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Photodimers of 1,1-Diphenyl-1-silacyclohexan-2-one. II. The Crystal and Molecular Structure of Dimer II, 2,2,8,8-Tetraphenyl-1-oxa-2,8-disilaspiro[7,7]tridecan-13-one

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Abstract. $C_{34}H_{36}O_2Si_2$, $M=532{\cdot}2$. Monoclinic, $P2_1/c$: $a=17{\cdot}866$ (5), $b=8{\cdot}352$ (3), $c=20{\cdot}718$ (7), $\beta=106{\cdot}20$ (2)°; $V=2924$ Å^3; D_c (for $Z=4$) = 1·23, $D_m=1{\cdot}22$ cm^{-3}; μ(Cu $K\alpha$) = 12·88 cm^{-1}. The molecules are composed of two different seven-membered hetero rings spiro-connected. One ring has atypical bond lengths and angles and is partially disordered. Attempts to improve the atomic coordinates of the disordered atoms did not lead to a significant improvement in R (0·079).

Introduction. Well formed colourless crystals crystallized from n-hexane were provided by A. G. Brook.

14 reflexions from a crystal approximately 0·1 × 0·1 × 0·2 mm were accurately centred on a computer-automated Picker diffractometer to yield the best least-squares crystal parameters. 5276 reflexions were measured with Ni-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) on the diffractometer in the θ–2θ scan mode at 1° min^{-1} and with a minimum scan width of 2·5°. Background counts B_1 and B_2 were measured for known periods comparable to the scanning time. Calibrated Al attenuators were used if the scan count exceeded 6×10^4. The standard reflexion used for monitoring stability changed by approximately ±5% from the mean during data collection.

No absorption corrections were made. The average values $\langle|E^2-1|\rangle$ and $\langle|E|\rangle$ were 1·006 and 0·825, respectively. The 458 $|E|$ values $>1{\cdot}4$ were related by the phase-determining program *LSAM* (Van der Heijden, 1974). Origin-determining reflexions were $81\underline{1}$, 016 and 722; symbolic phases were given to $71\bar{9}$, 085, 721 and $14,1,\bar{7}$. An E map calculated from the most probable set of phases revealed 22 out of 38 non-hydrogen atoms. The remaining atoms were found from difference maps which showed, at an early stage, two possible positions, C(8) and C(8′), for one C atom. These were given variable occupancy in subsequent refinement cycles using *XFLS*-3. In these refinement cycles the scattering factors for non-hydrogen atoms were those of Cromer & Mann (1968). For F_o weighting, $\sigma(I)$ was taken as $(\text{scan}+B_1+B_2)^{1/2}$ and reflexions having $[\text{scan}-(B_1+B_2)]$ less than this were omitted from refinement leaving 2858 independent reflexions; $\sigma(F_o)$ was taken as $[\{\sigma(I)/\text{Lp}\}^2+0{\cdot}02F_o^4]^{1/2}/2F_o$ where Lp is the Lorentz-polarization factor.

Virtually all H atoms were found on the final difference map including both peaks associated with C(8) and C(8′). All H atoms were given theoretically calculated positions (C–H = 1·0 Å) with isotropic temperature factors 6·0 Å^2. Those on C(8) and C(8′) showed occupancies 0·59 and 0·41. During final refinement cycles the data were divided into six groups according to the different attenuators used. The final residual was 0·079.

Discussion. The preceding paper (Cheng & Nyburg, 1976) reports the crystal structure of one of the two photodimers obtained from 1,1-diphenyl-1-silacyclohexan-2-one (Brook, Pierce & Duff, 1975). This paper reports the crystal and molecular structure of dimer II.

The atomic parameters obtained from the last cycle of least-squares refinement are given in Table 1. They confirm the molecular assignment tentatively ascribed by Brook *et al.* (1975). Bond lengths and angles are shown in Fig. 1. An *ORTEP* plot of the molecule is shown in Fig. 2. As we have noted, one C atom of ring B (Fig. 1) occupies either of two positions C(8), occupancy 0·59, and C(8′) occupancy 0·41. However, the bond lengths and angles involving these atoms seemed unlikely to be correct [see insets to Fig. 1(*a*) and (*b*)]. Note in particular C(7)–C(8) 1·45, C(7)–C(8′) 1·36, C(8)–C(9) 1·64, C(8′)–C(9) 1·66 Å, and also angles C(6)–C(7)–C(8′) 132·5° and C(8′)–C(9)–C(10) 104·9°. We made two unsuccessful attempts to improve the model. To see whether C(8) and C(8′) were primarily in error we calculated new final positions for CT(8) and CT(8′) such that they were coplanar with C(7)–C(8)–C(9) and C(7)–C(8′)–C(9), respectively, but at 1·54 Å from C(7) and C(9) in both cases. Coordinates are given in Table 2. Keeping the positions of C(7), CT(8), CT(8′) and C(9) fixed, anisotropic least-squares refinement gave a residual 0·0815. The Hamilton (1965) ratio test indicated that this is a significantly inferior model.

As an alternative it seemed possible that some of the atypical bond lengths and atypical angle are due to both C(7) and C(9) having pairs of disordered positions C(7′), C(7″) and C(9), C(9″) matching those of C(8) and C(8′). These two pairs of positions will undoubtedly be too close to be resolved by least-squares methods. Accordingly we attempted to infer where these pairs of disordered positions might be. From the outset it is clear that a compromise has to be made. If we accept that the coordinates of C(6), C(8), C(8′) and C(10) are without substantial error then any idealized bond lengths assumed from C(7′), C(7″) and C(9′), C(9″) to their neighbours will govern the internal angles at these atoms. However, C(6)–C(8) and C(6)–C(8′) differ quite significantly, 2·482 and 2·609 Å, so that any assumed bond lengths will give different angles at the two positions of C(7); similarly for the two positions of C(9) because C(8)–C(10) is 2·710 and C(8′)–C(10) is 2·516 Å. The best compromise was to choose what in fact are reasonable bond lengths, 1·54 Å, for the remainder. These give bond angles 109·4° at C(7′) and 118·2° at C(7″) (*i.e.*, one too small, one reasonable) and similarly at C(9′), C(9″) 124·7° and 110·6° (one too large, one too small).

Fixing the positions of C(7′), C(8), C(9′) (occupancies 0·59), C(7″), C(8′), C(9″) (occupancies 0·41) and of C(6), C(10) a least-squares refinement cycle gave non-positive definite temperature factors for C(9″). [The correlation of anisotropic temperature factors in these disordered pairs of atoms is extremely high. C(7′) and its image C(7″) are only 0·11 Å apart and C(9′), C(9″) are 0·22 Å apart.] Thus in a second cycle C(9″) was restricted to isotropic motion. The residual 0·0842 was slightly higher than previously (0·0785), as might be expected from the smaller number of variable parameters. However, for a significantly better model at the 0·5% level, R would have to be 0·079. We felt that further refinement cycles would not lower R significantly.

As far as the conformations of rings B and B' and the planarity of the carbonyl system are concerned, the conclusions are the same whether based on C(8), C(8′), C(7) and C(9) or their modified trial positions.

Because of our failure to find a significantly improved alternative set of positions for the disordered atoms F_c values were calculated from the parameters listed in Table 1.*

Both ring B and B' have chair conformations and the carbonyl system is closely coplanar. [Data for least-squares planes have been deposited.]*

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

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Si(1)	7426 (1)	4752 (2)	4604 (1)	44 (1)	172 (3)	29 (1)	2 (1)	10 (10)	−3 (1)
Si(2)	7735 (1)	5737 (2)	2667 (1)	39 (1)	178 (3)	28 (0)	0 (1)	8 (0)	−4 (1)
O(1)	7576 (2)	5091 (4)	3865 (2)	54 (2)	157 (6)	28 (1)	2 (3)	12 (1)	−2 (2)
O(2)	6343 (3)	7013 (6)	3643 (2)	50 (2)	276 (10)	47 (2)	18 (4)	18 (1)	11 (3)
C(1)	7602 (3)	6540 (7)	3504 (3)	41 (2)	142 (9)	32 (2)	2 (4)	7 (2)	8 (3)
C(2)	8290 (4)	7564 (7)	3898 (3)	60 (3)	168 (10)	35 (2)	−18 (4)	9 (2)	−12 (4)
C(3)	8182 (4)	8560 (8)	4483 (3)	66 (3)	190 (12)	42 (2)	−12 (5)	9 (2)	−21 (4)
C(4)	8196 (5)	7624 (8)	5122 (4)	83 (4)	201 (12)	37 (2)	−13 (6)	9 (2)	−29 (4)
C(5)	7465 (4)	6610 (8)	5102 (3)	74 (4)	236 (13)	34 (2)	1 (6)	15 (2)	−13 (4)
C(6)	6844 (4)	7449 (8)	3391 (3)	51 (3)	199 (12)	36 (2)	5 (5)	13 (2)	−8 (4)
C(7)	6682 (5)	8874 (9)	2940 (4)	100 (5)	237 (16)	47 (3)	51 (7)	30 (3)	32 (5)
C(8)	6448 (7)	8518 (14)	2228 (6)	75 (7)	235 (24)	37 (5)	55 (10)	5 (4)	7 (8)
C(8′)	7086 (10)	9576 (21)	2549 (9)	63 (10)	203 (38)	56 (9)	13 (14)	15 (7)	22 (13)
C(9)	7158 (6)	8601 (10)	1872 (4)	107 (5)	210 (16)	39 (3)	37 (8)	25 (3)	36 (5)
C(10)	7849 (4)	7493 (9)	2124 (3)	67 (3)	272 (15)	35 (2)	−9 (6)	16 (2)	15 (5)
C(11)	6500 (4)	3567 (8)	4498 (3)	46 (3)	221 (11)	35 (2)	−14 (4)	14 (2)	−7 (4)
C(12)	5800 (4)	4304 (9)	4488 (4)	52 (3)	257 (15)	52 (3)	21 (6)	18 (2)	29 (5)
C(13)	5112 (4)	3432 (12)	4370 (4)	49 (3)	350 (19)	64 (4)	6 (7)	18 (3)	8 (7)
C(14)	5133 (5)	1820 (13)	4266 (4)	54 (4)	346 (22)	58 (3)	−27 (7)	13 (3)	−13 (7)
C(15)	5815 (5)	1049 (10)	4280 (5)	67 (4)	267 (17)	80 (4)	−30 (7)	22 (3)	−51 (7)
C(16)	6496 (4)	1939 (10)	4405 (4)	61 (3)	249 (16)	70 (4)	−16 (6)	26 (3)	−52 (6)
C(17)	8259 (3)	3458 (7)	5045 (3)	48 (3)	177 (11)	29 (2)	−12 (4)	5 (2)	4 (3)
C(18)	8896 (4)	3131 (8)	4786 (3)	46 (3)	208 (12)	39 (2)	2 (5)	9 (2)	13 (4)
C(19)	9522 (4)	2225 (9)	5124 (4)	56 (3)	242 (14)	48 (3)	−1 (5)	11 (2)	11 (5)
C(20)	9548 (4)	1586 (9)	5737 (4)	50 (3)	221 (13)	54 (3)	−5 (5)	3 (3)	10 (5)
C(21)	8945 (5)	1856 (9)	6012 (4)	80 (4)	230 (14)	35 (2)	−15 (7)	2 (3)	18 (5)
C(22)	8308 (4)	2781 (8)	5670 (3)	63 (3)	208 (12)	38 (2)	−3 (5)	13 (2)	5 (4)
C(23)	8640 (3)	4455 (8)	2875 (3)	43 (2)	188 (12)	31 (2)	6 (4)	8 (2)	1 (4)
C(24)	8574 (4)	2814 (9)	2843 (4)	41 (3)	233 (13)	49 (3)	4 (5)	10 (2)	7 (4)
C(25)	9232 (5)	1852 (10)	3019 (4)	64 (4)	209 (15)	60 (3)	15 (6)	12 (3)	14 (5)
C(26)	9959 (4)	2531 (11)	3217 (4)	47 (3)	306 (16)	54 (3)	23 (6)	12 (2)	0 (5)
C(27)	10031 (4)	4127 (11)	3253 (4)	40 (3)	275 (19)	57 (3)	−5 (6)	10 (2)	−10 (6)
C(28)	9379 (4)	5114 (9)	3075 (4)	38 (2)	241 (14)	54 (3)	−7 (5)	13 (2)	−11 (5)
C(29)	6882 (3)	4509 (8)	2213 (3)	39 (2)	218 (13)	31 (2)	13 (4)	3 (2)	−10 (4)
C(30)	6805 (4)	4060 (9)	1550 (3)	56 (3)	268 (16)	38 (2)	14 (6)	8 (2)	−22 (5)
C(31)	6178 (5)	3111 (10)	1204 (4)	69 (4)	301 (16)	43 (3)	11 (7)	−4 (3)	−42 (5)
C(32)	5618 (5)	2634 (10)	1481 (5)	50 (4)	239 (16)	82 (4)	7 (6)	−11 (3)	−45 (6)
C(33)	5697 (4)	3032 (10)	2153 (5)	51 (3)	269 (15)	66 (4)	−13 (6)	12 (3)	−25 (6)
C(34)	6317 (4)	3928 (9)	2534 (4)	47 (3)	237 (14)	42 (2)	−18 (5)	5 (2)	−22 (5)

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* Lists of structure factors and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31387 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

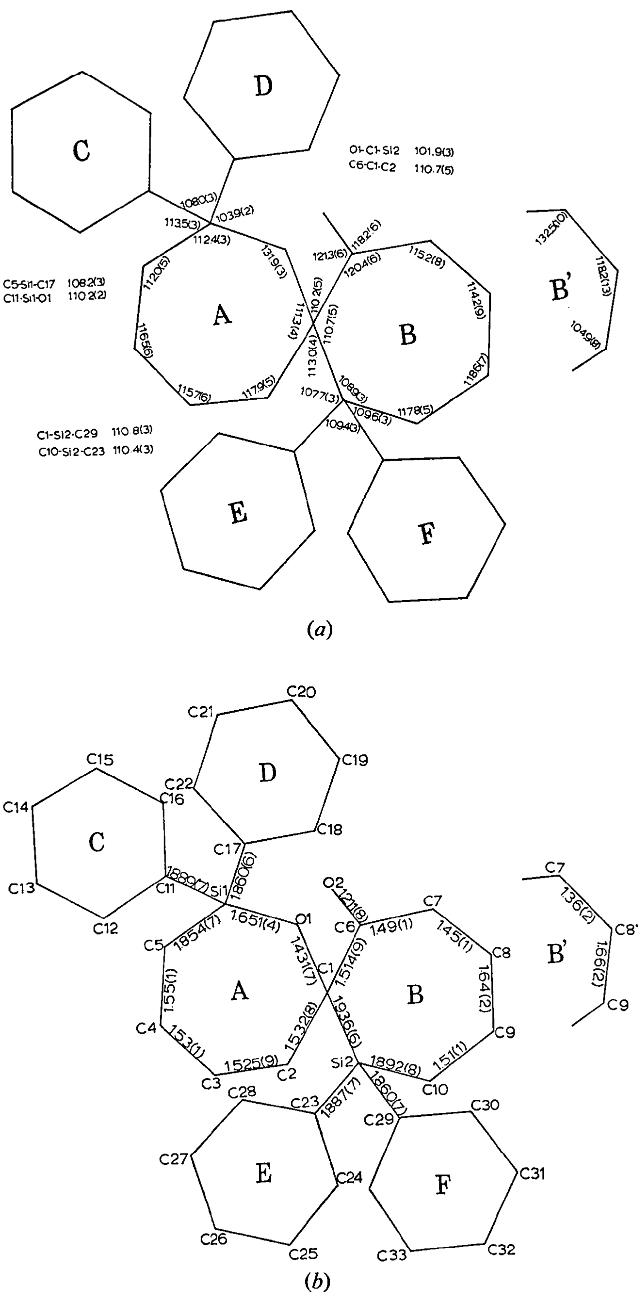

Fig. 1. (*a*) Bond lengths; (*b*) bond angles.

The phenyl rings attached to the Si atoms deserve no special comments except that all the bond angles at Si are tetrahedral.

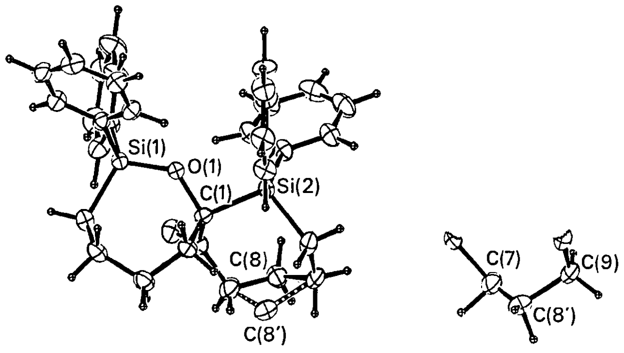

Fig. 2. *ORTEP* plot of dimer II showing 20% probability thermal ellipsoids. Hydrogen positions in main diagram are those when C(8) is as shown. In inset on right, hydrogen positions are those when C(8') is as shown.

There is a striking difference in the overall conformations of the oxaheterocyclic rings in this dimer and in dimer I. This is illustrated in Fig. 3 of the preceding paper where the two molecules are viewed normal to the 'flaps' C(6), C(7), O (dimer I) and C(2), C(1), O (dimer II). The corresponding internal angles in the two rings are virtually identical except for the crucial angles at C(7) 116·7 (3)° (dimer I) and at C(7) 109·4 (4)° (dimer II). The general effect to be excepted is the smaller this angle, the greater the angle between the 'flap' and the mean plane of the remaining atoms. Although not marked, this effect can be seen in the figure. Each conformer is still flexible, however, and in dimer I compared to dimer II C(4) has been flipped out of the mean plane. The consequence of twisting is so extreme that the ring of dimer I can no longer be said to have the chair conformation of the ring in dimer II.

There are no unusually short molecular contacts. In particular, there is ample room for C(8) and its attached H atoms to occupy either of the disordered positions.

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