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The Crystal and Molecular Structure of 2,6-*cis*-Diphenylhexamethylcyclotetrasiloxane

D. CARLSTRÖM and G. FALKENBERG

Department of Medical Physics, Karolinska Institutet, S-104 01 Stockholm, Sweden

The crystal structure of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane, $C_{18}H_{28}O_4Si_4$, has been determined and refined using three-dimensional X-ray diffractometer data. The unit cell is monoclinic, space group $C2/c$ with the constants $a = 15.155$, $b = 8.829$, $c = 18.020$ Å, $\beta = 93.44°$. There is half a formula unit in the asymmetric unit. The structure was solved by direct methods and refined by least-squares procedures. The final R-value was 0.048 for 2144 symmetry independent observed reflexions.

The eight-membered siloxane ring has a "boat form" and differs thereby from configurations earlier reported for cyclotetrasiloxanes. The intra- and intermolecular distances are discussed.

The material for the X-ray crystallographic analysis was synthesized by Dow-Corning, USA, and was, in the form of large colourless transparent crystals, placed at our disposal by AB Kabi, Stockholm. The substance has a very marked estrogen-like activity especially on the male sexual organs of the mouse, rat, rabbit, dog, and monkey (Åberg, B., personal communication).

EXPERIMENTAL

Preliminary rotation and Weissenberg diagrams showed that the crystals were monoclinic and the systematic absences indicated either of the two C-centered space groups Cc or $C2/c$. While the former is non-centrosymmetric with 4 general positions, the latter is centrosymmetric with 8 general positions. A rough determination of the density of the crystals showed that there were 4 molecules in the unit cell.

For the recording of the reflexion intensities an optically perfect crystal was trimmed to an almost spherical shape (diameter = 0.3 mm). The crystal was mounted about its b axis and was sealed within a capillary of Lindemann glass as it had been observed that crystals kept in open air slowly evaporated. Three-dimensional intensity data were collected with a Philips linear automatic diffractometer (PAILRED). The Mo$K\alpha$-radiation was monochromatized with a graphite crystal. Unit cell parameters: $a = 15.155 \pm 0.006$, $b = 8.829 \pm 0.004$, $c = 18.020 \pm 0.008$ Å, $\beta = 93.44 \pm 0.09°$. Integrated intensities were collected with the ω-scanning technique within $\sin\theta/\lambda < 0.66$ corresponding to the Cu-sphere. A scanning speed of 2.5° min^{-1} was employed and the scanning range was varied

between 1.6° and 2.5°. For reflexions giving less than 10 000 counts during one scan, the scan was repeated up to 3 times. Background was measured for one minute at the beginning and the end of each scan. As a check on the stability of the crystal and the instrument, standard reflexions were measured twice a day during the recording period. Excluding systematic absences, 2834 symmetry independent reflexions of the layers $h0l$ through $h11l$ were recorded. Out of these, 690 did not differ significantly from the background intensity. The integrated intensities were corrected for Lorentz and polarization factors but no corrections were made for extinction or absorption. The latter could be neglected altogether because of the spherical shape of the crystal and the low linear absorption coefficient of the material ($\mu = 2.63$ cm^{-1} for Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å). The corrected structure amplitudes were placed on an approximately absolute scale by Wilson statistics. The Wilson plot gave a correlation coefficient for the K-curve of -0.994 and the over all temperature factor, $B = 4.4$ Å^2, showed that the molecules had a high thermal mobility which was in accordance with the low melting point (+43°C) of the crystals. The normalized structure factors, $|E|$'s, were computed and the $|E|$ value distribution (Table 1) indicated the centrosymmetric space group ($C2/c$).

Table 1. Statistical averages and distribution of normalized structure factors.

	Experimental	Theoretical for centrosymmetric	Theoretical for non-centrosymmetric
$\langle\|E\|\rangle$	0.790	0.798	0.886
$\langle\|E\|^2-1\rangle$	0.912	0.968	0.736
$\langle\|E\|^2\rangle$	0.960	1.000	1.000
$\|E\|>1$	31.3 %	32.0 %	37.0 %
$\|E\|>2$	4.3 %	5.0 %	1.8 %
$\|E\|>3$	0.1 %	0.3 %	0.01 %

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Since 2,6-*cis*-diphenylhexamethyltetrasiloxane does not contain atoms with atomic numbers higher than 14 it was evident that the "heavy atom technique" probably would be difficult as the silicon atoms could not be located with certainty in the three-dimensional Patterson maps. However, the strong accumulation of vector maxima in $x0z$ was a further indication that the structure was centrosymmetric and it was decided to determine the structure by the symbolic addition procedure (*cf.* Karle and Karle [1]). Several attempts to solve the structure by this method failed, probably depending on the low $|E|$ values with $l = n + 1$. Through the courtesy of Dr. R. Norrestam, Stockholm University, a new attempt was made with his programme for direct methods (Norrestam [2]). The signs of the reflexions $\bar{7}$ 3 13 and 4 4 1 were used for the specification of origin. In addition the reflexions $\bar{9}$ 1 2, $\bar{10}$ 0 2 and $\bar{7}$ 1 14 were used as the basic set for solving the triple relations calculated for the 200 strongest $|E|$ values. The phases 0 or π in all combinations were assigned to the latter three reflexions. In the subsequent generation of eight different solutions of the sign relations, one solution was found to be superior to the other ones. In this solution all triple relations were utilized resulting in signs for 123 $|E|$ values. In the three-dimensional E-maps, based on these signs, four strong maxima were found separated by distances acceptable for Si – O bonds. These maxima fitted well half an eight-membered

Table 2. Fractional atomic coordinates($\times 10^5$) for non-hydrogen atoms and ($\times 10^4$) for hydrogen atoms. Anisotropic temperature parameters ($\times 10^5$) for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. Standard deviations in parentheses. β_{ij} are the coefficients in the expression: exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	38084 (4)	7538 (8)	18140 (4)	372 (3)	1551 (11)	298 (2)	194 (8)	−4 (4)	37 (7)
Si(2)	42510 (4)	575 (8)	34920 (4)	426 (3)	1568 (11)	266 (2)	−132 (8)	91 (4)	68 (7)
O(1)	46750 (11)	−1097 (21)	15262 (11)	427 (8)	1668 (27)	385 (6)	271 (22)	12 (11)	−147 (19)
O(2)	38677 (13)	8303 (25)	27193 (10)	561 (9)	2269 (34)	310 (6)	356 (28)	131 (11)	303 (22)
C(1)	38044 (16)	27408 (30)	14693 (14)	455 (11)	1639 (34)	300 (7)	356 (30)	61 (14)	27 (25)
C(2)	36983 (28)	30419 (43)	7112 (16)	1055 (25)	2028 (52)	312 (9)	593 (56)	−40 (23)	82 (34)
C(3)	37551 (34)	44969 (49)	4336 (22)	1116 (30)	2400 (59)	389 (13)	883 (69)	90 (30)	579 (45)
C(4)	38894 (37)	56915 (48)	9103 (27)	1322 (34)	1865 (63)	599 (17)	548 (74)	281 (37)	564 (52)
C(5)	39831 (47)	54373 (52)	16515 (29)	1913 (53)	1685 (51)	561 (19)	−66 (82)	183 (49)	−269 (52)
C(6)	39300 (32)	39622 (41)	19336 (20)	1183 (29)	1815 (49)	349 (11)	126 (56)	97 (28)	−132 (35)
C(7)	28203 (20)	−3328 (42)	14660 (23)	474 (12)	2112 (48)	640 (16)	16 (41)	−169 (22)	−134 (45)
C(8)	38021 (25)	−18641 (41)	35773 (21)	695 (18)	2078 (50)	534 (14)	−838 (50)	107 (25)	353 (42)
C(9)	39570 (29)	12994 (50)	42667 (19)	875 (22)	2817 (69)	397 (11)	491 (66)	197 (24)	−471 (46)

Atom	x	y	z	B	Atom	x	y	z	B
H(2)	3619 (27)	2211 (44)	350 (24)	6.5	H(7C)	2237 (24)	152 (38)	1660 (21)	5.5
H(3)	3630 (29)	4693 (52)	−108 (24)	7.0	H(8A)	3929 (24)	−2540 (39)	3080 (20)	5.5
H(4)	3867 (29)	6841 (50)	685 (25)	7.5	H(8B)	3158 (24)	−1886 (39)	3597 (19)	5.5
H(5)	4082 (27)	6487 (51)	2037 (23)	7.0	H(8C)	4122 (24)	−2401 (38)	3930 (20)	5.5
H(6)	4025 (26)	3716 (47)	2501 (23)	6.5	H(9A)	4208 (23)	2424 (41)	4200 (19)	5.5
H(7A)	2918 (23)	−1360 (43)	1610 (19)	5.5	H(9B)	3284 (23)	1325 (44)	4367 (20)	5.5
H(7B)	2754 (24)	−233 (41)	894 (20)	5.5	H(9C)	4218 (24)	994 (39)	4750 (21)	5.5

ring having a rotation diad through its centre. Phased by the four atomic positions of the *E*-maps, three-dimensional electron density maps were calculated from the 957 strongest structure amplitudes observed. It was now easy to locate all the 13 non-hydrogen atoms of the asymmetric unit. The positional coordinates were refined by the full-matrix least-squares method. Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[3] After two cycles of refinement using individual isotropic temperature factors the descrepancy index R ($R = \sum||F_o| - |F_c||/\sum|F_o|$) dropped from an initial value of 0.32 to 0.10. One cycle of refinement with anisotropic temperature factors lowered the R-value to 0.065. A difference Fourier synthesis prepared at this stage revealed the positions of the 14 hydrogen atoms. Two further cycles of refinement of the positional and thermal parameters of the non-hydrogen atoms and the positional coordinates of the hydrogen atoms gave a final R-index of 0.048. The hydrogen atoms were assigned isotropic temperature factors of the same magnitudes as those of the atoms to which they were bound. The atomic scattering factors for the hydrogen atoms were taken from the data of Stewart *et al.*[4] and the weighting scheme was that of Hughes.[5] The positional and thermal parameters for the final structure are given in Table 2. On request, a list of the final observed and calculated structure factors may be obtained from the authors.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Intramolecular bond distances and bond angles uncorrected for thermal motion are given in Table 3 and Fig. 1 which also shows the numbering system of the atoms. The average Si–O and Si–C distances are 1.631 and 1.851 Å, respectively. The angles around the silicon atoms are all close to the expected tetrahedral value and the mean Si–O–Si angle is 144.2°. These values may be compared with those reported for octamethylcyclotetrasiloxane by Steinfink *et al.*[6] who found the following average interatomic distances and angles: Si–O = 1.65 Å, Si–C = 1.92 Å, O–Si–O = 109.0°, C–Si–C = 106.0°, and Si–O–Si = 142.5°. The benzene ring attached to Si(1) is slightly distorted. The bonds around C(4) are thus considerably shorter than the standard aromatic C–C value (1.395 Å)[3] and the planarity of the ring is not very good; some of the carbon atoms deviate as much as 0.01 Å from the least-squares plane through the ring. The pronounced thermal movements of the atoms, especially of C(3), C(4), and C(5), strongly influencing the accuracy of their positional parameters may cause the descrepancies observed. All the C–H distances agree, within experimental errors, with accepted values and the angles involving hydrogen atoms are likewise quite normal.

The eight-membered siloxane ring has a twofold rotation symmetry with the rotation diad passing through the centre of the ring. The wide Si–O–Si angles make the ring relatively planar (the largest deviation from the plane for Si and O atoms is 0.4 Å) and prevents collision between phenyl and methyl groups. The two phenyl rings of the molecule are nearly parallel to each other and to the rotation diad which means that they are almost perpendicular to the plane of the siloxane ring. The overall configuration of the molecule can

Table 3. Interatomic distances and angles with estimated standard deviations in parentheses. Atoms with the superscript ′ belong to the symmetry related $(1-x, y, 0.5-z)$ half of the molecule.

Si(1) – O(1)	1.630 (2) Å	C(2) – H(2)	0.98 (4) Å
Si(1) – O(2)	1.630 (2)	C(3) – H(3)	1.00 (4)
Si(2) – O(2)	1.626 (2)	C(4) – H(4)	1.09 (5)
Si(2) – O(1′)	1.637 (2)	C(5) – H(5)	1.16 (4)
Si(1) – C(1)	1.861 (3)	C(6) – H(6)	1.05 (4)
Si(1) – C(7)	1.856 (3)	C(7) – H(7A)	0.95 (4)
Si(2) – C(8)	1.838 (4)	C(7) – H(7B)	1.03 (4)
Si(2) – C(9)	1.850 (4)	C(7) – H(7C)	1.06 (4)
C(1) – C(2)	1.392 (4)	C(8) – H(8A)	1.10 (4)
C(2) – C(3)	1.383 (6)	C(8) – H(8B)	0.98 (3)
C(3) – C(4)	1.368 (6)	C(8) – H(8C)	0.91 (4)
C(4) – C(5)	1.353 (7)	C(9) – H(9A)	1.07 (4)
C(5) – C(6)	1.402 (6)	C(9) – H(9B)	1.05 (3)
C(6) – C(1)	1.371 (4)	C(9) – H(9C)	0.97 (4)
O(1) – Si(1) – O(2)	109.9 (1)°	C(8) – Si(2) – C(9)	112.1 (2)°
O(1) – Si(1) – C(1)	108.7 (1)	Si(1) – O(2) – Si(2)	146.6 (2)
O(1) – Si(1) – C(7)	107.5 (2)	Si(2) – O(1′) – Si(1′)	141.7 (2)
O(2) – Si(1) – C(1)	107.1 (1)	Si(1) – C(1) – C(2)	120.4 (2)
O(2) – Si(1) – C(7)	110.8 (2)	Si(1) – C(1) – C(6)	122.7 (3)
C(1) – Si(1) – C(7)	112.8 (2)	C(1) – C(2) – C(3)	121.8 (4)
O(2) – Si(2) – O(1′)	109.0 (1)	C(2) – C(3) – C(4)	119.9 (4)
O(2) – Si(2) – C(8)	110.1 (1)	C(3) – C(4) – C(5)	119.7 (5)
O(2) – Si(2) – C(9)	107.9 (2)	C(4) – C(5) – C(6)	120.5 (6)
O(1′) – Si(2) – C(8)	107.0 (1)	C(5) – C(6) – C(1)	121.2 (4)
O(1′) – Si(2) – C(9)	110.7 (2)	C(6) – C(1) – C(2)	116.9 (3)

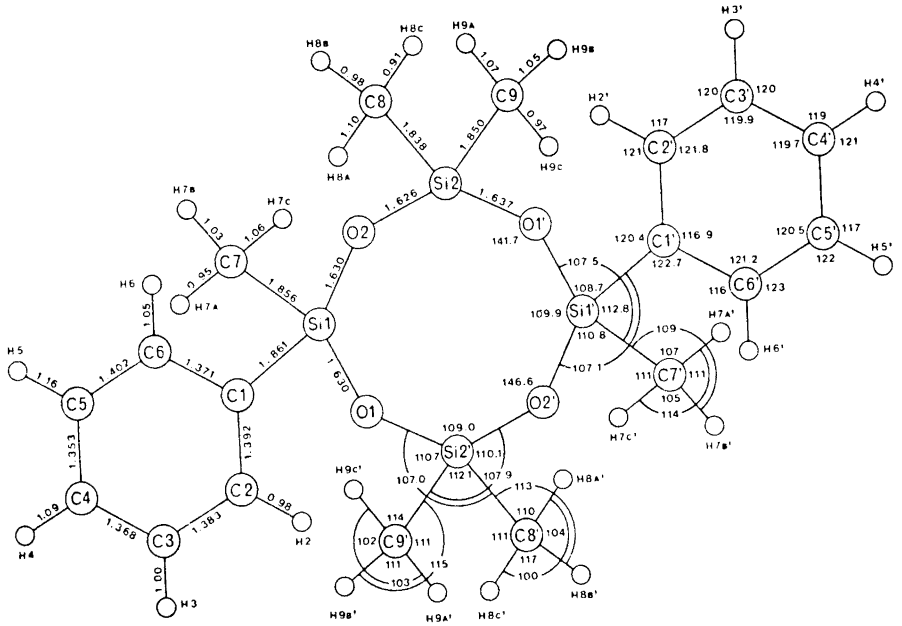

Fig. 1. The numbering of the atoms and bond distances and bond angles in the 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane molecule.

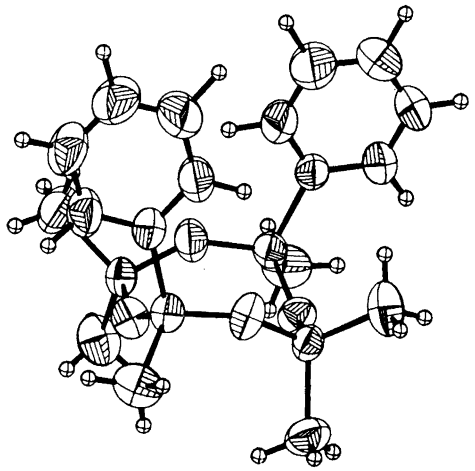

Fig. 2. The configuration of the 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane molecule. The thermal ellipsoids for the non-hydrogen atoms are scaled to 50 % probability. Hydrogen atoms are shown as equally large spheres. The drawing is made with the plotting programme ORTEP by Johnson.[9]

be seen in Fig. 2 which also depicts the ellipsoids of thermal motion scaled to 50 % probability. The cyclotetrasiloxane ring of the present structure can best be described as having a "boat form" which is quite different from the "cradle form" with a twofold rotation symmetry predicted by Yokoi [7] from electron diffraction on octamethylcyclotetrasiloxane in the gas phase. In the crystal structure determination of octamethylcyclotetrasiloxane already mentioned [6] the siloxane ring was found to possess a centre of symmetry and it

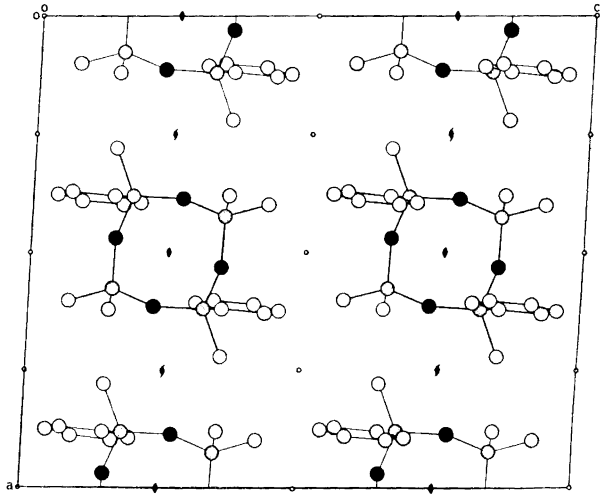

Fig. 3. Projection along *b* of the crystal structure of 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane. The atoms are represented by filled circles (oxygen atoms), dotted circles (silicon atoms), and open circles (carbon atoms). The unit cell contains four molecules each of which having a rotation diad through its center.

had accordingly a "chair form" configuration. It seems plausible that the large Si – O – Si angles contribute to a conformational instability in the eight-membered ring system and that the energy barriers between different conformations are small.

The packing of the molecules in the diphenylhexamethylcyclotetrasiloxane structure is shown in Fig. 3 which is a projection along the *b* axis. There are no intermolecular distances between non-hydrogen atoms less than 3.80 Å and the closest carbon-hydrogen approach is 2.99 Å which is well above the sum of the van der Waals radii. The rather loose packing of the structure is in accordance with the low density 1.16 g cm^{-3} of the compound.

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