

The Crystal and Molecular Structure of *r*-2,*cis*-4,*trans*-6,- *trans*-8-Tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane

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The crystal structure of the title compound ($C_{28}O_4Si_4H_{32}$) has been determined and refined using three-dimensional X-ray diffractometer data. The crystals are monoclinic, space group $P2_1/a$ with unit cell dimensions $a=11.832$, $b=13.511$, $c=9.591$ Å and $\beta=106.04^\circ$. There is half a formula unit in the asymmetric unit. The structure was solved by Patterson methods and refined by least-squares procedures to a final R -value of 0.043 for 2166 symmetry independent reflexions. The eight-membered siloxane ring has an unusual "chair-form" conformation with six nearly coplanar atoms and one atom above and one atom below the plane. The intramolecular bond distances and bond angles are discussed.

The present study forms part of a research project on organosilicon compounds. The title compound is of interest because of its close relationship to the biologically active *r*-2,*cis*-6-diphenylhexamethylcyclotetrasiloxane.¹ In addition it is representative of a class of substituted siloxanes used as precursors for the formation of polysiloxane polymers. The material used for the X-ray crystallographic analysis was synthesized by Dow-Corning, USA, and was in the form of small, colourless crystals placed at our disposal by Kabi AB, Stockholm. The material was recrystallized by slow evaporation of a methanolic solution. The name of the title compound as well as the names of the other cyclotetrasiloxanes mentioned in this paper are according to the latest IUPAC recommendation.

EXPERIMENTAL

A preliminary investigation of the crystals was made by oscillation and Weissenberg techniques. The systematic absences were:

$h00$ when $h=2n+1$ and $0k0$ when $k=2n+1$, indicating the monoclinic space group $P2_1/a$ which has four general positions. A rough determination of the density of the crystals showed that the unit cell contained 2 molecules. Unit cell parameters: $a=11.832\pm 0.005$, $b=13.511\pm 0.006$, $c=9.591\pm 0.004$ Å and $\beta=106.04\pm 0.09^\circ$. For the recording of the intensities a crystal with the dimensions $0.40\times 0.55\times 0.40$ mm was mounted along its b -axis. The integrated intensities were measured with a Philips linear automatic diffractometer (PAILRED), using graphite monochromatized $MoK\alpha$ -radiation ($\lambda=0.7107$ Å). The intensities were collected with the ω -scanning technique within $\sin\theta/\lambda\leq 0.66$ Å⁻¹ corresponding to the Cu-sphere. The scan-speed was 2.5°/min, the scanning range was 3° and the background was measured for 1 min. at the beginning and the end of each scan. Excluding systematic absences 3453 symmetry independent reflexions of the layers $h0l$ through $h17l$ were recorded. Out of these 1283 did not differ significantly from the background intensity. The standard reflexions, measured continuously during the collection of data, showed no significant changes in intensity. The net intensities were corrected for Lorentz and polarization factors but not for extinction or absorption. The latter could be neglected altogether because of the low linear absorption coefficient of the material ($\mu=2.32$ cm⁻¹ for $MoK\alpha$). The structure amplitudes were put on an approximately absolute scale by Wilson statistics. The Wilson plot gave a correlation coefficient for the K -curve of -0.979 and an overall temperature factor $B=2.2$ Å². An IBM 360/75 computer was employed for all calculations in this study, using our local crystallographic program system.²

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Preliminary coordinates of the silicon atoms were determined from a three-dimensional

Table 1. Fractional atomic coordinates for non-hydrogen atoms ($\times 10^6$) and for hydrogen atoms ($\times 10^4$). Anisotropic temperature parameters ($\times 10^6$) 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)	5738(6)	8004(5)	20892(7)	712(6)	451(4)	802(8)	-281(7)	626(10)	-381(8)
Si(2)	17798(6)	1868(5)	-3075(8)	625(5)	459(4)	990(9)	-200(7)	782(10)	-301(8)
O(1)	-7392(19)	3507(17)	15399(23)	1004(18)	906(16)	1458(28)	-1082(28)	1289(38)	-1162(34)
O(2)	11960(16)	7983(13)	7791(19)	765(16)	559(10)	1095(21)	-172(19)	921(29)	-439(24)
C(1)	4914(19)	21068(17)	26466(23)	672(16)	467(12)	700(23)	-40(22)	243(30)	-216(27)
C(2)	-3278(24)	24166(23)	33547(33)	763(22)	699(18)	1504(39)	-108(30)	1104(48)	-489(43)
C(3)	-3336(32)	33895(28)	38430(40)	1255(31)	798(23)	1968(54)	353(44)	1558(70)	-720(55)
C(4)	4740(35)	40575(23)	36186(38)	1575(40)	518(17)	1668(44)	157(39)	888(69)	-488(42)
C(5)	12921(30)	37690(22)	29492(33)	1245(31)	500(16)	1464(41)	-405(34)	720(58)	-185(39)
C(6)	13029(23)	28014(19)	24528(28)	770(21)	509(14)	1089(30)	-176(26)	659(40)	-119(32)
C(7)	25015(19)	10698(17)	-12747(24)	545(16)	450(12)	942(26)	-51(21)	559(34)	-195(28)
C(8)	36541(23)	13832(23)	-6422(33)	632(19)	774(19)	1402(39)	-272(31)	117(43)	380(44)
C(9)	42321(25)	19995(26)	-13744(40)	676(23)	798(21)	2154(55)	-352(34)	744(56)	488(56)
C(10)	36734(29)	23034(23)	-27671(36)	1184(31)	622(18)	1650(45)	-286(36)	1608(62)	18(43)
C(11)	25256(35)	20394(27)	-33936(32)	1384(36)	801(22)	1046(36)	-398(43)	323(56)	316(46)
C(12)	19467(24)	14199(23)	-26556(30)	792(22)	725(18)	1091(33)	-324(32)	85(44)	-1(38)
C(13)	14150(37)	583(23)	36397(36)	1735(42)	570(17)	1258(40)	250(41)	830(66)	39(41)
C(14)	28321(33)	-7353(25)	7305(40)	1375(36)	668(19)	1992(53)	530(41)	1796(74)	596(50)

Atom	x	y	z	B	Atom	x	y	z	B
H(2)	-919(21)	1941(20)	3470(26)	3.5	H(11)	2131(22)	2278(19)	-4312(26)	3.5
H(3)	-1014(21)	3599(19)	4272(27)	3.5	H(12)	1156(22)	1203(20)	-3139(27)	3.5
H(4)	563(22)	4731(19)	3980(27)	3.5	H(13a)	1089(23)	59(19)	4414(29)	3.5
H(5)	1859(22)	4190(19)	2836(27)	3.5	H(13b)	2197(22)	394(20)	4096(27)	3.5
H(6)	1875(22)	2611(20)	2021(26)	3.5	H(13c)	1607(21)	-485(20)	3358(28)	3.5
H(8)	4152(22)	1124(19)	3457(27)	3.5	H(14a)	2507(22)	-1266(20)	1105(27)	3.5
H(9)	5036(22)	2205(20)	-860(26)	3.5	H(14b)	3532(22)	-348(19)	1574(28)	3.5
H(10)	4042(22)	2702(19)	-3276(27)	3.5	H(14c)	3153(22)	-1083(20)	50(27)	3.5

Patterson calculation. In the subsequent Fourier synthesis phased by the silicon atoms it was easy to locate the oxygen atoms of the siloxane ring. After two more cycles of Fourier syntheses the positions of the 14 carbon atoms in the asymmetric unit could be established. The refinement was carried out by a full-matrix least-squares procedure. After one cycle of isotropic refinement of the non-hydrogen atoms the R -index ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) dropped from an initial value of 0.27 to 0.14. When the atoms were given anisotropic temperature factors the R -value decreased to 0.062. Weights were then applied to F_o according to $w = 1 / (a + |F_o| + b|F_o|^2 + c|F_o|^3)$ with $a = 10.0$, $b =$

0.01 and $c = 0.002$. One further cycle of anisotropic refinement resulted in an R -value of 0.055. A difference synthesis revealed the positions of the 18 hydrogen atoms in the asymmetric unit. One additional cycle of anisotropic refinement of the non-hydrogen atoms with the hydrogen atoms kept in the positions derived from the difference map lowered the R -value to 0.048. The positional parameters of the hydrogen atoms were then refined in one cycle in which they were given isotropic temperature factors of 3.5 \AA^2 . The four strongest reflexions showed $F_o < F_c$ which was interpreted as caused by secondary extinction. Accordingly these four reflexions

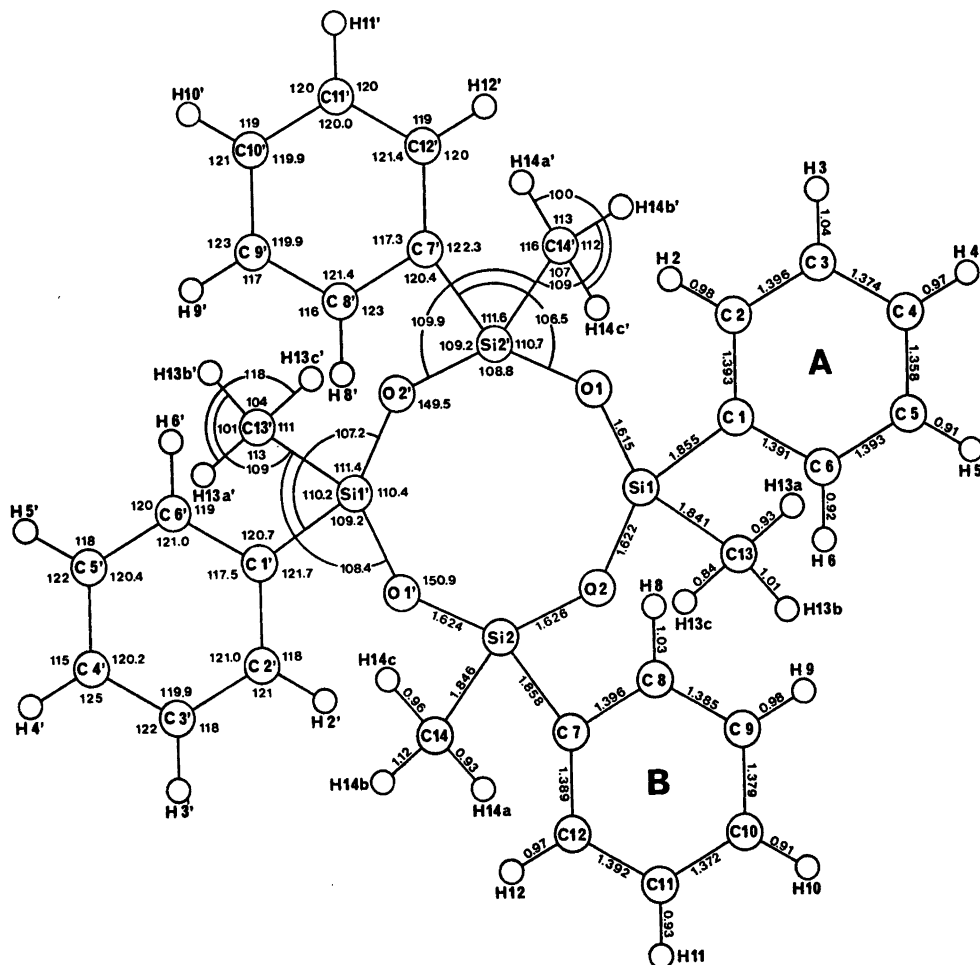


Fig. 1. The numbering of the atoms and bond distances and bond angles in the *r*-2,*cis*-4,*trans*-6,*trans*-8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane molecule.

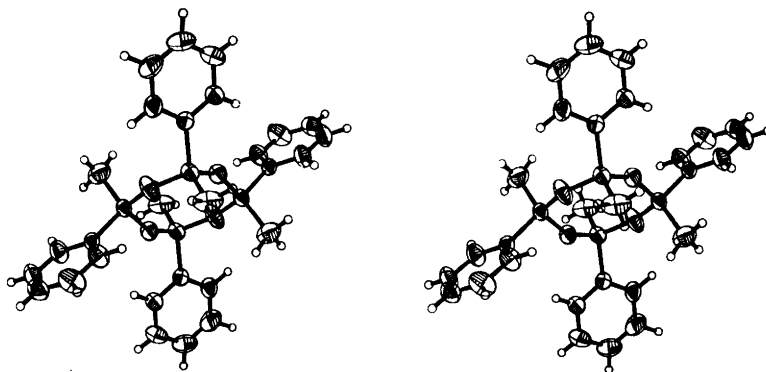


Fig. 2. The conformation of the *r*-2,*cis*-4,*trans*-6,*trans*-8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane molecule. The thermal ellipsoids for the non-hydrogen atoms are scaled to 50 % probability. Hydrogen atoms are shown as equally large spheres. The drawing is made with the plotting program ORTEP by Johnson.¹⁹

were excluded from further refinements. The non-hydrogen atoms were then refined until the shifts were below the e.s.d.'s resulting in a final *R*-value of 0.043 for 2166 observed reflexions. The atomic scattering factors for the non-hydrogen atoms and the hydrogen atoms were those of International Tables for X-ray Crystallography³ and of Stewart *et al.*,⁴ respectively. 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 author.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A schematic representation of the molecule with bond distances and bond angles uncorrected for thermal motion and showing the atomic numbering is seen in Fig. 1. A stereo view of the molecule is given in Fig. 2. The estimated standard deviations for bond lengths are: Si–O = 0.002 Å, Si–C = 0.002–0.003 Å, C–C = 0.003–0.005 Å and C–H = 0.02–0.03 Å. The e.s.d.'s for bond angles involving silicon atoms are 0.1–0.2° and for C–C–C angles 0.3–0.4°. The average intramolecular bond lengths are: Si–O = 1.622 Å, Si–C_{meth} = 1.844 Å and Si–C_{phen} = 1.856 Å. The mean Si–O–Si angle is 150.2° and the angles around the silicon atoms are all close to the expected tetrahedral value. All these parameters are in good agreement with corresponding data given

for the *cis*¹ and *trans*⁵ forms of 2,6-diphenylhexamethylcyclotetrasiloxane, for 2,2,4,4-tetramethyl-6,6,8,8-tetraphenylcyclotetrasiloxane⁶ and for octamethylcyclotetrasiloxane.⁷ An exception is the Si–O–Si angles which in the present molecule are slightly larger than in the other cyclotetrasiloxanes. It is quite interesting to note that the Si–C_{phen} bonds invariably are longer than the Si–C_{meth} bonds in the present structure as well as in the above-mentioned phenyl-substituted cyclotetrasiloxanes.^{1,5,6} Since no corrections for thermal motion have been made and it is apparent that the methyl carbons have larger thermal motions than the phenyl carbons, part of this effect can be attributed to thermal motions. However, in six-membered cyclosiloxane rings one has the reverse situation *i.e.* Si–C_{phen} is shorter than Si–C_{meth}. This is in agreement with the standard values Si–C_{phen} = 1.84 ± 0.01 and 1.843 ± 0.005 and Si–C_{meth} = 1.865 ± 0.008 and 1.870 ± 0.005 given by International Tables for X-ray Crystallography⁸ and Sutton,⁹ respectively. The eight-membered siloxane ring is relatively planar because of the wide Si–O–Si angle (around 150°). The largest deviation from the plane is 0.24 Å for O atoms. see Table 2. The angles between the least-squares plane through the siloxane ring and the planes through the benzene rings are 41 and 55° for ring A and B, respectively.

The cyclotetrasiloxane ring of the title compound like those of *r*-2,*trans*-6-diphenylhexamethylcyclotetrasiloxane⁵ and octamethyl-

Table 2. Least-squares planes and deviations in Å of individual atoms. The equations of the planes are in the form $AX+BY+CZ=D$, where X, Y, Z are coordinates in orthogonal Ångström space. Asterisks indicate atoms not included in the calculations of the planes.

Plane of siloxane ring			
$0.2337X - 0.8277Y + 0.5102Z = 0.0000$			
Si(1)	0.1166	Si(1')	-0.1166
Si(2)	0.1575	Si(2')	-0.1575
O(1)	0.0322	O(1')	-0.0322
O(2)	-0.2439	O(2')	0.2439
Plane of siloxane ring except two atoms			
$-0.1698X + 0.8683Y - 0.4660Z = 0.0000$			
Si(1)	0.0203	Si(1')	-0.0203
Si(2)	-0.0202	Si(2')	0.0202
O(1)	-0.0322	O(1')	0.0322
O(2)*	0.3966	O(2)*	-0.3966
Plane of benzene ring A			
$0.3982X - 0.2588Y + 0.8800Z = 1.3658$			
C(1)	-0.0034	C(4)	-0.0078
C(2)	0.0020	C(5)	0.0063
C(3)	0.0036	C(6)	-0.0007
Plane of benzene ring B			
$0.4557X - 0.8018Y - 0.3865Z = 0.7836$			
C(7)	0.0143	C(10)	0.0215
C(8)	-0.0056	C(11)	-0.0125
C(9)	-0.0123	C(12)	-0.0055
Plane of benzene ring B except one atom			
$0.4621X - 0.7958Y - 0.3914Z = 0.8266$			
C(7)	0.0071	C(10)*	0.0427
C(8)	-0.0054	C(11)	0.0018
C(9)	0.0019	C(12)	-0.0053

cyclotetrasiloxane⁷ possesses a centre of symmetry. While the latter two have the common "chair form" conformation with four coplanar atoms and with two atoms above and two atoms below the plane, the present molecule has six almost coplanar atoms, Si(1) Si(2), O(1), Si(1'), Si(2') and O(1') (largest deviation 0.03 Å) with two atoms O(2) and O(2'), lying 0.4 Å above respectively below the plane (see Table 2). This conformation is very similar to that of the *r*-2,*cis*-4,*trans*-6,*trans*-8-tetramethyl-2,4,6,8-tetraphenylcyclo-2,4,6,8-tetrasiloxane-1,5-diaza-3,7-dioxane¹⁰ molecule. However, in this structure there are two silicon atoms that lie above and below the six atoms plane.

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The benzene ring A attached to Si(1) is essentially planar whereas the atoms of the benzene ring B attached to Si(2) are far from coplanar (see Table 2). The non-planarity of the B-ring can be attributed to the atom C(10). When this atom is excluded from the calculations the planarity of the B-ring is as good as that of the A-ring. As seen in Fig. 1 both rings are slightly distorted. The deviation from the regular hexagonal geometry of the benzene ring upon substitution for a hydrogen atom with an electron-withdrawing functional group, affects the bond lengths and the bond angles.¹¹ Such distortions are found in many organosilicon compounds where benzene rings are attached to silicon atoms.^{1,5,12-18}

The packing of the molecules in the present structure is shown in Fig. 3 which is a projection along the *b*-axis. It should be noted that the molecular conformation and the packing of the molecules in the present structure and in the structure of *r*-2,*cis*-4,*trans*-6,*trans*-8-tetramethyl-2,4,6,8-tetraphenylcyclo-2,4,6,8-tetrasiloxane-1,5-diaza-3,7-dioxane¹⁰ are very similar although the latter compound crystallizes in the space group *Pbca* with 4 molecules in the unit cell.

The closest carbon-hydrogen and hydrogen-hydrogen approaches are 3.03 and 2.48 Å, respectively.

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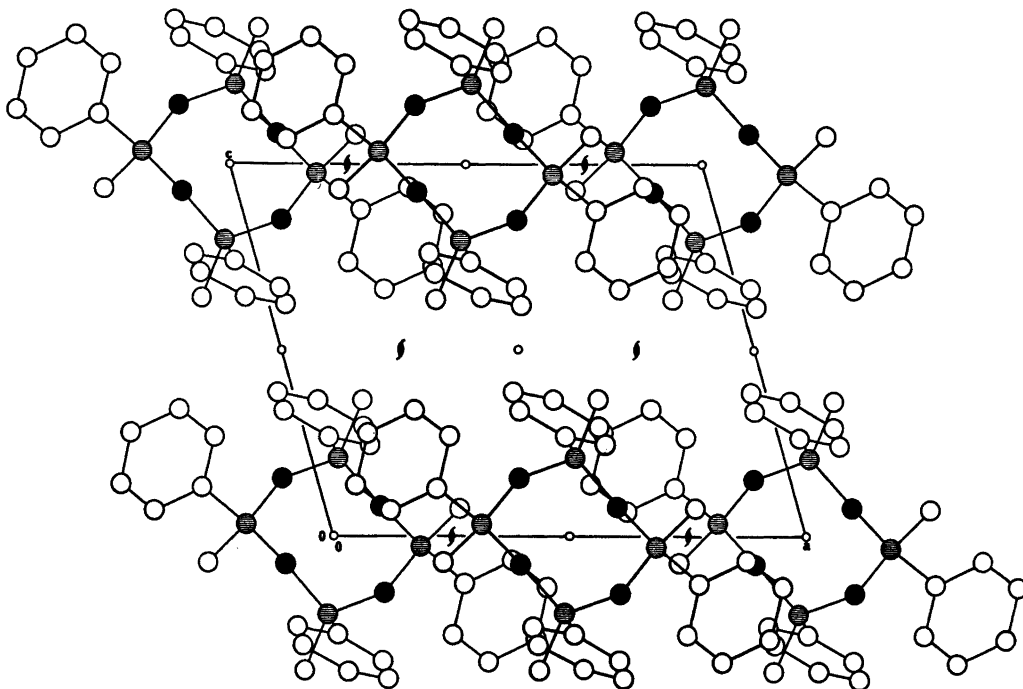


Fig. 3. Projection along b of the crystal structure of *r*-2,*cis*-4,*trans*-6,*trans*-8-tetramethyl-2,4,6,8-tetraphenylcyclotetrasiloxane. The filled, striped and open circles represent the atoms O, Si and C, respectively.

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