3)–Si(1)	173·7
C(3)–Si(2)–Si(1)–Si(3)	173·5
C(5)–Si(3)–Si(2)–Si(1)	174·1
C(5)–Si(3)–Si(1)–Si(2)	173·4
C(2)–Si(1)–Si(2)–Si(3)	69·3
C(2)–Si(1)–Si(3)–Si(2)	69·9
C(4)–Si(2)–Si(3)–Si(1)	67·3
C(4)–Si(2)–Si(1)–Si(3)	69·1
C(6)–Si(3)–Si(2)–Si(1)	68·3
C(6)–Si(3)–Si(1)–Si(2)	67·9
C(1)–Si(1)–Si(2)–C(3)	67·2
C(1)–Si(1)–Si(3)–C(5)	67·0
C(3)–Si(2)–Si(3)–C(5)	65·8
C(2)–Si(1)–Si(2)–C(4)	168·0
C(2)–Si(1)–Si(3)–C(6)	169·0
C(4)–Si(2)–Si(3)–C(6)	170·9
C(1)–Si(1)–Si(2)–C(4)	50·1
C(1)–Si(1)–Si(3)–C(6)	51·7
C(3)–Si(2)–Si(1)–C(2)	50·6
C(3)–Si(2)–Si(3)–C(6)	51·8
C(5)–Si(3)–Si(1)–C(2)	50·3
C(5)–Si(3)–Si(2)–C(4)	53·2

The axial Si–C bonds are bent away from the principal ring axis on average about 5·5°. This inclination appears to be primarily a consequence of the flattened cyclohexasilane ring, since there do not appear to be any strong interactions between the axial methyl groups across the ring. The average cross-ring axial methyl carbon distance is 4·21 Å, a distance which is much larger than twice the van der Waals radius, 4·0 Å for methyl groups.

Conclusion

From the present study of $[Si(CH_3)_2]_6$ in the solid state, it would seem that the preferred conformation of this molecule is the chair conformation. The fact that $[Si(CH_3)_2]_6$ seems to prefer the chair conformation reinforces the idea that in solution the molecule undergoes rapid conformational flips between chair conformations, so that on a time-average basis the methyl protons are equivalent as indicated by both the n.m.r. spectrum of $[Si(CH_3)_2]_6$ and the e.s.r. spectrum of its anion radical at low temperatures, as previously noted.

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The Crystal Structure of a Sodium Triborate Modification, β-$Na_2O.3B_2O_3$

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The β-modification of sodium triborate, β-$Na_2O.3B_2O_3$, is monoclinic with the following unit-cell dimensions (at 22°C): $a=8·990\pm0·003$, $b=11·033\pm0·002$, $c=12·107\pm0·004$ Å, $\beta=90·50\pm0·03°$; $Z=6$, calculated density 2·246 g.cm^{-3}; space group $P2_1/c$. Three-dimensional X-ray intensity data were measured with a Picker automatic single-crystal diffractometer, using Cu $K\alpha$ radiation. The structure was determined by direct methods and refined by full-matrix least squares to an R value of 0·065. The weighted R value was 0·043. The borate polyanion in this phase is built up from three different kinds of groups, *viz.* pentaborate groups, triborate groups and BO_4 tetrahedra. The groups share corners with each other and in this way are mutually connected to an infinite double layer. The average B–O bond lengths for the BO_4 tetrahedra and the BO_3 triangles are normal, 1·474 and 1·368 Å respectively, but significant deviations from the averages depending on local surroundings are observed. The three crystallographically different sodium atoms are surrounded by 6, 7 and 8 oxygen atoms at distances ranging from 2·2 Å to 3·1 Å.

Introduction

The only anhydrous triborate for which the structure is known is the caesium compound (Krogh-Moe, 1960). In this compound the anion structure consists of a single infinite three-dimensional network of triborate groups sharing corners. Triborates of a number of different cations are known to exist, however. In the system sodium oxide–boron oxide Tilman & Bouaziz (1968) reported the presence of three different crystalline triborate phases. The phase labelled β by Tilman & Bouaziz is the subject of the present study. This modification seemed interesting inasmuch as its infrared spectrum was more similar to that of a pentaborate than that of a triborate. Apart from an interest in the main features of this structure, accurate knowledge of boron–oxygen bond lengths and angles is desirable. Thus recent work (Krogh-Moe, 1972) has revealed