Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System.* Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sriraghavan, K. & Ramakrishnan, V. T. (1997). Unpublished results.

Acta Cryst. (1997). **C53**, 1867–1869

Two Cyclotetrasiloxanes at 143 K

Karl Hensen,[a] Frank Gebhardt,[a] Markus Kettner,[a] Peter Pickel[a] and Michael Bolte[b]

[a]*Institut für Physikalische und Theoretische Chemie der J. W. Goethe-Universität Frankfurt, Marie-Curie-Str. 11, 60439 Frankfurt/Main, Germany, and* [b]*Institut für Organische Chemie der J. W. Goethe-Universität Frankfurt, Marie-Curie-Str. 11, 60439 Frankfurt/Main, Germany. E-mail: pickel@chemie.uni-frankfurt.de*

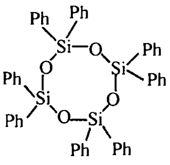
(*Received 6 May 1997; accepted 9 July 1997*)

Abstract

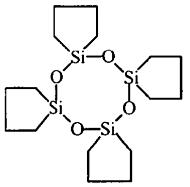
The crystal structures of octaphenylcyclotetrasiloxane [$C_{48}H_{40}O_4Si_4$, (I)] and 2,4,6,8-tetrakis(tetramethylene)cyclotetrasiloxane [a tetraspiro compound: cyclotetrasiloxane-2,4,6,8-tetraspiro-tetrakis(cyclopentane), $C_{16}H_{32}O_4Si_4$, (II)] were determined at 143 K. Compound (I) is compared with the room-temperature structure and the structure of the monoclinic polymorph, both reported previously. Whereas the siloxane ring of (I) is nearly planar, the siloxane ring of (II) exhibits a chair conformation. The angles between the siloxane ring and the various phenyl substituents of (I) vary considerably and are on average smaller in the triclinic form than in the monoclinic form. Greatly differing Si—O—Si angles, as found in the monoclinic form (153 and 167°), appear only in one of the molecules in the asymmetric unit of (I) [153.4 (1) and 163.7 (1)°]; the Si—O—Si angles of the second molecule differ by only 3.0°. The Si—O—Si angles of (II) display a difference of 5.2°. The silacyclopentane rings of (II) exhibit different conformations.

Comment

Octaphenylcyclotetrasiloxane, (I), and 2,4,6,8-tetrakis(tetramethylene)cyclotetrasiloxane, (II), were obtained from the reaction of diphenyldibromosilane or 1,1-dibromosilacyclopentane with *N*-methylimidazole in low yields. During preparation, the reactants must have been affected by atmospheric humidity and the associated hydrolysis must be the cause of the formation of the cyclosiloxanes.



(I)



(II)

Compound (I) crystallizes in the triclinic crystal system with two half molecules in the asymmetric unit, each molecule being situated on an inversion centre (Fig. 1). In contrast, the monoclinic form of (I) [as determined by Hossain, Hursthouse & Malik (1979), hereinafter referred to as mon1, and as determined by Braga & Zanotti (1980), hereinafter mon2] does not show any crystallographic symmetry. A comparison with the crystal structure of the triclinic form of (I), which has been determined at room temperature by Ovchinnikov *et al.*, (1988) and is hereinafter referred to as tric1, shows some remarkable differences. Firstly, there are differences in the cell parameters. *a* and *b* of (I) are slightly smaller than in tric1 [10.731 (1) and 10.764 (2) Å, respectively], whereas *c* is considerably shorter than in tric1 [19.147 (2) Å]. γ is nearly equal in both structures [76.12 (1)° in tric1], but whereas α was found to be larger than β in tric1 [83.79 (1) and 83.08 (1)°, respectively], the reverse was found for (I) at low temperature.

The siloxane ring is nearly planar [r.m.s. deviations: 0.051 Å in molecule 1 of (I) and 0.057 Å in molecule 2 of (I); 0.057 and 0.048 Å in tric1; 0.046 and 0.048 Å in mon1 and mon2, respectively]. All Si—O bond lengths of (I), ranging from 1.620 (1) to

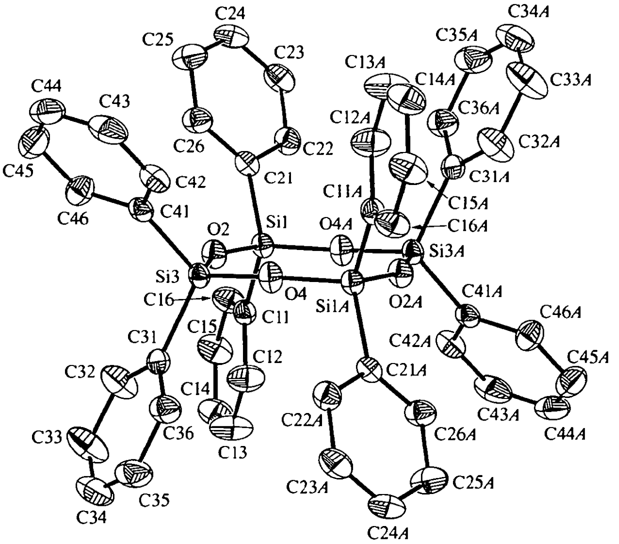


Fig. 1. Perspective view of molecule 1 of (I) with the atom numbering. Displacement ellipsoids are at the 50% probability level and H atoms have been omitted for clarity.

1.630 (1) Å, are in excellent agreement with the Si—O distances in other siloxanes (*International Tables for Crystallography*, Vol. C, 1992).

An unusual feature of the structure is the significant difference of the Si—O—Si angles: adjacent angles are significantly different in the monoclinic form [153 (2×) and 167° (2×)], but this is found only for one of the molecules in the triclinic form [153.4 (1) at O2 and 163.7 (1)° at O4 in (I); 152.5 and 165.0° in tric1]. The corresponding angles of the second molecule are similar to each other [156.8 (1) at O6 and 159.8 (1)° at O8 in (I); 157.3 and 158.9° in tric1].

Another interesting feature is the angles between the siloxane ring and the phenyl substituents. The values range from 57 to 88° [mean 71 (12)°] in each of the monoclinic structures, from 52 to 86° [mean 65 (13)°] in tric1, and from 51 to 83° [mean 65 (12)°] in (I). Thus, the molecule is conformationally flexible with respect to this angle.

Compound (II) (Fig. 2) is also an eight-membered cyclic siloxane. It crystallizes with half a centrosymmetric molecule in the asymmetric unit. Instead of carrying two phenyl ligands, each Si atom is incorporated in a silacyclopentane ring. In this case, the siloxane ring is not planar, but displays a chair-like conformation with O2, Si3, O4, O2*A*, Si3*A* and O4*A* [symmetry code: (*A*) $1-x$, $1-y$, $1-z$] in a common plane (r.m.s. deviation 0.006 Å), while Si1 and Si1*A* are 0.717 (3) Å above and below this plane, respectively. The two Si—O—Si bond angles are different: whereas O4 encloses an angle of 144.5 (2)°, O2 forms an angle of 139.3 (2)° with the two Si neighbours.

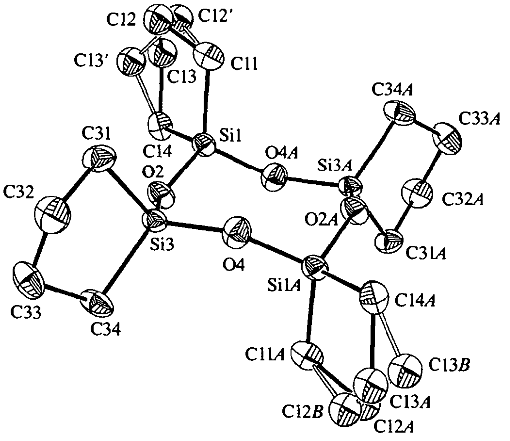


Fig. 2. Perspective view of (II) with the atom numbering. Displacement ellipsoids are at the 50% probability level and H atoms have been omitted for clarity.

Two methylene groups of one of the silacyclopentane rings are disordered [ratio of site occupation factors 0.58 (2):0.42 (2)]. The main conformer exhibits a twist conformation [q = 0.409 and φ = 273.4 (Cremer & Pople, 1975)], while the other conformer has an envelope conformation (q = 0.417 and φ = 79.9), like that of the ordered ring (q = 0.413 and φ = 287.2).

Experimental

N-Methylimidazole (6.2 equivalents) was added to 3 mmol of diphenyldibromosilane [prepared from diphenyldichlorosilane according to Rühlmann & Mansfeld (1964)] in 25 ml of hexane. The single crystals of (I) were obtained by slow evaporation of hexane from the solution. 1,1-Dibromosilacyclopentane was prepared following the procedure of West (1954) for the synthesis of cyclic silanes. 1,1-Dibromosilacyclopentane (2.01 mmol) was dissolved in 20 ml of hexane. During addition of nearly 5 equivalents of *N*-methylimidazole, a white powder precipitated. After isolation and drying, the single crystals of (II) were grown by sublimation at 2–3 Torr (1 Torr = 133.322 kPa).

Compound (I)

Crystal data

$C_{48}H_{40}O_4Si_4$
M_r = 793.16
Triclinic
$P\overline{1}$
a = 10.6688 (1) Å
b = 10.7353 (1) Å
c = 18.8291 (2) Å
α = 83.323 (1)°
β = 83.735 (1)°
γ = 76.030 (1)°
V = 2071.21 (4) Å^3
Z = 2
D_x = 1.272 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 7927 reflections
θ = 1–25°
μ = 0.188 mm^{-1}
T = 143 K
Block
0.80 × 0.60 × 0.20 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996*a*)
$T_{\min}$ = 0.847, $T_{\max}$ = 1.000
32949 measured reflections
8383 independent reflections

7270 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.018
$\theta_{\max}$ = 26.40°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -23 \rightarrow 23$
501 standard reflections frequency: 720 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.083
S = 1.031
8383 reflections
505 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.9123P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.356 e Å^{-3}
$\Delta\rho_{\min}$ = −0.255 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (II)

Crystal data

$C_{16}H_{32}O_4Si_4$
M_r = 400.78

Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$P2_1/c$
$a = 6.3603$ (1) Å
$b = 17.8106$ (3) Å
$c = 9.3363$ (1) Å
$\beta = 99.036$ (1)°
$V = 1044.50$ (3) Å^3
$Z = 2$
$D_x = 1.274$ Mg m^{-3}

Cell parameters from 4336 reflections
$\theta = 1–25°$
$\mu = 0.301$ mm^{-1}
$T = 143$ K
Plate
0.40 × 0.20 × 0.05 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996*a*)
$T_{\min} = 0.874$, $T_{\max} = 1.000$
13687 measured reflections
2122 independent reflections

1531 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.082$
$\theta_{\max} = 26.43°$
$h = -7 \rightarrow 7$
$k = -19 \rightarrow 21$
$l = -11 \rightarrow 11$
130 standard reflections frequency: 600 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.123$
$S = 1.048$
2122 reflections
108 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 1.5197P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.460$ e Å^{-3}
$\Delta\rho_{\min} = -0.394$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

The data collection nominally covered a sphere of reciprocal space, by a combination of eight, for (I), and seven, for (II), sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.95 cm. Coverage of the unique set is over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. The data were corrected for Lorentz and polarization effects. All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\rm H) = 1.2U_{\rm eq}(\rm C)$] using a riding model with C—H(aromatic) = 0.95 and C—H(secondary) = 0.99 Å.

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structures: *SHELXS*96 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*96 (Sheldrick, 1996*b*); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

FG thanks the Fonds der Chemischen Industrie for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1227). Services for accessing these data are described at the back of the journal.

References

Braga, D. & Zanotti, G. (1980). *Acta Cryst.* **B36**, 950–935.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **89**, 6193–6200.

Hossain, M. A., Hursthouse, M. B. & Malik, K. M. A. (1979). *Acta Cryst.* **B35**, 522–524.

Ovchinnikov, Y. E., Shklover, V. E., Struchkov, Y. T., Dement'ev, V. V. & Frunze, T. M. (1988). *Metalloorg. Khim.* (*Organomet. Chem. USSR*), **1**, 1117–1120.

Rühlmann, K. & Mansfeld, M. (1964). *J. Prakt. Chem.* **24**, 226–230.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1996*a*). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.

Sheldrick, G. M. (1996*b*). *SHELXL96. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT. Area-Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

West, R. (1954). *J. Am. Chem. Soc.* **76**, 6012–6014.

Acta Cryst. (1997). **C53**, 1869-1871

A Tetragonal-Looking But Twinned Orthorhombic Structure

MICHAEL BOLTE AND MARIA SCHOLTYSSIK

Institut für Organische Chemie der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany. E-mail: bolte@chemie.uni-frankfurt.de

(*Received 9 May 1997; accepted 25 June 1997*)

Abstract

2,2′-Methylenebis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one), $C_{17}H_{24}O_4$, forms crystals which appear tetragonal, but are actually orthorhombic. They are twinned on (110). The asymmetric unit consists of two very similar molecules, each with exact crystallographic C_2 symmetry. Each molecule forms two strong intramolecular hydrogen bonds connecting the two cyclohexenone rings.

Comment

Recently we determined the crystal structure of (1) (see Scheme), which appeared to be twinned (Bolte, Degen & Rühl, 1997). The title compound, (2), was synthesized in order to compare it with (1) and to find out whether it was similarly twinned. The two independent half molecules in the asymmetric unit of (2) are very similar in geometry; a least-squares fit of all non-H atoms shows