

Photodimers of 1,1-Diphenyl-1-silacyclohexan-2-one. I. The Crystal and Molecular Structure of Dimer I, *trans*-7,7'-Bicyclo-(2,2-diphenyl-1-oxa-2-silacycloheptylidene)

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Abstract. $C_{34}H_{36}Si_2O_2$, $M = 532.2$. Triclinic, $P1$ or $P\bar{1}$ (latter confirmed): $a = 10.047$ (4), $b = 9.934$ (4), $c = 9.226$ (3) Å; $\alpha = 122.96$ (1), $\beta = 76.70$ (1), $\gamma = 112.68$ (1)°; $V = 712.6$ (2) Å³; $D_m = 1.23$ (1), $D_c = 1.24$ g cm⁻³ for $Z = 1$; $\mu(\text{Mo } K\alpha) = 1.57$ cm⁻¹. The structure, refined to a final residual of 0.083, consists of one (centrosymmetric) molecule per cell which has two seven-membered oxasila-heterocyclic rings joined by a central ethylenic double bond.

Introduction. Colourless, well formed crystals of known elemental analysis were supplied by Professor A. G. Brook.

The crystal used for data collection was a parallelepiped of dimensions *ca* 0.3 × 0.2 × 0.5 mm. It was mounted about **b**, parallel to its longest dimension. The cell parameters and their standard deviations were obtained from diffractometer angular settings of 12 well-centred axial reflexions using Cu $K\alpha$ radiation. Intensities were collected on a computer-controlled Picker four-circle diffractometer equipped with pulse-height analyser using filtered Mo $K\alpha$ radiation. Scanning was in the θ - 2θ mode at 1° min⁻¹. Backgrounds were determined for 1 min at each end of the scan range of 2° adjusted for α splitting. The take-off angle was 3.0°. During the course of data collection there was a random deviation of $\leq 8\%$ from the mean in the intensity of the standard reflexion, recorded every 30

reflexions. Counting statistics and an Abrahams factor (Abrahams & Bernstein, 1965) of 0.02 were used to calculate $\sigma(I)$. Of the 3131 independent reflexions measured, 2844 were considered significant on the criterion $|F_o| > \sigma(F_o)$. Absorption corrections were not applied. Direct methods were used in phasing the structure factors after the Patterson function failed to show the positions of the Si atoms unambiguously. The distribution of normalized structure factors indicated space group $P\bar{1}$. Assuming this, three reflexions (8 $\bar{2}1$, 4 $\bar{1}\bar{5}$, 36 $\bar{1}$), having $|E| > 3.0$, were chosen to define the origin. Three more were used as 'symbols', and a total of 298 reflexions with $|E| > 1.62$ were used as input to the program *TANFOR* (Drew, unpublished) to generate and refine phases using the tangent formula. A unique non-trivial solution ($R_{\text{Karle}} = 12\%$, average consistency = 99%) was obtained, and the computed E map revealed the positions of all 19 non-hydrogen atoms. Refinement was by *XFLS-3* using $1/[\sigma^2(F_o)]$ as weights and Hartree-Fock scattering factors (Cromer & Mann, 1968) with appropriate corrections for anomalous dispersion applied for Si. Three cycles of 'isotropic' refinement gave a conventional unweighted R of 0.134 for all observed reflexions. Another two cycles using anisotropic temperature factors, applied to all non-hydrogen atoms, lowered it to 0.107. A difference map at this stage revealed all H atoms, which were then included in later refinement.

Table 1. Atomic fractional coordinates ($\times 10^4$) and anisotropic temperature factors ($\times 10^4$) of form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si	2346 (1)	4723 (1)	1806 (1)	74 (1)	110 (2)	104 (2)	38 (1)	7 (1)	48 (1)
O	804 (3)	4433 (4)	2877 (3)	85 (3)	195 (5)	115 (4)	60 (3)	18 (3)	78 (4)
C(3)	3853 (4)	5032 (5)	2942 (5)	86 (4)	156 (7)	143 (6)	53 (4)	4 (4)	74 (5)
C(4)	3807 (4)	6280 (6)	4873 (5)	110 (5)	155 (7)	153 (6)	36 (5)	-35 (4)	53 (5)
C(5)	2861 (4)	5462 (6)	5900 (5)	105 (5)	218 (9)	143 (6)	66 (5)	-9 (4)	81 (6)
C(6)	1417 (4)	4142 (5)	5114 (5)	110 (4)	175 (7)	144 (6)	72 (5)	21 (4)	95 (6)
C(7)	526 (3)	4686 (4)	4540 (4)	75 (3)	107 (5)	111 (5)	29 (3)	2 (3)	52 (4)
C(8)	2692 (4)	6632 (4)	1675 (4)	95 (4)	99 (5)	108 (5)	41 (4)	3 (3)	39 (4)
C(9)	1578 (4)	7013 (5)	1467 (5)	94 (4)	152 (7)	193 (7)	40 (5)	-7 (4)	91 (6)
C(10)	1822 (5)	8412 (6)	1325 (6)	129 (5)	187 (8)	230 (9)	54 (5)	-12 (5)	130 (7)
C(11)	3204 (5)	9490 (6)	1433 (7)	142 (6)	159 (8)	253 (10)	44 (5)	-8 (6)	124 (7)
C(12)	4349 (5)	9178 (7)	1645 (8)	106 (5)	172 (3)	327 (12)	16 (5)	-10 (6)	150 (9)
C(13)	4086 (4)	7759 (5)	1776 (6)	89 (4)	151 (7)	234 (9)	31 (4)	-5 (5)	108 (7)
C(14)	2069 (3)	2795 (4)	-393 (4)	78 (3)	110 (5)	107 (5)	39 (4)	9 (3)	43 (4)
C(15)	1734 (4)	1223 (5)	-557 (5)	108 (4)	123 (6)	158 (7)	38 (4)	2 (4)	64 (4)
C(16)	1564 (5)	-246 (5)	-2195 (6)	159 (6)	108 (7)	187 (8)	58 (5)	-14 (5)	36 (6)
C(17)	1734 (5)	-141 (6)	-3662 (6)	154 (6)	163 (8)	152 (7)	68 (6)	-3 (5)	13 (6)
C(18)	2056 (5)	1405 (6)	-3523 (5)	167 (7)	188 (9)	113 (6)	59 (6)	4 (5)	43 (6)
C(19)	2229 (4)	2857 (5)	-1881 (4)	118 (5)	140 (7)	123 (6)	56 (5)	14 (4)	57 (5)

Table 1 (cont.)

	x	y	z	B
H(3A)	3934 (49)	4032 (64)	2756 (59)	4.67 (98)
H(3B)	4663 (63)	5524 (71)	2557 (70)	5.97 (123)
H(4A)	4589 (45)	6750 (55)	5470 (53)	3.25 (79)
H(4B)	3387 (58)	7126 (72)	4926 (69)	5.89 (118)
H(5A)	3366 (71)	4792 (83)	5833 (80)	7.29 (147)
H(5B)	2797 (68)	6409 (88)	7161 (79)	7.43 (144)
H(6A)	1501 (58)	2980 (71)	4107 (70)	5.56 (110)
H(6B)	740 (41)	3772 (49)	5817 (48)	2.66 (68)
H(9)	605 (54)	6257 (62)	1303 (57)	4.51 (94)
H(10)	1085 (46)	8723 (56)	1201 (53)	3.85 (84)
H(11)	3392 (66)	10471 (79)	1351 (77)	7.08 (143)
H(12)	5279 (74)	9860 (87)	1350 (83)	8.12 (161)
H(13)	4879 (47)	7650 (55)	2060 (52)	3.88 (85)
H(15)	1678 (50)	1172 (63)	381 (61)	4.56 (100)
H(16)	1165 (68)	-1372 (88)	-2272 (77)	7.05 (138)
H(17)	1989 (68)	-827 (85)	-4742 (83)	7.47 (147)
H(18)	1953 (70)	1340 (87)	-4483 (84)	7.64 (159)
H(19)	1587 (49)	4005 (64)	-1770 (57)	4.33 (94)

Two more cycles using mixed temperature factors (anisotropic for non-hydrogen atoms, isotropic otherwise) and refining all variable parameters gave a final unweighted R of 0.083* and a value of 1.63 for the e.s.d. of a unit observation. (The space group $P\bar{1}$ was thus confirmed.) The final difference map showed no peaks greater than $0.6 \text{ e } \text{Å}^{-2}$, the largest being situated near the Si atoms. Atomic coordinates and thermal parameters are given in Table 1, bond lengths and angles in Fig. 1.

Discussion. Ultraviolet photolysis of 1,1-diphenyl-1-silacyclohexan-2-one (III) yields two isomeric dimers whose structures (I) and (II) were tentatively assigned by chemical and spectroscopic methods (Brook, Pierce & Duff, 1975).

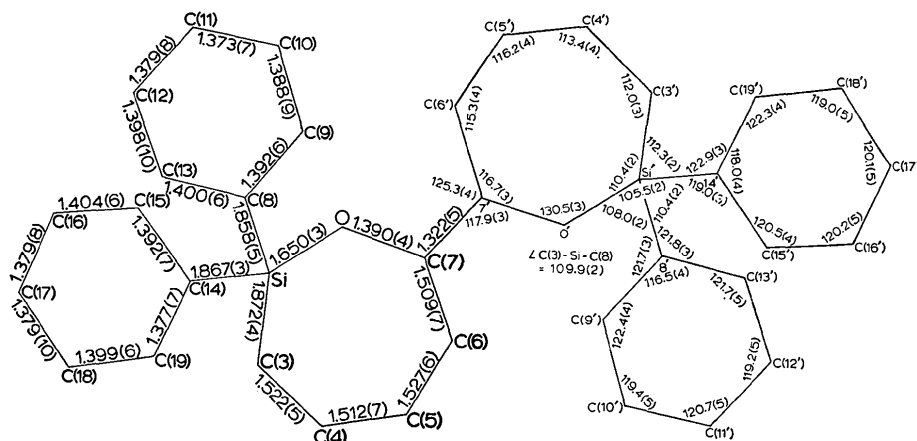
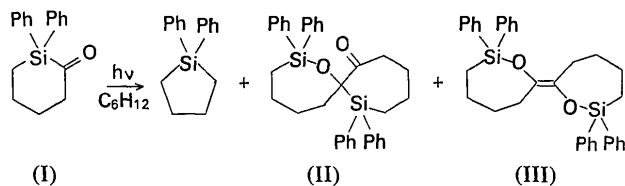


Fig. 1. Bond lengths and angles in dimer I.

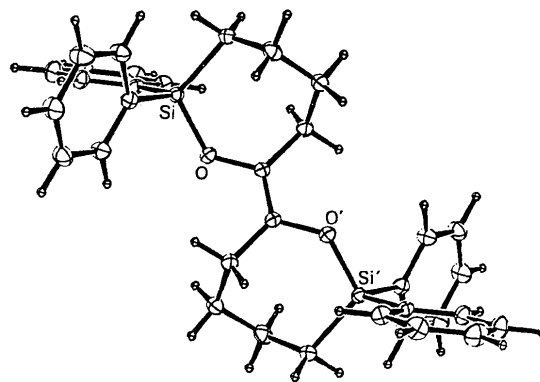


Fig. 2. ORTEP plot of dimer I molecule with thermal ellipsoids of 20% probability.

Both structures have been confirmed by crystal structure analysis. This paper reports the results for dimer I, the following paper (Cheng, Wong-Ng, Nyburg & Van der Heijden, 1976) the results for dimer II.

The crystal structure consists of discrete centrosymmetric molecules, one of which is shown in Fig. 2. The centrosymmetric dimer molecule has a planar ethylenic system at its centre (Table 2 gives various least-squares planes).

The internal angles of the ring are (except at Si) larger than tetrahedral as is always the case for such strained systems. The Si-C lengths are very close to those usually found [see e.g. Nyburg, Brook, Pascoe & Szymanski (1972)]; similarly for Si-O at 1.650 (3) Å [compare the mean length of 1.657 Å in β -1-phenylsilitrane (Parkanyi, Simon & Nagy, 1974)].

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31386 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Best least-squares planes*

(a) Coefficients of planes $AX + BY + CZ = D$ where X, Y, Z are real orthogonal coordinates (in Å) where X is along x , Z along z^* and Y furnishes a right-handed system.

Plane		A	B	C	D
1	Oxasila-ring	0.296 (2)	-0.849 (3)	-0.438 (3)	-3.319 (1)
2	Ethylenic	-0.380 (3)	-0.850 (4)	-0.365 (3)	-3.048 (2)
3	Phenyl (B)	0.115 (2)	-0.044 (2)	-0.992 (6)	-1.463 (2)
4	Phenyl (C)	0.984 (5)	0.171 (8)	-0.046 (4)	1.392 (2)

(b) Deviations from planes (10^{-3} Å). Asterisked atoms were not included in the calculation of the best least-squares plane.

Plane						
1	Si	6 (1)	O	-75 (3)	C(3)	305 (5)
	C(4)	-608 (5)	C(5)	-48 (6)	C(6)	613 (5)
	C(7)	-201 (4)				
2	O	2 (3)	C(6)	5 (5)	C(7)	-13 (4)
	C(7')	13 (4)	C(6')	-5 (5)	Si*	-797 (1)
	C(3)*	-1540 (5)	C(4)*	-2267 (5)	C(5)*	-1364 (6)
3	C(8)	4 (3)	C(9)	-7 (4)	C(10)	6 (5)
	C(11)	-3 (5)	C(12)	2 (6)	C(13)	-4 (5)
	Si*	29 (1)				
4	C(14)	0 (4)	C(15)	0 (5)	C(16)	-2 (6)
	C(17)	4 (6)	C(18)	-5 (6)	C(19)	2 (5)
	Si*	59 (1)				

(c) Angles between normals to planes ($^{\circ}$)

Plane	2	3	4
1	39.8 (3)	59.6 (3)	80.4 (1.5)
2		69.2 (3)	120.2 (1.5)
3			81.3 (1.5)

The Si-O-C angle at $130.5(3)^{\circ}$ also indicates strain. Thus although the angle in methyl silyl ether Me-O-SiH₃ is 120.6° (Glidewell, Rankin, Robiette, Sheldrick,

Beagley & Freeman, 1970) it can apparently be easily opened up. An angle of 131.4° , comparably large to that found here, is present in the six-membered ring examined by Boer & Van Remoortere (1969).

The conformation of the ring is not easily described but is approximately a boat [see Fig. 3(a)]. More details are given in the following paper (Cheng *et al.*, 1976) where the conformational effect of having a central ethylenic bond rather than a spiro C atom (in dimer II) is discussed. The phenyl rings attached to Si warrant no special comment. The shortest intermolecular contact is O...H(6'B), $2.44(5)$ Å.

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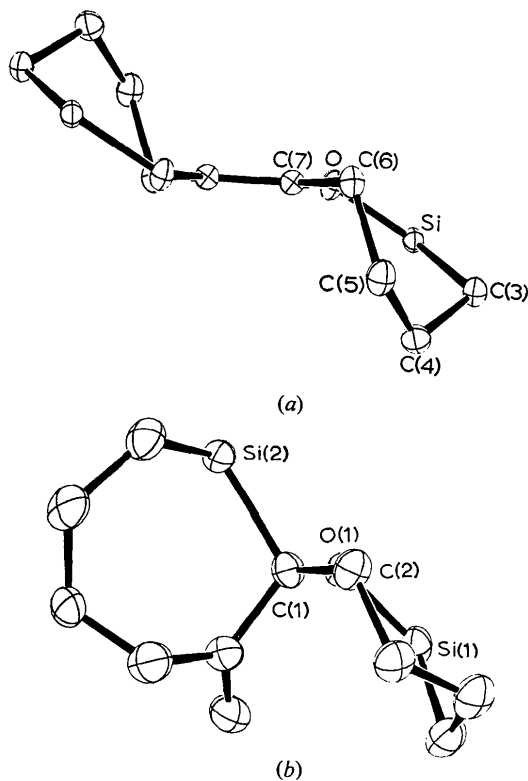


Fig. 3. Comparison of conformation of (a) ring of dimer I with (b) corresponding ring (A) of dimer II.