

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

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The crystal structure of 2,6-*trans*-diphenylhexamethylcyclotetrasiloxane,  $C_{18}H_{26}O_4Si_4$ , has been determined and refined using three-dimensional X-ray diffractometer data. The unit cell is monoclinic, space group  $C2/c$  with the constants  $a=23.147$  Å,  $b=8.759$  Å,  $c=14.877$  Å,  $\beta=128.08^\circ$ . There is half a formula unit in the asymmetric unit. The structure was solved by the "heavy atom" technique and refined by least-squares procedures. The final  $R$ -value was 0.050 for 1635 symmetry independent reflexions. The eight-membered siloxane ring has a "chair form" configuration. The intramolecular bond distances and bond angles are discussed. The present structure is compared with that of the *cis* form.

The structure of the *trans* form of 2,6-diphenylhexamethylcyclotetrasiloxane was determined in order to compare it with the structure of the *cis* form<sup>1</sup> which has a very marked estrogenic activity.<sup>2</sup> Unlike the *cis* form the *trans* form has no pronounced biological activity. The material used for the X-ray crystallographic analysis was synthesized by Dow-Corning, USA, and was in the form of large, colourless crystals placed at our disposal by Kabi AB, Stockholm. The material was recrystallized by slow evaporation of a methanolic solution.

## EXPERIMENTAL

A number of crystals were investigated by oscillation and Weissenberg diagrams which indicated a monoclinic system with systematic absences characteristic for either of the space groups  $Cc$  or  $C2/c$ . Unit cell parameters:  $a=23.147$ ,  $b=8.759$ ,  $c=14.877$  Å,  $\beta=128.08^\circ$ . The density of the crystals showed that the unit cell contained 4 molecules. For the recording

of the intensities a crystal with the dimensions  $0.2 \times 0.4 \times 0.25$  mm was mounted about its  $b$ -axis and sealed within a capillary of Lindemann glass since the crystals slowly evaporated in open air. A Philips linear automatic diffractometer (PILRED) with graphite monochromatized  $MoK\alpha$ -radiation ( $\lambda=0.7107$  Å) was used for collecting the intensity data. Excluding systematic absences, 2788 symmetry independent reflexions of the layers  $h0l$  through  $h1l$  were recorded within  $\sin \theta/\lambda \leq 0.66$  Å<sup>-1</sup>, using the  $\omega$ -scanning technique. Out of these 1137 did not differ significantly from the background intensity which was measured for 40 s at the beginning and the end of each scan. The standard reflexions measured two times in each layer as a check of the stability of the crystal and the instrument showed no significant changes. The integrated intensities were corrected for Lorentz and polarization factors but not for extinction or absorption. The latter could be neglected because of the low linear absorption coefficient of the material ( $\mu=2.67$  cm<sup>-1</sup> for  $MoK\alpha$ ). The structure factors were placed on an approximately absolute scale by Wilson statistics and the Wilson plot gave a correlation coefficient for the  $K$ -kurve of  $-0.961$  and an overall temperature factor  $B=2.6$  Å<sup>2</sup>. The normalized structure factors,  $|E|$ 's, were computed, but the  $|E|$  value distribution did not clearly indicate whether the structure was centrosymmetric or not. For that reason the non-centrosymmetric space group  $Cc$  was assumed for the structure determination.

An IBM 360/75 computer was employed for all calculations in this study, using our local crystallographic program system.<sup>3</sup>

## DETERMINATION AND REFINEMENT OF THE STRUCTURE

The structure was solved by the "heavy atom" technique. In the three-dimensional Patterson maps several of the strongest peaks

Table 1. Fractional atomic coordinates for non-hydrogen atoms ( $\times 10^5$ ) and for hydrogen atoms ( $\times 10^4$ ). Anisotropic temperature parameters ( $\times 10^5$ ) for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms. Standard deviations in parentheses.  $\beta_{ij}$  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	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Si(1)	31833 (5)	32707(10)	44922 (7)	278 (3)	1307(13)	657 (7)	-146 (9)	599 (8)	-18(14)
Si(2)	15294 (5)	27098(11)	32670 (7)	232 (3)	1307(13)	559 (6)	-85 (9)	401 (7)	71(14)
O(1)	34679(12)	23226(26)	56370(18)	367 (8)	1363(33)	795(18)	111(26)	760(21)	251(38)
O(2)	22981(12)	34308(32)	36635(19)	283 (8)	1980(45)	835(20)	-373(28)	532(21)	221(46)
C(1)	35582(16)	52377(38)	48863(25)	258(10)	1362(45)	633(22)	-49(32)	479(25)	170(49)
C(2)	43015(20)	55170(48)	55373(36)	278(11)	1748(65)	1218(38)	-140(40)	590(35)	-6(76)
C(3)	45891(24)	69703(60)	58626(43)	344(15)	2312(91)	1449(49)	-832(56)	639(44)	-394(98)
C(4)	41391(31)	81882(55)	55462(46)	563(22)	1621(74)	1512(52)	-659(63)	975(56)	-421(94)
C(5)	34143(28)	79652(55)	49184(50)	514(20)	1456(70)	1970(64)	51(54)	1014(60)	183(99)
C(6)	31197(20)	65093(48)	45812(37)	307(13)	1561(61)	1389(42)	-31(42)	613(39)	154(80)
C(7)	34822(26)	22168(50)	37835(38)	628(19)	1738(64)	1313(40)	-76(54)	1471(50)	-194(79)
C(8)	14348(25)	7642(51)	27370(33)	576(18)	1884(67)	934(33)	-502(55)	943(41)	-856(75)
C(9)	7827(22)	39607(58)	21762(35)	384(14)	2541(86)	1015(35)	547(55)	724(38)	1098(87)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(2)	4621(21)	4646(47)	5748(31)	5.5	H(7C)	3322(21)	1198(51)	3600(33)	5.5
H(3)	5116(20)	7055(47)	6266(31)	5.5	H(8A)	1833(22)	102(47)	3352(33)	5.5
H(4)	4307(20)	9195(47)	5746(31)	5.5	H(8B)	1397(21)	690(48)	2066(32)	5.5
H(5)	3091(20)	8818(47)	4728(31)	5.5	H(8C)	1092(22)	146(46)	2605(32)	5.5
H(6)	2609(20)	6401(49)	4119(31)	5.5	H(9A)	846(21)	4897(46)	2515(31)	5.5
H(7A)	3946(22)	2011(50)	4179(33)	5.5	H(9B)	803(20)	3969(48)	1522(31)	5.5
H(7B)	3336(21)	2846(47)	3096(32)	5.5	H(9C)	296(21)	3820(50)	1812(32)	5.5

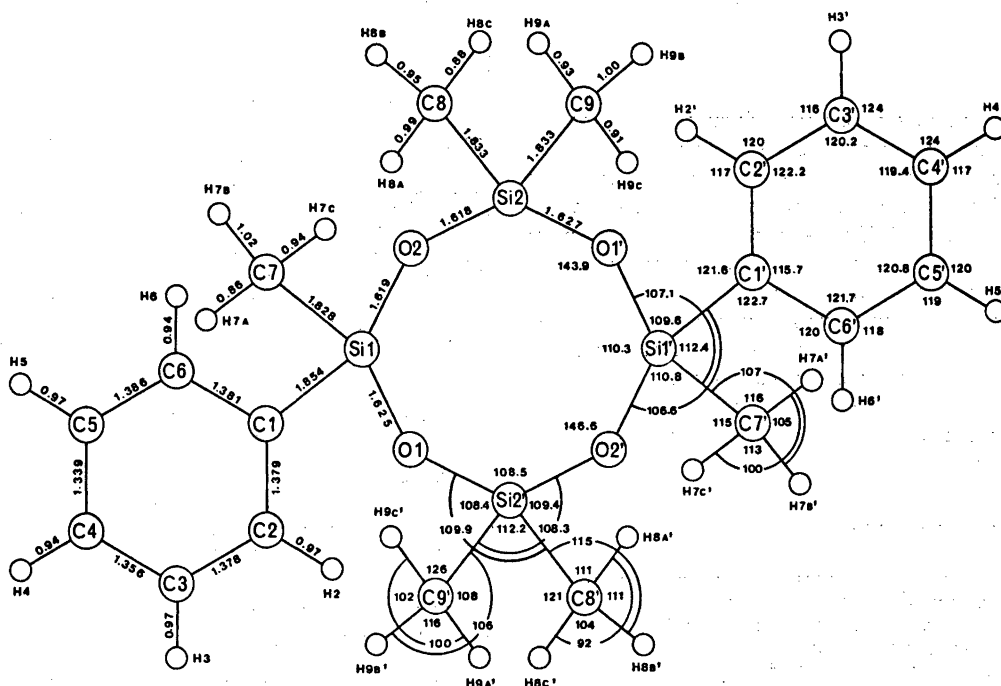


Fig. 1. The numbering of the atoms and bond distances and bond angles in the 2,6-*trans*-diphenylhexamethylcyclotetrasiloxane molecule.

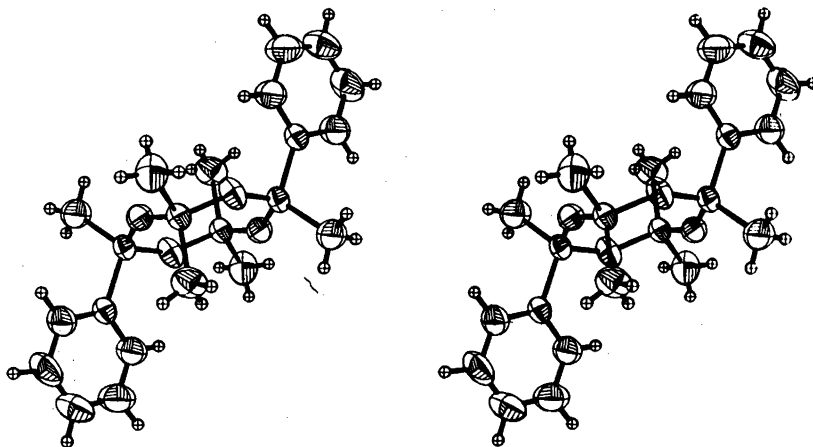


Fig. 2. The configuration of the 2,6-*trans*-diphenylhexamethylcyclotetrasiloxane molecule. The thermal ellipsoids for the non-hydrogen atoms are scaled to 50 % probability. Hydrogen atoms are shown as equally large spheres. The drawing is made with the plotting program ORTEP by Johnson.<sup>12</sup>

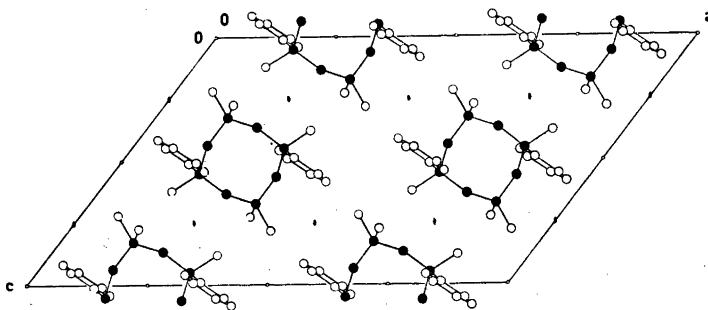


Fig. 3. Projection along *b* of the crystal structure of 2,6-*trans*-diphenylhexamethylcyclotetrasiloxane. The filled, dotted and open circles represent the atoms O, Si, and C, respectively.

could be interpreted as caused by four silicon atoms arranged in a slightly distorted square parallel to the *a*–*c* plane at a height of  $y \approx 0.30$ . Phased by the four atomic positions of the silicon atoms thus determined, three-dimensional electron density maps were calculated. After a few cycles of Fourier syntheses it was easy to locate all the 26 non-hydrogen atoms of the molecule. The positional coordinates were subsequently refined by the full-matrix least-squares method. Atomic scattering factors were taken from International Tables for X-Ray Crystallography<sup>4</sup> except for those of the hydrogen atoms which were taken from the data of Stewart *et al.*<sup>5</sup> After one cycle of refinement using individual isotropic tempera-

ture factors the discrepancy index  $R$  ( $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ) dropped from an initial value of 0.25 to 0.165. One cycle of refinement with anisotropic temperature factors lowered the  $R$ -value to 0.086. At this stage it became clear that the structure indeed was centrosymmetric. After one further cycle of refinement with anisotropic temperature factors for the 13 non-hydrogen atoms of the asymmetric unit the  $R$ -value dropped to 0.080 when the centrosymmetric space group  $C2/c$  was adopted. A difference Fourier synthesis prepared at this stage revealed the positions of the 14 hydrogen atoms. Three additional cycles of refinement of the positional and thermal parameters of the non-hydrogen atoms and one cycle of refine-

ment of the positional parameters of the hydrogen atoms gave a final  $R$ -value of 0.050 for 1635 observed structure amplitudes. Eight reflexions which obviously were erroneous were excluded from the last refinements. The shifts were all below the e.s.d.'s in the last cycle. The hydrogen atoms were assigned isotropic temperature factors of  $5.5 \text{ \AA}^2$ . Weights were applied to  $|F_o|$  according to  $w = 1/(a + |F_o| + b|F_o|^2)$  with  $a = 25.0$  and  $b = 0.01$ . The positional and thermal parameters for the final structure are given in Table 1. 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 Fig. 1 which also shows the numbering system of the atoms. The estimated standard deviations for bond lengths are: Si-O = 0.002 Å, Si-C = 0.004 Å, C-C = 0.005–0.006 Å and C-H = 0.03–0.05 Å. For bond angles involving silicon atoms the e.s.d.'s are 0.2–0.3° and for C-C-C angles 0.4–0.6°. The average Si-O and Si-C<sub>meth</sub> distances are 1.622 Å and 1.831 Å, respectively, and the Si-C<sub>phen</sub> distance is 1.828 Å. The angles around the silicon atoms are all close to the expected tetrahedral value and the mean Si-O-Si angle is 145.2°. These values are in good agreement with corresponding parameters reported for 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane,<sup>1</sup> for 1,1,2,2-tetramethyl-3,3,4,4-tetraphenylcyclotetrasiloxane,<sup>6</sup> and for octamethylcyclotetrasiloxane.<sup>7</sup> The benzene ring attached to Si(1) is planar (maximal deviation 0.003 Å) but slightly distorted. The angle C(6)-C(1)-C(2) of the benzene ring is thus quite small (115.7°). This type of distortion is also found in the 2,6-*cis*-diphenylhexamethylcyclotetrasiloxane<sup>1</sup> as well as in several other compounds where benzene rings are attached to a silicon compound.<sup>8–10</sup> The deviation from the regular hexagonal geometry of the benzene ring upon substitution for a hydrogen atom with an electron-withdrawing functional group also effects the bond lengths.<sup>11</sup> In the present structure the bonds C(3)-C(4) and C(4)-C(5) are considerably shorter than the aromatic standard value but

this shortening can mainly be attributed to the effects of thermal motion.

The eight-membered siloxane ring possesses a centre of symmetry. Since the Si-O-Si angles are large (around 145°) the ring is relatively planar with a largest deviation from the plane for Si and O atoms of 0.3 Å. Owing to the symmetry the planes of the benzene rings are parallel and the angle between the least-squares plane through the siloxane ring and the plane through the benzene ring is 105°. The shape of the molecule can be seen in Fig. 2 which also depicts the ellipsoids of thermal motion. The cyclotetrasiloxane ring has a "chair form" configuration. The atoms Si(1) and O(2) lie 0.75 Å below and Si(1') and O(2') 0.75 Å above a plane through the atoms Si(2), O(1'), Si(2') and O(1). This configuration ( $\bar{1}$ ) differs from that of the *cis* form<sup>1</sup> (42 m) but is the same as found in the structure of octamethylcyclotetrasiloxane.<sup>7</sup> The packing of the molecules in the present structure is shown in Fig. 3 which is a projection along the  $b$ -axis. It was most interesting to find that in this projection the packings of the *cis*<sup>1</sup> and *trans* forms are virtually identical. This is also reflected in the cell parameters. When the cell edges and angles of the *cis* form are transferred to fit the shape of the unit cell of the present compound one obtains:  $a = 24.232 \text{ \AA}$ ,  $b = 8.829 \text{ \AA}$ ,  $c = 15.155 \text{ \AA}$  and  $\beta = 132.07^\circ$ .

There are no short intermolecular distances. The closest carbon-hydrogen and hydrogen-hydrogen approaches are 3.00 Å and 2.51 Å, respectively. The rather loose packing of the structure is in accordance with the low density (1.17 g cm<sup>-3</sup>) of the compound.

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## REFERENCES

1. Carlström, D. and Falkenberg, G. *Acta Chem. Scand.* 27 (1973) 1203.
2. Bennet, D. R. and Åberg, B., *Acta Pharmacol. Toxicol.* 36 (1975) Suppl. III.
3. Bergin, R. *Internal Report I/71*, Dept. of Medical Physics, Karolinska Institutet, Stockholm 1971.
4. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4, p. 71.

5. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
6. Shklover, V. E., Kalinin, A. E. and Gusev, A. I. *Zh. Strukt. Khim.* 14 (1973) 692.
7. Steinfink, H., Post, B. and Fankuchen, I. *Acta Crystallogr.* 8 (1955) 420.
8. Alexander, L. E., Northolt, M. G. and Engmann, E. *J. Phys. Chem.* 71 (1967) 4298.
9. Chieh, P. C. and Trotter, J. *J. Chem. Soc. A* (1969) 1778.
10. Turley, J. W. and Boer, F. P. *J. Am. Chem. Soc.* 90 (1968) 4026.
11. Domenicano, A., Vaciago, A. and Coulson, C. A. *Acta Crystallogr. B* 31 (1975) 221.
12. Johnson, C. K. *ORTEP*, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge 1965.

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