ring (Fig. 3) fusion in (1) and a *cis* ring fusion in (2) necessitates the following differences. Ring *B* in (1) is in a chair conformation as is easily seen in the figure and by the torsional angles around this ring (3a—4—4a—8a—9—9a, beginning with ∠9a—3a—4—4a: −53·1, 40·2, −37·8, 47·6, −60·1, 64·0°). In contrast, in (2) ring *B* has a twist-boat conformation (torsional angles 57·6, −25·9, −33·6, 66·2, −34·6, −25·4°). In addition, there are certain bond-angle differences as shown in Table 3. The largest differences are seen at the ring-junction C atoms 3a, 4a, 8a and 9a.

Dienes (4) and (5) were synthesized from hydrindanones (11) and (12), respectively.* Stereospecific syntheses of (11) and (12) have been previously reported (Corey & Engler, 1984) and the crystal structures presently reported establish the relative configuration of the ring fusion of (11) and (12) as well as the stereochemical course of the 4 + 2 cycloadditions between dienes (4) and (5) and dienophile (6).

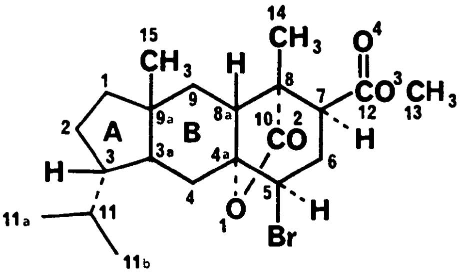

Fig. 3. IUPAC numbering scheme for (1) and (2).

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* The details of the syntheses of (4) and (5) will be reported at a later date.

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Hexaphenylcyclotrisiloxane, $C_{36}H_{30}O_3Si_3$, a Redetermination

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Abstract. $M_r = 594·89$, orthorhombic, $P2_12_12_1$, $a = 20·247$ (6), $b = 15·807$ (3), $c = 10·109$ (2) Å, $V = 3235·3$ Å^3, $Z = 4$, $D_m = 1·234$, $D_x = 1·221$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 1·514$ mm^{-1}, $F(000) = 1248$, $T = 293$ K. Final $R = 0·0718$ for 2211 unique observed reflections. A redetermination of the structure described by Bokii, Zakharova & Struchkov [*Zh. Strukt. Khim.* (1972), **13**, 291–297] who had insufficient data to carry out an independent refinement of every atom and assumed that the phenyl groups were perfect hexagons (their *R* 17%) is presented. This structure determination gives the same major features and shows that there are small but significant distortions of the phenyl rings, presumably resulting from the $\pm M$ effect of the silicon atoms.

Introduction. This structure determination is part of a programme of investigation of cyclic oligomers of silane derivatives, prompted by our interest in the unique liquid-crystalline phase of diisobutylsilanediol which we have suggested is of the columnar discotic type.

In general, discogenic molecules have well defined and clearly characteristic types of structures with a central rigid aromatic core, surrounded by an annulus of radiating alkyl chains (usually of the range C_5—C_9). When viewed in this light, diisobutylsilanediol appears to be totally unsuitable for mesophase formation and we have therefore postulated that the basic structural unit of the mesophase was actually a cyclic dimer rather than an individual molecule. Following a preliminary investigation of the crystalline solid, we modified our model to a cyclic trimer.

The structure of the title compound (I) has previously been determined by Bokii *et al.* (1972). The model, which they used for refinement, assumed that the phenyl rings had idealized bond lengths (of 1·4 Å)

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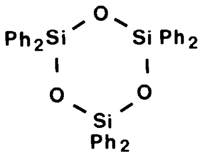
and C—C—C bond angles (of 120°) and behaved as rigid bodies. Their data refined to a final $R = 0{\cdot}167$. In view of the appreciable distortion of aromatic rings observed in other silane derivatives, we considered it desirable to carry out a more accurate structure determination, with enough data to allow a full refinement of all the atom parameters.



(I)

Experimental. Compound prepared by Dr R. Bushby by a condensation reaction of diphenylsilanediol, recrystallized from ethyl acetate, rectangular prism, $0{\cdot}40 \times 0{\cdot}35 \times 0{\cdot}15$ mm. D_m by flotation in ethanol/carbon tetrachloride. Data collected with an Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$; reflections measured for two octants to $2\theta = 140°$ for the ranges of h, k and l ± 24, 0 to 19 and 0 to 12 respectively; reflections $36\bar{1}$ and $\bar{3}\bar{6}1$ used as intensity controls (104 measurements each) gave average counts of 1219 and 913 with σ's (calculated) of 41 and 42. Lattice parameters determined from 67 θ measurements ($13 < \theta < 24°$). No absorption correction. 6751 reflections measured, 2651 of comparable height to background rejected; data merged using *SHELX*76 (Sheldrick, 1976), 2516 unique reflections, $R = 0{\cdot}044$, 305 reflections eliminated with $F < 3\sigma(F)$; structure solved with *MULTAN*80 (Main *et al.*, 1980), non-H atoms refined by least squares (using F's) first with isotropic thermal parameters then anisotropic, H-atom coordinates established from a difference Fourier map (22) or calculated (8) and their thermal vibration parameters fixed at equivalent $U_{\rm iso}$ of atom to which each is attached; anisotropic scale factors applied (Shakked & Rabinovich, 1977); for final cycle, max. shift/error $= 0{\cdot}034$, av. $= 0{\cdot}004$, final $R = 0{\cdot}0718$ for 2211 reflections, unit weights used. Difference Fourier map max. 0·36, min. $-0{\cdot}40$ e Å^{-3}; atom scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. *Fractional atom coordinates* ($\times 10^4$), *with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$)

	x	y	z	$U_{\rm eq}$*
Si(1)	9071 (1)	291 (2)	5396 (3)	537
Si(2)	10370 (1)	−605 (2)	5210 (3)	541
Si(3)	9128 (1)	−1471 (2)	4287 (3)	531
O(1)	9868 (3)	183 (4)	5560 (7)	541
O(2)	9924 (3)	−1334 (4)	4450 (6)	507
O(3)	8776 (3)	−609 (4)	4852 (6)	507
C(11)	11010 (5)	−236 (6)	4028 (11)	597
C(12)	11610 (5)	99 (7)	4504 (13)	706
C(13)	12084 (6)	436 (9)	3649 (15)	849
C(14)	11980 (6)	409 (9)	2337 (19)	991
C(15)	11384 (8)	103 (10)	1850 (13)	1061
C(16)	10915 (7)	−256 (9)	2679 (14)	896
C(21)	10707 (5)	−1043 (6)	6728 (11)	567
C(22)	11292 (5)	−1540 (7)	6758 (12)	716
C(23)	11516 (7)	−1930 (9)	7884 (17)	1000
C(24)	11193 (9)	−1787 (9)	9037 (14)	1000
C(25)	10608 (9)	−1309 (10)	9057 (15)	1143
C(26)	10395 (7)	−921 (8)	7933 (13)	875
C(31)	8715 (5)	546 (6)	7038 (11)	577
C(32)	9073 (6)	986 (7)	7978 (12)	803
C(33)	8799 (8)	1246 (8)	9136 (13)	893
C(34)	8127 (7)	1071 (8)	9426 (13)	855
C(35)	7788 (6)	656 (9)	8534 (14)	846
C(36)	8038 (5)	380 (8)	7328 (13)	734
C(41)	8889 (5)	1125 (6)	4140 (10)	563
C(42)	8247 (6)	1366 (7)	3911 (12)	730
C(43)	8108 (6)	1997 (8)	3027 (14)	827
C(44)	8586 (8)	2428 (8)	2389 (13)	895
C(45)	9259 (7)	2212 (9)	2635 (15)	965
C(46)	9392 (6)	1555 (8)	3490 (12)	782
C(51)	8871 (5)	−2404 (6)	5283 (11)	592
C(52)	9266 (5)	−2773 (7)	6231 (13)	791
C(53)	9059 (7)	−3450 (9)	7005 (15)	1071
C(54)	8419 (6)	−3771 (8)	6804 (13)	815
C(55)	8005 (5)	−3400 (7)	5911 (13)	745
C(56)	8211 (5)	−2718 (7)	5149 (13)	693
C(61)	8941 (5)	−1611 (7)	2522 (11)	588
C(62)	8908 (6)	−919 (7)	1645 (11)	739
C(63)	8794 (7)	−1012 (8)	324 (13)	880
C(64)	8740 (7)	−1813 (10)	−252 (15)	945
C(65)	8763 (8)	−2506 (9)	626 (15)	1055
C(66)	8872 (7)	−2397 (7)	1919 (12)	843

* $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Discussion. Table 1* lists the atom coordinates and equivalent $U_{\rm iso}$'s. Table 2 contains bond distances and angles. Fig. 1 shows the molecule and the numbering scheme and Fig. 2 is a c-axis projection of the unit cell. Although an isolated molecule (*e.g.* in solution) might be expected to take up the structure of highest possible symmetry (with point-group symmetry of perhaps $3m$ or 32), in the crystal structure the molecules lie in sites with no symmetry. Packing considerations would, therefore, be expected to lead to some slight departure from perfect threefold symmetry and the tables have been laid out with corresponding parameters from each part of the molecule on the same lines to facilitate their comparison.

It is apparent that the overall departure from the idealized structure of Bokii *et al.* (1972) is not very great. Those distortions which occur can be considered to be of two types:

(1) those due to 'chemical' effects within the molecule such as I and M effects;

(2) those due to the difference of local environment, *i.e.* the fact that the phenyl groups do not occupy identical sites.

Distortions of the first type should occur symmetrically and should, therefore, be apparent in the molecular parameters averaged over corresponding parts of the molecule. Distortions of the second type, however, will be apparently random and should, in most instances, give an average of zero.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, torsion angles and least-squares best planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39774 (20 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* (°)

$i =$	1	2	3	4	5	6	Av.
C(*i*1)—C(*i*2)	1·410 (14)	1·422 (13)	1·382 (14)	1·375 (14)	1·379 (14)	1·410 (14)	1·396
C(*i*2)—C(*i*3)	1·397 (16)	1·371 (17)	1·359 (16)	1·368 (16)	1·391 (15)	1·363 (16)	1·375
C(*i*3)—C(*i*4)	1·343 (20)	1·356 (20)	1·420 (18)	1·347 (17)	1·407 (17)	1·398 (17)	1·378
C(*i*4)—C(*i*5)	1·390 (19)	1·404 (20)	1·309 (17)	1·426 (18)	1·363 (16)	1·410 (18)	1·384
C(*i*5)—C(*i*6)	1·387 (17)	1·361 (18)	1·390 (16)	1·378 (16)	1·390 (15)	1·337 (17)	1·374
C(*i*6)—C(*i*1)	1·378 (16)	1·385 (15)	1·426 (13)	1·390 (14)	1·432 (13)	1·392 (15)	1·400
Av.	1·384	1·383	1·381	1·381	1·394	1·395	

Si(1)—O(1)	1·632 (6)	Si(2)—O(1)	1·646 (6)	Si(3)—O(2)	1·633 (6)
Si(1)—O(3)	1·637 (6)	Si(2)—O(2)	1·654 (7)	Si(3)—O(3)	1·640 (6)

$i =$	1	2	3	4	5	6
C(*i*6)—C(*i*1)—C(*i*2)	117·8 (11)	116·0 (19)	117·1 (11)	118·6 (10)	117·5 (19)	114·4 (11)
C(*i*1)—C(*i*2)—C(*i*3)	121·6 (12)	122·7 (12)	122·1 (12)	120·4 (11)	122·7 (11)	122·7 (11)
C(*i*2)—C(*i*3)—C(*i*4)	119·4 (13)	118·7 (14)	120·6 (13)	122·2 (12)	118·3 (12)	121·3 (12)
C(*i*3)—C(*i*4)—C(*i*5)	119·8 (13)	120·5 (14)	117·2 (12)	118·8 (12)	120·5 (11)	116·0 (13)
C(*i*4)—C(*i*5)—C(*i*6)	121·5 (14)	119·8 (15)	124·8 (12)	118·5 (12)	121·1 (10)	121·4 (14)
C(*i*5)—C(*i*6)—C(*i*1)	119·6 (13)	121·8 (13)	118·2 (12)	121·4 (11)	119·7 (11)	124·0 (13)

O(3)—Si(1)—O(1)	107·7 (3)	O(1)—Si(2)—O(2)	106·8 (3)	O(2)—Si(3)—O(3)	106·5 (3)
C(31)—Si(1)—O(1)	108·4 (4)	C(11)—Si(2)—O(2)	107·5 (4)	C(61)—Si(3)—O(3)	110·4 (4)
C(31)—Si(1)—O(3)	110·4 (4)	C(11)—Si(2)—O(1)	109·3 (4)	C(61)—Si(3)—O(2)	108·5 (4)
C(41)—Si(1)—O(1)	109·7 (4)	C(21)—Si(2)—O(2)	109·4 (4)	C(51)—Si(3)—O(3)	110·4 (4)
C(41)—Si(1)—O(3)	108·3 (4)	C(21)—Si(2)—O(1)	109·8 (4)	C(51)—Si(3)—O(2)	109·1 (4)
C(41)—Si(1)—C(31)	112·3 (5)	C(21)—Si(2)—C(11)	113·7 (5)	C(51)—Si(3)—C(61)	111·8 (5)

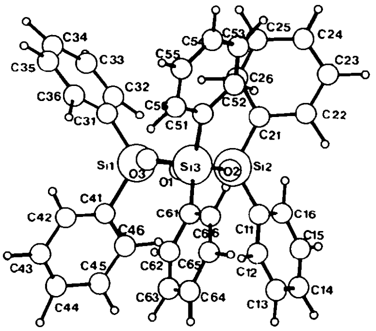

Fig. 1. View of the title compound with atom labels drawn by the program *PLUTO*78 (Motherwell & Clegg, 1978).

The six-membered siloxane ring is virtually planar with threefold symmetry. The maximum deviation from the best plane is only 0·084 (7) Å. The Si—O—Si angles are appreciably greater than expected for pure sp^2 hybridization, being 132–133°. This feature has been found in other cyclic trisiloxanes, *e.g. trans*- and *cis*-1,2,3-trimethyl-1,2,3-triphenylcyclotrisiloxane (Shklover, Bokii, Struchkov, Andrianov, Zavin & Svistunov, 1974*a,b*). The phenyl rings are all virtually planar, the maximum deviation from the best plane being only 0·03 (2) Å. They are, however, not perfect hexagons, as assumed by Bokii *et al.* (1972). There is an appreciable shortening of the C—C bonds in the 2,3 and 5,6 positions, the mean length of the twelve bonds of this type being 1·375 Å together with a small but significant decrease in the C(*i*2)—C(*i*1)—C(*i*6) angle to a mean value of 116·9 (13)°. We interpret this in terms of a significant $\pm M$ effect of the silicon atoms on the aromatic rings.

We thank the University Computing Service of the University of Leeds for the provision of facilities and Dr R. Bushby, Department of Organic Chemistry, University of Leeds, for the preparation of the title compound.

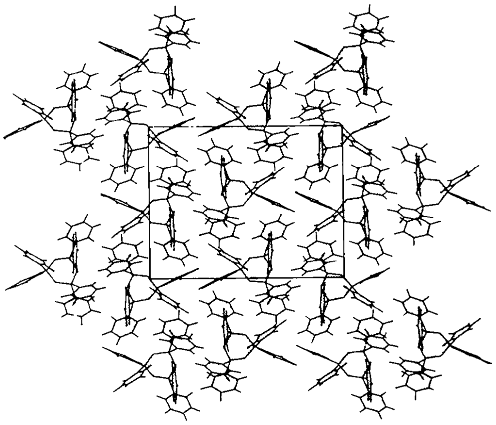

Fig. 2. Projection of the crystal structure along **c** (*PLUTO*78 plus shading). **a** horizontal, **b** vertical, origin: lower left-hand corner.

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