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Octaphenylcyclotetrasiloxane: The Monoclinic Form

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Abstract. $C_{48}H_{40}O_4Si_4$, $M_r = 792.34$, $a = 21.962$ (2), $b = 10.139$ (1), $c = 21.722$ (1) Å, $\beta = 115.99$ (1)°, $U = 4347.5$ Å^3, $D_m = 1.20$, $D_c = 1.21$ Mg m^{-3}, $Z = 4$, space group $P2_1/c$, $F(000) = 1664$, λ(Cu $K\alpha$) = 1.5418 Å, μ(Cu $K\alpha$) = 1.502 mm^{-1}. The structure was refined to $R = 0.0711$ for 4009 unique reflections. The Si_4O_4 ring is unusually flat.

Introduction. Previous work has shown that octaphenylcyclotetrasiloxane is polymorphic, occurring in monoclinic and triclinic forms and also as a benzene solvate (Hyde, Frevel, Nutting, Petrie & Purcell, 1947). As part of an investigation of the structure and conformation of cyclosiloxanes and related species, we have begun a crystallographic study of this system. Here we report the analysis of the monoclinic form.

The compound was prepared by the condensation of phenylsilanediol in alkaline medium and recrystallized from benzene–95% ethanol to obtain colourless needles. The cell parameters were initially determined from photographs and subsequently refined on a Nonius CAD-4 diffractometer from the setting angles for 25 reflections. The intensities of 7191 reflections (3 < θ < 60°) were recorded on the diffractometer with Ni-filtered Cu $K\alpha$ radiation, an ω–2θ scan technique and a crystal 0.40 × 0.15 × 0.12 mm. Two reference reflections, measured periodically, showed only minor fluctuations. The intensities were corrected for Lp factors but not for absorption. 4009 unique reflections with $F_o > 3\sigma(F_o)$ were considered observed and used in the analysis.

The structure was determined by direct methods and refined by a full-matrix least-squares procedure to a final R of 0.0711. All non-hydrogen atoms were treated anisotropically. The H atoms were inserted in calculated positions (C–H = 1.08 Å) but individual U_{iso} values were refined. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0.0004F_o^2]$, which gave flat analysis of $w\Delta^2$ with $\sin \theta$ and $[F_o/F_{max}]^{1/2}$. The final non-hydrogen atomic coordinates are given in Table 1, selected interatomic distances and angles in Table 2, and least-squares plane data in Table 3.* Neutral-atom scattering factors were taken from Stewart, Davidson & Simpson (1965) for H and from Cromer & Mann (1968) for Si, O and C.

Discussion. The molecular structure is illustrated in Fig. 1, which also shows the atom numbering. The Si–O and Si–C lengths are in good agreement with values found in other cyclotetrasiloxanes (Steinfink, Post & Fankuchen, 1955; Shklover, Kalinin, Gusev, Bokii, Struchkov, Andrianov & Petrova, 1973; Carlström & Falkenberg, 1973; Söderholm & Carlström, 1977; Söderholm, 1978). In addition the angles around Si are close to expected tetrahedral values but with the C–Si–C angles consistently a few degrees larger. An unusual feature of the structure however is the size of the Si–O–Si angles, 152 (×2) and 167° (×2). These are correlated with a much

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* Lists of structure factors, thermal parameters, H atom positional parameters and dimensions of the phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34092 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* (×10⁴) *of the non-hydrogen atoms with e.s.d.'s in parentheses*

	x	y	z
Si(1)	1685 (1)	4298 (1)	3357 (1)
Si(2)	1754 (1)	5180 (1)	2002 (1)
Si(3)	3267 (1)	6227 (1)	2901 (1)
Si(4)	3240 (1)	5108 (1)	4234 (1)
O(1)	2464 (1)	4627 (3)	3870 (1)
O(2)	1556 (1)	4539 (3)	2574 (1)
O(3)	2510 (1)	5788 (3)	2376 (1)
O(4)	3434 (1)	5797 (3)	3669 (1)
C(11)	1546 (2)	2524 (4)	3449 (2)
C(12)	1022 (2)	2036 (5)	3575 (2)
C(13)	926 (3)	698 (6)	3619 (3)
C(14)	1352 (3)	−192 (6)	3534 (3)
C(15)	1876 (3)	269 (5)	3404 (3)
C(16)	1974 (2)	1605 (5)	3368 (3)
C(21)	1142 (2)	5427 (4)	3572 (2)
C(22)	1346 (2)	5869 (5)	4239 (2)
C(23)	945 (3)	6714 (5)	4406 (3)
C(24)	332 (3)	7121 (6)	3912 (4)
C(25)	122 (3)	6714 (6)	3252 (3)
C(26)	522 (3)	5862 (5)	3082 (3)
C(31)	1152 (2)	6518 (5)	1539 (2)
C(32)	603 (2)	6298 (6)	913 (3)
C(33)	144 (3)	7307 (8)	586 (3)
C(34)	235 (4)	8523 (8)	872 (4)
C(35)	777 (4)	8762 (7)	1489 (5)
C(36)	1229 (3)	7765 (6)	1816 (4)
C(41)	1751 (2)	3893 (4)	1400 (2)
C(42)	1603 (2)	2583 (5)	1447 (3)
C(43)	1633 (3)	1649 (6)	979 (4)
C(44)	1802 (3)	2044 (8)	473 (4)
C(45)	1944 (3)	3326 (8)	417 (3)
C(46)	1912 (2)	4233 (6)	866 (2)
C(51)	3333 (2)	8045 (4)	2875 (2)
C(52)	3152 (3)	8669 (6)	2258 (3)
C(53)	3202 (3)	10064 (7)	2226 (4)
C(54)	3443 (3)	10774 (7)	2813 (5)
C(55)	3627 (3)	10183 (6)	3433 (4)
C(56)	3574 (3)	8818 (5)	3462 (3)
C(61)	3877 (2)	5408 (4)	2652 (2)
C(62)	3710 (3)	4300 (5)	2231 (2)
C(63)	4183 (4)	3722 (6)	2046 (3)
C(64)	4816 (4)	4251 (7)	2275 (4)
C(65)	4996 (3)	5322 (7)	2696 (4)
C(66)	4531 (3)	5900 (5)	2883 (3)
C(71)	3795 (2)	3658 (4)	4619 (2)
C(72)	4412 (2)	3499 (5)	4605 (3)
C(73)	4833 (3)	2435 (7)	4926 (4)
C(74)	4629 (4)	1537 (7)	5265 (4)
C(75)	4023 (4)	1649 (6)	5280 (3)
C(76)	3603 (3)	2709 (6)	4956 (3)
C(81)	3338 (2)	6353 (5)	4886 (2)
C(82)	3817 (3)	6276 (6)	5561 (3)
C(83)	3880 (4)	7277 (8)	6032 (3)
C(84)	3455 (5)	8343 (8)	5817 (4)
C(85)	2989 (4)	8440 (7)	5173 (4)
C(86)	2924 (3)	7453 (5)	4706 (3)

greater tendency to flattening of the Si₄O₄ ring than found previously. Thus in Table 3 we see that the maximum deviation of an atom from the best plane through all eight ring atoms is 0·1 Å. A variety of trial calculations showed that the ring conformation can be most conveniently described as a shallow, distorted

Table 2. *Important bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Si(1)–O(1)	1·616 (3)	Si(1)–C(11)	1·851 (4)
Si(1)–O(2)	1·616 (3)	Si(1)–C(21)	1·854 (5)
Si(2)–O(2)	1·621 (4)	Si(2)–C(31)	1·854 (4)
Si(2)–O(3)	1·617 (3)	Si(2)–C(41)	1·844 (5)
Si(3)–O(3)	1·613 (3)	Si(3)–C(51)	1·852 (5)
Si(3)–O(4)	1·604 (3)	Si(3)–C(61)	1·846 (6)
Si(4)–O(4)	1·623 (4)	Si(4)–C(71)	1·857 (4)
Si(4)–O(1)	1·609 (3)	Si(4)–C(81)	1·837 (5)
Mean	1·615	Mean	1·849

Si(1)–O(1)–Si(4)	167·4 (2)	Si(2)–O(3)–Si(3)	166·9 (2)
Si(1)–O(2)–Si(2)	152·3 (2)	Si(3)–O(4)–Si(4)	152·6 (2)

C(11)–Si(1)–C(21)	114·7 (2)	C(51)–Si(3)–C(61)	111·3 (2)
C(11)–Si(1)–O(1)	107·5 (2)	C(51)–Si(3)–O(3)	108·8 (2)
C(11)–Si(1)–O(2)	107·5 (2)	C(51)–Si(3)–O(4)	108·4 (2)
C(21)–Si(1)–O(1)	107·6 (2)	C(61)–Si(3)–O(3)	108·9 (2)
C(21)–Si(1)–O(2)	109·7 (2)	C(71)–Si(3)–O(4)	108·6 (2)
O(1)–Si(1)–O(2)	109·8 (2)	O(3)–Si(3)–O(4)	110·8 (2)

C(31)–Si(2)–C(41)	110·7 (2)	C(71)–Si(4)–C(81)	111·4 (2)
C(31)–Si(2)–O(2)	109·9 (2)	C(71)–Si(4)–O(1)	109·0 (2)
C(31)–Si(2)–O(3)	109·0 (2)	C(71)–Si(4)–O(4)	110·1 (2)
C(41)–Si(2)–O(2)	109·9 (2)	C(81)–Si(4)–O(1)	109·1 (2)
C(41) Si(2)–O(3)	108·1 (2)	C(81)–Si(4)–O(4)	107·8 (2)
O(2)–Si(2)–O(3)	109·2 (1)	O(1)–Si(4)–O(4)	109·0 (2)

Table 3. *Least-squares planes and deviations* (Å) *of individual atoms*

The equations of the planes are in the form $Ax + By + Cz = D$, where x,y,z are fractional coordinates. Asterisks indicate atoms not included in the calculation of the planes.

Plane 1: $-9·5209x + 9·0508y + 6·5276z = 4·3710$

Si(1)	0·1061	O(1)	−0·0037
Si(2)	−0·0464	O(2)	−0·0641
Si(3)	0·0473	O(3)	0·0283
Si(4)	−0·0692	O(4)	0·0017

Plane 2: $-10·0386x + 8·9142y + 6·9703z = 4·2649$

Si(1)*	0·2148	O(1)*	0·0829
Si(2)	−0·0133	O(2)	0·0133
Si(3)*	0·0276	O(3)*	0·0305
Si(4)	−0·0133	O(4)	0·0132

Plane 3: $-7·4604x + 9·5162y + 4·4040z = 4·2950$

Si(1)	0·0164	O(1)	−0·0264
Si(2)*	0·2070	O(2)	−0·0029
Si(3)*	0·4703	O(3)*	0·3863
Si(4)	0·0129	O(4)*	0·2759

Plane 4: $-10·4423x + 8·8015y + 7·3063z = 4·1960$

Si(1)*	0·2801	O(1)*	0·1303
Si(2)	−0·0062	O(2)*	0·0548
Si(3)	−0·0081	O(3)	0·0128
Si(4)*	0·0096	O(4)	0·0015

Angles between normals to planes (°)

Plane 2–Plane 3	8·66
Plane 2–Plane 4	1·32

boat (plane 2, Table 3) with Si(2), Si(4), O(2), O(4) forming the planar base and Si(1), O(1) and Si(3), O(3) the stern and prow.
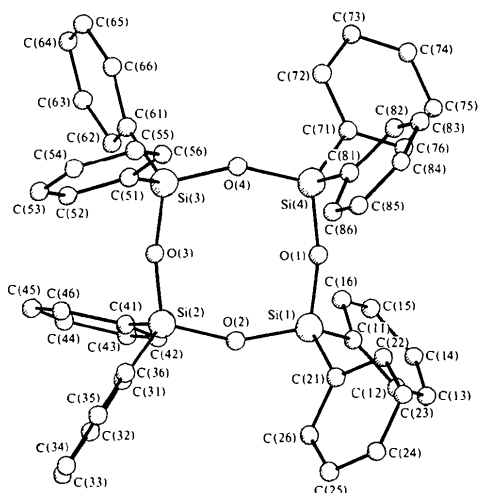
Fig. 1. The molecular structure of octaphenylcyclotetrasiloxane showing the numbering scheme.

We consider that the flattening of the ring may be due to intramolecular crowding. Although there are no unacceptably short C···C contacts between phenyl groups on different Si atoms the orientations of these groups result in a fairly evenly distributed set of C_β···O contacts, four at each O atom, lying between 3·13–3·59 Å.

The molecular packing is shown in Fig. 2. Although there are no intermolecular C···C contacts <3·63 Å, the rather unsymmetrical arrangement of phenyl-ring orientations on each molecule may have been influenced by intermolecular interactions. The molecular packing although fairly loose may therefore have an indirect effect on the molecular configuration. We have commenced an investigation of the triclinic form of this compound for comparison.
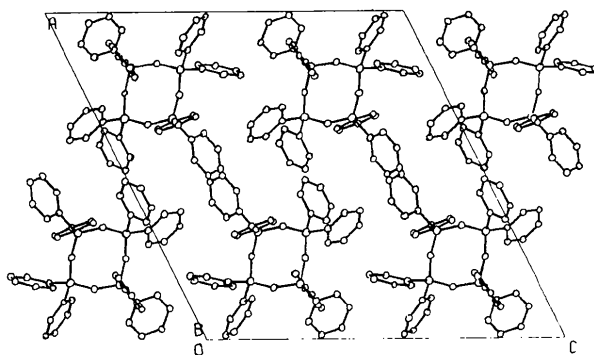
Fig. 2. The molecular packing looking down [010].

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