The Room-Temperature Structure of Octaphenylcyclotetra(siloxane) (OPCTS)

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Abstract. $C_{48}H_{40}O_4Si_4$, $M_r = 793 \cdot 21$, $P2_1/c$, $a = 21 \cdot 918\,(8)$, $b = 10 \cdot 138\,(6)$, $c = 21 \cdot 743\,(8)$ Å, $\beta = 116 \cdot 0\,(1)°$, $V = 4342 \cdot 4$ Å^3, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0 \cdot 7107$ Å, $d_{calc} = 1 \cdot 22$ Mg m^{-3}, $\mu = 0 \cdot 140$ mm^{-1}. The structure was determined by direct methods and refined to $R = 0 \cdot 095$ for 3008 unique observed reflections. The eight-membered ring is almost planar; two types of Si–O–Si angles have been found with mean values of $153 \cdot 2$ and $167 \cdot 4°$.

Introduction. Differential thermal analyses have shown that when pure octaphenylcyclotetra(siloxane) (OPCTS) is heated, two phase transitions are observed: a solid–solid transition at about 349 K and a solid–mesomorphic one at about 461 K. The latter is optically isotropic and has been assumed to be a plastic crystalline phase, containing globular molecules, which extends from 461 K to the melting point at 478 K (Keyes & Daniels, 1975).

Successive powder neutron diffraction studies have suggested that the mesophase is a smectic *A* phase (Volino & Dianoux, 1978). As the molecular conformation and the crystal packing were uncertain the interpretation of the diffraction patterns was difficult. We have determined the crystal and molecular structure of OPCTS at room temperature in order to obtain precise information on its molecular structure and to provide a valuable model of rationalization of the solid-phase properties.

Transparent needle-shaped crystals of commercial OPCTS (Eastman Organics Chemicals) were obtained from a dichloromethane/hexane mixture.

The intensities were collected from a crystal approximately $0 \cdot 35 \times 0 \cdot 20 \times 0 \cdot 10$ mm on a Philips PW 1100 four-circle diffractometer, operating in the $\theta/2\theta$ scan mode (scan width $= 1 \cdot 1°$, scan speed $= 0 \cdot 033°$ s^{-1}) with Mo $K\alpha$ radiation monochromatized by a graphite crystal. 5832 independent reflections up to $\theta = 23°$ were collected; 3008 of these $[I > 2 \cdot 5\sigma(I)]$ were used for the structure determination. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the direct methods included in *SHELX* 76 (Sheldrick, 1976). An *E* map generated from the phase set (50 reflections, $E \geq 1 \cdot 5$) located the tetra(siloxane) ring. The remaining non-hydrogen atoms were located from a difference Fourier synthesis. The structure was refined by full-matrix least squares, with the phenyl rings treated as rigid groups (D_{6h} symmetry, C–C $= 1 \cdot 395$ Å, C–H $= 1 \cdot 08$ Å). Each C atom was assigned an individual isotropic thermal parameter; the remaining non-hydrogen atoms were allowed to vibrate anisotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$ in which $w = 2 \cdot 9[\sigma^2(F_o) + 0 \cdot 0011(F_c)^2]$. The relatively high *R* value is probably due to the limited number of structure parameters used in the refinement.†

The calculations were carried out on the Cyber 76 computer of the CINECA centre with the *SHELX* 76 system of crystallographic programs (Sheldrick, 1976). All atomic scattering factors were those of *International Tables for X-ray Crystallography* (1974).

Discussion. A perspective view of the molecule is shown in Fig. 1. The final positional parameters with their e.s.d.'s in parentheses for the non-hydrogen atoms are listed in Table 1; bond lengths, and shorter intramolecular distances and angles are reported in Table 2. The Si–C and Si–O distances range from $1 \cdot 855$ to $1 \cdot 867\,(6)$ Å (mean $1 \cdot 860$ Å) and $1 \cdot 606–1 \cdot 619\,(6)$ Å (mean $1 \cdot 613$ Å), respectively, in very good agreement with those reported for 2,6-*cis*-diphenylhexamethylcyclotetra(siloxane) (Carlström & Falkenberg, 1973), 2,2,4,4-tetramethyl-6,6,8,8-tetraphenylcyclotetra(siloxane) (Shklover, Kalinin & Gusev, 1973), octamethylcyclotetra(siloxane) (Steinfink, Post & Fan-

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34810 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final positional parameters* $(\times 10^4)$ *and equivalent isotropic thermal parameters* $(\times 10^3)$, *with e.s.d's in parentheses*

|	x	y	z	$U\,(\text{Å}^2)$
Si(1)	1683 (3)	5699 (3)	3355 (1)	40 (2)
Si(2)	1754 (1)	4818 (3)	2002 (1)	45 (2)
Si(3)	3268 (1)	3772 (3)	2900 (1)	44 (2)
Si(4)	3242 (1)	4894 (3)	4233 (1)	42 (2)
O(1)	2464 (3)	5373 (6)	3870 (3)	49 (4)
O(2)	1561 (3)	5465 (7)	2575 (3)	45 (4)
O(3)	2508 (3)	4215 (7)	2381 (3)	52 (5)
O(4)	3425 (3)	4201 (6)	3671 (3)	50 (4)
C(11)	1541 (3)	7484 (7)	3446 (4)	43 (3)
C(12)	1011 (3)	7941 (7)	3580 (4)	56 (3)
C(13)	921 (3)	9293 (7)	3629 (4)	73 (4)
C(14)	1361 (3)	10188 (7)	3543 (4)	78 (4)
C(15)	1891 (3)	9730 (7)	3408 (4)	85 (4)
C(16)	1981 (3)	8379 (7)	3359 (4)	71 (4)
C(21)	1138 (4)	4568 (8)	3573 (3)	44 (3)
C(22)	1361 (4)	4136 (8)	4247 (3)	57 (3)
C(23)	957 (3)	3284 (8)	4415 (3)	64 (3)
C(24)	331 (3)	2865 (8)	3911 (3)	75 (4)
C(25)	109 (3)	3297 (8)	3238 (3)	83 (4)
C(26)	512 (3)	4149 (8)	3069 (3)	66 (3)
C(31)	1154 (4)	3474 (7)	1536 (7)	48 (3)
C(32)	600 (4)	3722 (7)	909 (4)	68 (3)
C(33)	137 (4)	2718 (7)	575 (4)	88 (4)
C(34)	228 (4)	1466 (7)	869 (4)	87 (4)
C(35)	782 (4)	1219 (7)	1497 (4)	105 (5)
C(36)	1245 (4)	2223 (7)	1830 (4)	89 (4)
C(41)	1739 (4)	6113 (7)	1388 (4)	45 (3)
C(42)	1594 (4)	7434 (7)	1447 (7)	68 (3)
C(43)	1630 (4)	8366 (7)	992 (7)	90 (3)
C(44)	1811 (4)	7977 (7)	478 (7)	96 (5)
C(45)	1955 (4)	6656 (7)	420 (7)	83 (4)
C(46)	1919 (4)	5724 (7)	875 (7)	62 (3)
C(51)	3339 (3)	1939 (7)	2875 (4)	48 (4)
C(52)	3152 (3)	1327 (7)	2244 (4)	71 (3)
C(53)	3204 (3)	−40 (7)	2209 (4)	89 (4)
C(54)	3444 (3)	−794 (7)	2805 (4)	88 (4)
C(55)	3632 (3)	−182 (7)	3437 (4)	97 (4)
C(56)	3579 (3)	1185 (7)	3472 (4)	68 (3)
C(61)	3883 (3)	4602 (7)	2653 (4)	43 (3)
C(62)	3699 (3)	5700 (7)	2222 (4)	58 (3)
C(63)	4168 (3)	6276 (7)	2031 (4)	77 (4)
C(64)	4821 (3)	5756 (7)	2270 (4)	85 (4)
C(65)	5005 (3)	4658 (7)	2700 (4)	89 (4)
C(66)	4536 (3)	4082 (7)	2892 (4)	77 (4)
C(71)	3791 (3)	6349 (8)	4620 (3)	43 (3)
C(72)	4413 (3)	6484 (8)	4594 (4)	67 (5)
C(73)	4835 (3)	7548 (8)	4918 (4)	108 (5)
C(74)	4636 (3)	8477 (8)	5268 (4)	96 (4)
C(75)	4014 (3)	8341 (8)	5294 (4)	91 (4)
C(76)	3592 (3)	7277 (8)	4969 (4)	75 (4)
C(81)	3340 (3)	3646 (8)	4900 (3)	48 (3)
C(82)	3834 (3)	3747 (8)	5575 (3)	78 (4)
C(83)	3898 (3)	2756 (8)	6045 (3)	104 (5)
C(84)	3467 (3)	1664 (8)	5839 (3)	93 (4)
C(85)	2973 (3)	1564 (8)	5163 (3)	94 (4)
C(86)	2909 (3)	2555 (8)	4694 (3)	74 (4)
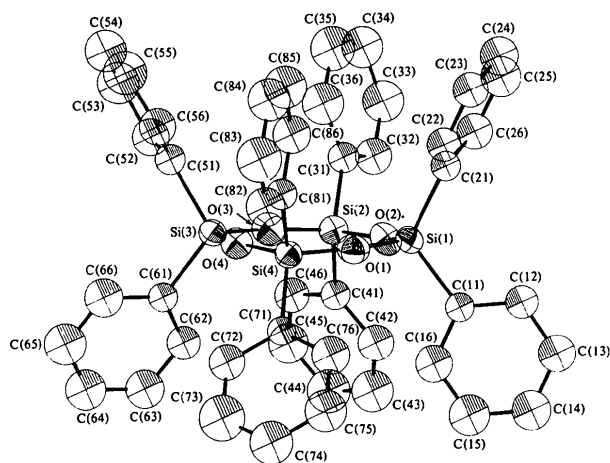
Fig. 1. *ORTEP* drawing (Johnson, 1965) of the OPCTS molecule with the atomic nomenclature.

Table 2. *Distances* (Å) *and relevant angles* (°) *with estimated standard deviations in parentheses*

Si(1)–O(1)	1·616 (7)	Si(1)–C(11)	1·861 (7)
Si(1)–O(2)	1·615 (6)	Si(1)–C(21)	1·861 (8)
Si(2)–O(2)	1·619 (6)	Si(2)–C(31)	1·855 (8)
Si(2)–O(3)	1·610 (7)	Si(2)–C(41)	1·861 (8)
Si(3)–O(3)	1·613 (7)	Si(3)–C(51)	1·867 (8)
Si(3)–O(4)	1·616 (6)	Si(3)–C(61)	1·858 (8)
Si(4)–O(4)	1·606 (6)	Si(4)–C(71)	1·856 (8)
Si(4)–O(1)	1·608 (7)	Si(4)–C(81)	1·864 (8)
Si(1)–O(1)–Si(4)	167·1 (5)	Si(2)–O(3)–Si(3)	167·8 (5)
Si(1)–O(2)–Si(2)	152·8 (4)	Si(3)–O(4)–Si(4)	153·7 (4)
C(11)–Si(1)–C(21)	114·6 (3)	C(51)–Si(3)–C(61)	111·2 (3)
C(11)–Si(1)–O(1)	107·5 (3)	C(51)–Si(3)–O(3)	109·3 (4)
C(11)–Si(1)–O(2)	107·2 (3)	C(51)–Si(3)–O(4)	108·4 (3)
C(21)–Si(1)–O(1)	107·5 (3)	C(61)–Si(3)–O(3)	109·2 (3)
C(21)–Si(1)–O(2)	110·4 (3)	C(61)–Si(3)–O(4)	109·1 (3)
O(1)–Si(1)–O(2)	109·5 (4)	O(3)–Si(3)–O(4)	109·6 (3)
C(31)–Si(2)–C(41)	109·9 (3)	C(71)–Si(4)–C(81)	110·9 (3)
C(31)–Si(2)–O(2)	110·8 (4)	C(71)–Si(4)–O(1)	108·7 (3)
C(31)–Si(2)–O(3)	108·9 (4)	C(71)–Si(4)–O(4)	111·3 (3)
C(41)–Si(2)–O(2)	109·7 (3)	C(81)–Si(4)–O(1)	108·9 (3)
C(41)–Si(2)–O(3)	109·1 (3)	C(81)–Si(4)–O(4)	108·2 (3)
O(2)–Si(2)–O(3)	108·4 (3)	O(1)–Si(4)–O(4)	108·9 (3)

O(1)···C(16)	3·26	O(3)···C(36)	3·20
O(1)···C(22)	3·13	O(3)···C(46)	3·32
O(1)···C(76)	3·22	O(3)···C(52)	3·32
O(1)···C(86)	3·28	O(3)···C(62)	3·16
O(2)···C(16)	3·33	O(4)···C(56)	3·13
O(2)···C(26)	3·22	O(4)···C(66)	3·53
O(2)···C(36)	3·60	O(4)···C(72)	3·20
O(2)···C(42)	3·19	O(4)···C(86)	3·35

kuchen, 1955) and 2,6-*trans*-diphenylhexamethylcyclotetra(siloxane) (Söderholm & Carlström, 1977). The O—Si—O (mean 109·2°), the C—Si—C (mean 111·6°) and the O—Si—C angles (mean 109·0°) are

close to the expected tetrahedral value. However, the Si—O—Si angles are significantly larger (from 152·8 to 167·8°) than those found (from 142 to 145°) for the previously reported tetra(siloxane) compounds. The Si—O—Si angles are of two types with mean values of 153·2 and 167·4°. The oxygen atoms O(2) and O(4), which exhibit the largest Si—O—Si angles, are also

Table 3. *Mean planes*

Equation of the O_4Si_4 root-mean-square plane

$$0.3379x + 0.8919y - 0.3005z = 4.6785$$

Deviations (Å) from the O_4Si_4 root-mean-square plane

Si(1)	−0.111 (4)	O(1)	0.003 (7)
Si(2)	0.044 (4)	O(2)	0.071 (7)
Si(3)	−0.043 (4)	O(3)	−0.029 (7)
Si(4)	0.075 (4)	O(4)	−0.009 (7)

Dihedral angles (°) between planes

Plane O_4Si_4−phenyl ring C(11)−C(16)	94.0
phenyl ring C(21)−C(26)	65.1
phenyl ring C(31)−C(36)	100.6
phenyl ring C(41)−C(46)	66.1
phenyl ring C(51)−C(56)	59.5
phenyl ring C(61)−C(66)	65.1
phenyl ring C(71)−C(76)	123.2
phenyl ring C(81)−C(86)	88.2

Phenyl ring C(11)−C(16)−phenyl ring C(21)−C(26)	87.1
Phenyl ring C(31)−C(36)−phenyl ring C(41)−C(46)	108.0
Phenyl ring C(51)−C(56)−phenyl ring C(61)−C(66)	84.4
Phenyl ring C(71)−C(76)−phenyl ring C(81)−C(86)	97.2

Important torsion angles (°)

The sign convention used for the torsion angles is such that the sign is negative if an anticlockwise rotation is required for atom (1) to eclipse atom (4) whilst looking down the (2)−(3) bond.

O(1)−Si(1)−C(11)−C(12)	−127.3 (4)
O(1)−Si(1)−C(21)−C(22)	−149.4 (4)
O(2)−Si(2)−C(31)−C(32)	96.4 (4)
O(2)−Si(2)−C(41)−C(42)	1.3 (4)
O(3)−Si(3)−C(51)−C(52)	53.6 (4)
O(3)−Si(3)−C(61)−C(62)	17.0 (4)
O(4)−Si(4)−C(71)−C(72)	162.3 (4)
O(4)−Si(4)−C(81)−C(82)	−63.7 (4)

involved in the highest number of shorter intra-molecular distances from neighbouring C atoms not directly bonded to Si (mean 3.24 Å), as can be seen in Table 2. The eight-membered O_4Si_4 ring is almost planar, the maximum deviation from the root-mean-square plane being 0.1 Å (Table 3).

The molecule as a whole does not possess symmetry elements, but, owing to the planarity of the O_4Si_4 ring and the almost perfect tetrahedral hybridization of the Si atoms, the $O_4Si_4C_8$ moiety has idealized D_{4h} symmetry. This structure, unusual for this kind of ring, may be determined by the steric hindrance of the eight phenyl rings, which are rotated in a different way with respect to the inner ring (Table 3). The eight phenyls, anyway, are roughly pointing towards the eight vertices of a parallelepiped, with approximate dimensions $6.5 \times 6.5 \times 4.7$ Å.

This conformation is quite different from that predicted by Volino & Dianoux (1978). Consequently, the interpretation of neutron diffraction data on the high-temperature behaviour of OPCTS should be reconsidered.

The crystal packing is determined by van der Waals forces, the closest C−C approach being 3.63 Å, greater than the sum of the van der Waals radii. The eight-membered rings are almost parallel to the (101) plane and approximately arranged on planes spaced at 5 Å along (010); on these planes the molecules are disposed on alternate strips along the [101] or [202] directions in turn, with an extra repeat after 10 Å.

Note added in proof: After revising the proofs of this work we received information of an earlier publication of the same structure in this journal (Hossain, Hursthouse & Malik, 1979). A comparison of the results of these two independent structure determinations is useful and suggests the following comments.

The first structure was determined using 4009 reflections and a structure model of 545 parameters (all non-hydrogen atoms having been treated independently and anisotropically, observations/parameters ratio: 7.4). We used 3008 reflections and a structure model of 170 parameters (all the phenyl groups being treated as rigid with regular hexagonal geometry, observations/ parameters ratio: 17.7). These data account for the lower R factor (0.0711) found in the first structure determination.

A comparison of the atomic coordinates shows that there are no significant differences between the two sets of values.

When a comparison of the bond parameters is made the average values are found to be equal within experimental errors, but the individual values of the Si−C and Si−O bond parameters are less scattered in our structure, as shown by the following figures (the values for the first structure are in parentheses): Si−C: range 1.855–1.867 Å (1.837–1.857), mean: 1.860 Å (1.849); Si−O: range 1.606–1.619 Å (1.604–1.623), mean: 1.613 Å (1.615).

The only significant difference has been found for the Si−C(phenyl) distance which in our structure is 0.01 Å longer. This is the only drawback of our model, which is one that ignores the well established deformation of substituted phenyl rings (Domenicano, Vaciago & Coulson, 1975).

The bond angles are equal within experimental errors [Si−O−Si: 167.4° (167.1), 153.2° (152.4); O−Si−O: 109.1° (109.7); C−Si−C: 111.6° (112.0)] and even the smallest deviations from the idealized symmetry are unambiguously detectable in both structure models, indicating that there are true packing effects.

However, we were particularly interested in the molecular conformation and crystal packing and felt that our model was appropriate. In summary, we feel that it was well worth using a reduced structure model

as considerable computing time was saved and we obtained exactly the same values for the bond parameters that were of interest to us.

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Structure of (±)-N-Methyl-2-(3,4-dihydroxyphenyl)ethylammonium-2-sulfonate Hemihydrate [(±)-Epinine β-Sulfonate Hemihydrate]

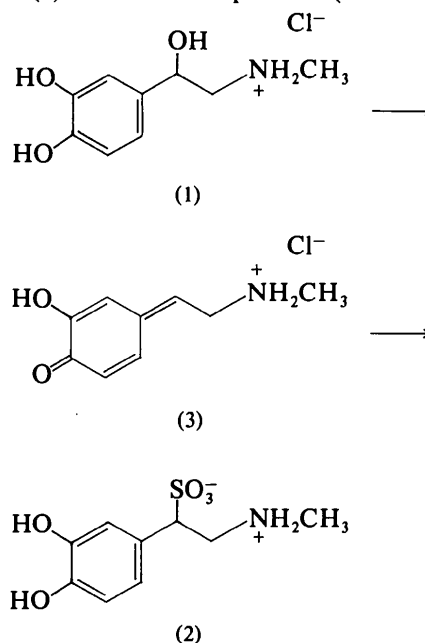BY J. G. HENKEL,* J. B. ANDERSON, M. RAPPOSCH AND G. HITE

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Abstract. $C_9H_{13}NO_3S.\frac{1}{2}H_2O$, m.p. 532–533 K (decomposition), *Pbna*, $a = 13\cdot588$ (3), $b = 14\cdot885$ (4), $c = 10\cdot616$ (3) Å, $Z = 8$, $D_x = 1\cdot585$, D_m (C_6H_6–CCl_4) $= 1\cdot58$ Mg m^{-3}, Mo $K\alpha$ ($\lambda = 0\cdot7093$ Å), 1017 reflections, $2\theta < 40°$, $217 < 3\sigma(F_o)$. The structure was solved by *MULTAN* with magic integers. Full-matrix least-squares refinement converged with $R(F) = 0\cdot040$. This confirms the previous assignment of structure to the racemic degradation product of (−)-epinephrine in the presence of aqueous bisulfite.

Introduction. The degradation of (−)-epinephrine (1) in the presence of aqueous bisulfite or sulfite was first reported by Schroeter, Higuchi & Schuler (1958). They speculated that (±)-epinine β-sulfonate (2) is the reaction product. Although there has been general acceptance of the identity of the product based upon its elemental analysis, melting point, ultraviolet spectrum, pKa and X-ray powder diffraction pattern, there have been occasional reports of confusion in the literature regarding its identity (Kawazu, Inoue, Tomino & Iwao, 1973, and references therein). The kinetics of degradation have been thoroughly studied but fail to unambiguously characterize the mechanism or course of the reaction (Hajratwala, 1975, and references

therein) or the structure of the product. The occurrence of the *o*- or *p*-hydroxybenzyl alcohol structure in this and other molecules appears to favor this type of reactivity (Higuchi & Schroeter, 1959) in which dienones (3) have been implicated (Cohen & Jones,

(1)

(3)

(2)

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