The methyl substituent on C(9) is equatorial; C(9) has the R configuration according to the notation of Cahn, Ingold & Prelog (1966). The cyclohexenone ring C is approximately a half-chair (the maximum deviation from ideal cyclohexene half-chair torsion angles is 8·7°), with an axial phenylselenyl substituent. This conformation minimizes repulsion between the Se atom and the carbonyl group. The plane of the phenyl ring is at right angles to that of the molecular skeleton, which enables efficient molecular packing.

References

CAHN, R. S., INGOLD, C. K. & PRELOG, V. (1966). *Angew. Chem.* **78**. 413–447.

CLEGG, W. (1981). *Acta Cryst.* A**37**. In the press.

KLYNE, W. & PRELOG, V. (1960). *Experientia*. **16**. 521–523.

SHELDRICK, G. M. (1980). To be published.

Dodeca(phenylsilasesquioxane)*

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Abstract. $C_{72}H_{60}O_{18}Si_{12}$, $M_r = 1550·3$, tetragonal, $P4/n$, $a = 17·449(4)$, $c = 14·156(4)$ Å, $U = 4310·0$ Å³, $D_x = 1·194$ Mg m⁻³, $Z = 2$, $F(000) = 1608$; final $R = 0·077$ for 1666 unique reflexions. The $(PhSi)_{12}O_{18}$ molecule contains four ten-membered and four eight-membered silicon–oxygen rings and has crystallographic $\bar{4}$ (S_4) symmetry. The $Si_{12}O_{18}$ core approximates to $\bar{4}2m$ (D_{2d}) symmetry.

with $I > 2\sigma(I)$; the discrepancy index for equivalent reflexions was 0·067.

The structure was solved by direct methods, and refined to a minimum value of $\sum w\Delta^2$ [$\Delta = |F_o| -$

Introduction. Very small crystals of this compound were obtained in small quantities from an attempt to recrystallize the silicon–nitrogen ring compound $(PhSiF.NMe)_3$ from acetone. The nature of the material obtained was established by a preliminary crystal structure determination based on data collected at high speed from a crystal of dimensions *ca* 0·1 mm. A second data set was subsequently obtained from a slightly larger crystal, including measurements of several sets of equivalent reflexions. All measurements were made with a Stoe–Siemens AED diffractometer (Clegg, 1981) and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å). 11 444 intensities were obtained in the range $7<2\theta<50°$. Cell dimensions were derived from the setting angles of 42 automatically centred reflexions.

Equivalent reflexions were averaged and the two data sets combined, without application of absorption corrections ($\mu = 0·23$ mm⁻¹), to give 1666 unique data

* 1,3,5,7,9,11,13,15,17,19,21,23-Dodecaphenylheptacyclo-[11.11.1.1³·⁹.1⁵·²³.1⁷·¹⁹.1¹¹·¹⁷.1¹⁵·²¹]dodecasiloxane.

Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* (Å² $\times 10^4$)

$U_{eq} = \frac{1}{3}$ of the trace of the orthogonalized U matrix.

	x	y	z	U_{eq}
Si(1)	7745 (1)	4178 (1)	5953 (2)	394 (7)
Si(2)	6981 (1)	4119 (1)	4003 (2)	408 (7)
Si(3)	8095 (1)	3184 (1)	2724 (2)	408 (7)
O(1)	7355 (3)	4427 (3)	4973 (3)	450 (18)
O(2)	7650 (3)	3855 (3)	3289 (4)	485 (20)
O(3)	8799 (3)	2881 (3)	3350 (4)	495 (20)
O(4)	6464 (3)	3381 (3)	4274 (3)	513 (19)
O(5)	7500	2500	2508 (5)	507 (29)
C(11)	8158 (4)	5037 (4)	6507 (6)	459 (30)
C(12)	8281 (5)	5074 (6)	7463 (7)	752 (43)
C(13)	8581 (7)	5723 (8)	7888 (9)	1026 (55)
C(14)	8770 (7)	6329 (7)	7372 (12)	1038 (61)
C(15)	8664 (7)	6314 (6)	6416 (11)	1121 (60)
C(16)	8350 (6)	5675 (5)	5985 (8)	801 (40)
C(21)	6410 (5)	4875 (5)	3423 (6)	564 (34)
C(22)	5794 (6)	5184 (6)	3890 (9)	1036 (53)
C(23)	5355 (7)	5779 (8)	3400 (12)	1293 (72)
C(24)	5516 (9)	5999 (8)	2547 (10)	1325 (71)
C(25)	6091 (8)	5636 (7)	2078 (8)	1203 (60)
C(26)	6509 (7)	5080 (7)	2513 (8)	1070 (53)
C(31)	8470 (4)	3558 (4)	1599 (5)	412 (27)
C(32)	7990 (5)	3757 (6)	858 (7)	701 (39)
C(33)	8241 (6)	4056 (6)	34 (7)	899 (46)
C(34)	9013 (6)	4164 (6)	−91 (7)	845 (46)
C(35)	9503 (6)	3987 (6)	608 (7)	835 (46)
C(36)	9235 (5)	3690 (5)	1452 (6)	639 (36)

$|F_c|$; $w^{-1} = \sigma^2(F_o) + 0.001F_o^2$]. Anisotropic thermal parameters were refined for all Si, O and C atoms. H atoms were included in the refinement with constraints [H on external bisector of C–C–C angle with C–H = 0.96 Å, $U(H) = 1.2\ U_{eq}(C)$]. The final values of R and R_w[$=(\sum w\varDelta^2/\sum wF_o^2)^{1/2}$] were 0.077 and 0.089.

A final difference synthesis contained several peaks of height 0.5–0.85 e Å^{-3}, which are probably due to disordered acetone molecules located in cavities between the $(PhSi)_{12}O_{18}$ molecules, but no simple disorder model could be successfully refined. The crystal data quoted are for the molecular formula without acetone. Final coordinates and geometrical parameters are given in Tables 1 and 2.*

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* Lists of structure factors, thermal parameters and hydrogen atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35578 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°)

Si(1)–O(1)	1.606 (5)	Si(2)–O(1)	1.612 (5)
Si(2)–O(2)	1.612 (5)	Si(3)–O(2)	1.617 (5)
Si(3)–O(3)	1.604 (5)	Si(1^i)–O(3)	1.613 (5)
Si(2)–O(4)	1.618 (5)	Si(1^{ii})–O(4)	1.609 (5)
Si(3)–O(5)	1.612 (3)		
Si(1)–C(11)	1.839 (8)	Si(2)–C(21)	1.847 (9)
Si(3)–C(31)	1.842 (8)		
C(11)–C(12)	1.373 (13)	C(11)–C(16)	1.377 (12)
C(12)–C(13)	1.384 (17)	C(13)–C(14)	1.326 (19)
C(14)–C(15)	1.367 (22)	C(15)–C(16)	1.385 (15)
C(21)–C(22)	1.373 (14)	C(21)–C(26)	1.348 (14)
C(22)–C(23)	1.466 (18)	C(23)–C(24)	1.298 (23)
C(24)–C(25)	1.359 (20)	C(25)–C(26)	1.360 (17)
C(31)–C(32)	1.386 (12)	C(31)–C(36)	1.370 (12)
C(32)–C(33)	1.350 (14)	C(33)–C(34)	1.373 (16)
C(34)–C(35)	1.344 (15)	C(35)–C(36)	1.383 (14)
O(1)–Si(1)–O(3^{ii})	110.7 (3)	O(1)–Si(1)–O(4^i)	107.9 (3)
O(3^{ii})–Si(1)–O(4^i)	107.7 (3)	O(1)–Si(1)–C(11)	108.2 (3)
O(3^{ii})–Si(1)–C(11)	109.8 (3)	O(4^i)–Si(1)–C(11)	112.5 (3)
O(1)–Si(2)–O(2)	109.7 (3)	O(1)–Si(2)–O(4)	106.8 (3)
O(2)–Si(2)–O(4)	109.0 (3)	O(1)–Si(2)–C(21)	111.0 (3)
O(2)–Si(2)–C(21)	108.4 (3)	O(4)–Si(2)–C(21)	111.9 (3)
O(2)–Si(3)–O(3)	109.5 (3)	O(2)–Si(3)–O(5)	108.7 (2)
O(3)–Si(3)–O(5)	110.7 (3)	O(4)–Si(2)–O(1)	106.8 (3)
O(3)–Si(3)–C(31)	108.8 (3)	O(5)–Si(3)–C(31)	109.1 (4)
Si(1)–O(1)–Si(2)	144.7 (3)	Si(2)–O(2)–Si(3)	149.9 (4)
Si(3)–O(3)–Si(1^i)	151.0 (4)	Si(2)–O(4)–Si(1^{ii})	152.8 (4)
Si(3)–O(5)–Si(3^{iii})	158.1 (5)		
Si(1)–C(11)–C(12)	121.3 (7)	Si(1)–C(11)–C(16)	121.7 (7)
C(12)–C(11)–C(16)	117.0 (8)	C(11)–C(12)–C(13)	121.7 (10)
C(12)–C(13)–C(14)	120.4 (12)	C(13)–C(14)–C(15)	119.8 (12)
C(14)–C(15)–C(16)	120.4 (11)	C(11)–C(16)–C(15)	120.7 (10)
Si(2)–C(21)–C(22)	119.2 (8)	Si(2)–C(21)–C(26)	123.1 (8)
C(22)–C(21)–C(26)	117.2 (10)	C(21)–C(22)–C(23)	117.3 (11)
C(22)–C(23)–C(24)	122.4 (13)	C(23)–C(24)–C(25)	118.4 (14)
C(24)–C(25)–C(26)	120.5 (12)	C(21)–C(26)–C(25)	123.6 (11)
Si(3)–C(31)–C(32)	121.9 (6)	Si(3)–C(31)–C(36)	122.4 (6)
C(32)–C(31)–C(36)	115.6 (8)	C(31)–C(32)–C(33)	123.7 (9)
C(32)–C(33)–C(34)	118.9 (10)	C(33)–C(34)–C(35)	119.8 (10)
C(34)–C(35)–C(36)	120.5 (10)	C(31)–C(36)–C(35)	121.5 (8)

Symmetry operators: (i) $\tfrac{1}{2} + y, 1 - x, 1 - z$; (ii) $1 - y, -\tfrac{1}{2} + x, 1 - z$. (iii) $\tfrac{1}{2} - x, \tfrac{1}{2} - y, z$.

Discussion. The existence of compounds with the general formula $(PhSi)_{2n}O_{3n}$ has been recognized for some time. A method of preparation described by Brown (1965) involves polycondensation of $PhSi(OH)_3$, which can be generated *in situ* by hydrolysis of a variety of phenylsilicon compounds, such as $PhSiCl_3$ in a water/acetone mixture. Our fortuitous preparation of $(PhSi)_{12}O_{18}$ from $(PhSiF.-NMe)_3$ was probably basically by this method, the acetone being presumably not completely dry.

The structural nature of the silasesquioxanes is less well established. The proposal that $(PhSi)_8O_{12}$ is based on a cube of Si atoms (Brown, Vogt & Prescott, 1964) has been supported by a crystal structure analysis (Hossain, Hursthouse & Malik, 1979). This proposal was based on spectroscopic evidence, which suggested that for $(PhSi)_{2n}O_{3n}$ with $n = 4$, 5 and 6 no silicon–oxygen rings were present with fewer than eight atoms. Thus, a single possibility exists also for $(PhSi)_{10}O_{15}$, based on a pentagonal prismatic arrangement of Si atoms. For $(PhSi)_{12}O_{18}$, however, there are two possible arrangements, which are shown in Fig. 1. Of these, the hexagonal-prismatic arrangement (I) was favoured (Brown, Vogt & Prescott, 1964).

The structure analysis reported here shows that $(PhSi)_{12}O_{18}$ actually contains a $Si_{12}O_{18}$ core of approximate $\bar{4}2m$ (D_{2d}) symmetry, consisting of fused eight- and ten-membered silicon–oxygen rings. The molecule is depicted in Fig. 2, and the numbering scheme
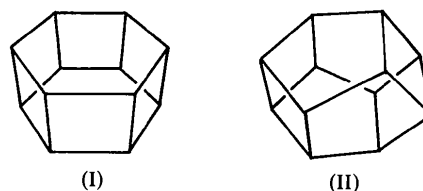

(I)   (II)

Fig. 1. Proposed arrangements for the $Si_{12}O_{18}$ core of $(PhSi)_{12}O_{18}$. Each vertex represents a Si atom and each edge a Si–O–Si linkage.
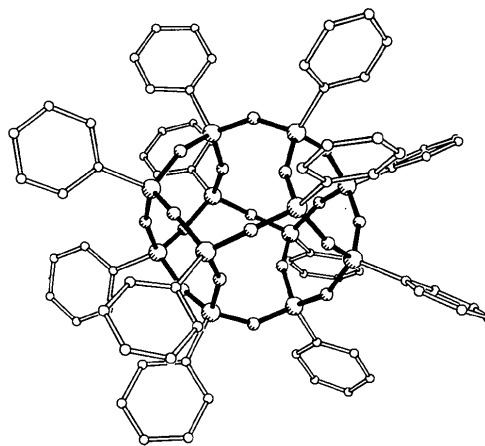

Fig. 2. Molecular structure of $(PhSi)_{12}O_{18}$ (H atoms omitted); perspective view along a direction parallel to y. The $\bar{4}$ axis runs left–right.

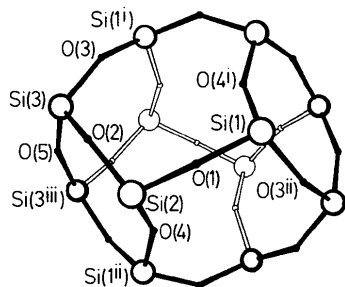indicated in Fig. 3, which shows the central core. The Si atom arrangement is that of possibility (II) in Fig. 1.

Fig. 3. The $Si_{12}O_{18}$ core, showing the numbering scheme. For symmetry operators, see Table 2.

Bond lengths and angles are similar to those in $(PhSi)_8O_{12}$ (Hossain, Hursthouse & Malik, 1979).

References

Brown, J. F. Jr (1965). *J. Am. Chem. Soc.* **87**, 4317–4324.
Brown, J. F. Jr, Vogt, L. H. & Prescott, P. I. (1964). *J. Am. Chem. Soc.* **86**, 1120–1125.
Clegg, W. (1981). *Acta Cryst.* A**37**. In the press.
Hossain, M. A., Hursthouse, M. B. & Malik, K. M. A. (1979). *Acta Cryst.* B**35**, 2258–2260.

Structure of Dimethyl 3a,4,9,9a-Tetrahydro-9-oxo-*cis*-furo-[3,2-*b*]quinoline-2,3-dicarboxylate

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Abstract. $C_{15}H_{13}NO_6$, monoclinic, $P2_1/c$, $Z = 4$, $a = 11.635$ (4), $b = 10.442$ (3), $c = 12.347$ (3) Å, $\beta = 108.81$ (2)°, $D_m = 1.417$, $D_x = 1.422$ Mg m^{-3}. The structure was solved by the direct method; block-diagonal least-squares refinement led to a final R of 0.047 for 2198 observed reflexions. Molecules are held together by van der Waals interactions and strong NH···O hydrogen bonds. The furan ring has abnormal bond angles, indicating distortion caused by the cycloaddition. The pyridine ring in the quinoline moiety has a conformation of a slightly creased hinge.

Introduction. During the course of studies on the 1,3-dipolar cycloaddition of quinoline 1-oxides, reaction of 4-methoxyquinoline 1-oxide with dimethyl acetylenedicarboxylate was found to afford the title compound (*A*), though in a small yield of 8·1%, together with the 2-substituted quinoline (*B*) and the furo[3,2-*c*]quinoline (*C*) as shown in Fig. 1 (Ishiguro, Funakoshi, Saeki, Hamana & Ueda, 1980). Although the demethylation of the 4-methoxy group of the quinoline ring is inevitable, the formation of *A* is very noticeable because *A* is the first example of 2,3-

dihydroquinolines obtained from the 1,3-dipolar cycloaddition of quinoline 1-oxides. By an X-ray diffraction method the conformation of *A* was determined as given in the title.

The title compound was recrystallized from an ethanol solution as yellow plates. Preliminary Weissenberg photographs showed the systematic absences of the space group $P2_1/c$. The unit-cell parameters were determined by a least-squares procedure using the 2θ values of 15 reflexions measured on a Syntex $P1$ four-circle diffractometer. The density was measured by flotation in an aqueous KI solution. A single crystal
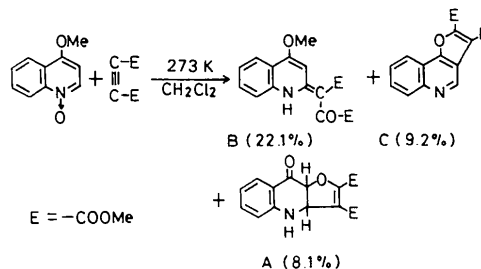

Fig. 1. A diagram for the reaction.

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