Crystal and Molecular Structure of 3,7-Dihydro-1,1,3,3,5,5,7,7-octamethyl-1*H*,5*H*-benzo[1,2-*c*:4,5-*c'*]bis[1,2,5]oxadisilole

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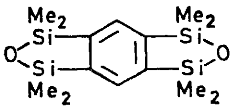
Crystals of the title compound are monoclinic, space group $P2_1/c$ with a = 10·669(9), b = 9·159(8), c = 11·518(10) Å, β = 115·2(1)°. Diffractometer data for 1401 planes were refined by least squares to R 0·045. The nature of the molecule was unknown and the structure was determined by direct methods. Bond lengths in the oxadisilole ring, which has approximate C_{2v} symmetry, are: C–C 1·411, Si–C 1·882, and Si–O 1·647 Å.

THE work-up of the products of the silylation of hexabromobenzene with Me_2SiHCl and magnesium in tetrahydrofuran yields, besides the expected $(CSiMe_2H)_6$, well formed crystals m.p. 244 °C in insufficient quantity for identification by the usual chemical and spectroscopic methods.[1] We have carried out a single-crystal X-ray analysis on this material and have established its structure as (I).



(I)

EXPERIMENTAL

Crystal Data.—$C_{14}H_{26}Si_4O_2$, M = 338·7, Monoclinic, a = 10·669(9), b = 9·159(8), c = 11·518(10) Å, β = 115·2(1)°, U = 1018·4 Å^3, D_m = 1108, Z = 2, D_c = 1104 kg. m^{-3}. Space group $P2_1/c$ (C^5_{2h}, No. 14). Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 249 m^{-1}.

Unit-cell dimensions were obtained from precession photographs by a least-squares process, the standard deviations being multiplied by 1·5 to allow for systematic errors. Intensity data were collected around c on a linear diffractometer equipped with a graphite monochromator. The maximum value of θ was 25° and the 1401 strongest planes were used for the analysis.

Structure Determination and Refinement.—The signs of the 148 planes with the largest E values were found by a computer, by direct methods.[2] Seven planes with large E values and many interactions were used as a starting set. Three were given a positive sign to fix the origin and the symbols a, b, c, and d were assigned to the other four. Symbols and/or signs were accepted for other planes involved in sign relations of high probability. The E map based on these phases showed the molecule but the nature of the atom bonded to the two silicon atoms was not clear. This atom was identified as oxygen from chemical evidence. This trial structure was refined by a block-diagonal (3 × 3 and 1 × 1 or 6 × 6) least-squares method; weights[3] were given by $w^{-1} = 1{\cdot}15 + |F_o| + 0{\cdot}0053|F_o|^2$. Hydrogen atoms were found from a difference-Fourier map when R was 0·067 and refinement converged with R 0·045. Hydrogen atoms were given isotropic temperature factors 0·01 unit of U higher than the carbon atoms to which they are bonded.

RESULTS AND DISCUSSION

Tables 1—3 give co-ordinates, thermal parameters, and bond lengths and angles, with their corresponding standard deviations. The Figure shows the molecule projected on the least-square plane through the benzoid ring, together with the atoms labelling. Final observed and calculated structure factors are listed in

TABLE 1

Final co-ordinates (Å) and standard deviations

	X	Y	Z
Si(1)	1·9317(9)	0·6582(10)	5·2485(10)
Si(2)	3·3956(10)	−1·3445(11)	7·3605(12)
O	1·8888(26)	−0·4606(28)	6·4329(30)
C(1)	0·5319(42)	0·3021(58)	3·3600(46)
C(2)	1·6709(49)	2·3600(46)	5·8232(56)
C(3)	2·9751(57)	−3·1476(47)	6·9967(64)
C(4)	4·1110(54)	−1·0176(67)	9·3637(51)
C(5)	4·6028(32)	−0·6434(32)	6·5143(34)
C(6)	3·8716(32)	0·3565(30)	5·4596(33)
C(7)	4·6141(32)	0·9906(32)	4·7249(34)
H(11)	−0·38(5)	0·36(6)	3·34(4)
H(12)	0·66(8)	−0·45(6)	2·90(8)
H(13)	0·79(7)	0·77(9)	2·72(7)
H(21)	0·67(7)	2·50(7)	5·59(6)
H(22)	2·07(7)	3·04(7)	5·26(11)
H(23)	2·22(5)	2·49(4)	6·83(4)
H(31)	2·27(7)	−3·45(6)	7·37(5)
H(32)	2·48(7)	−3·25(7)	5·88(6)
H(33)	3·79(4)	−3·66(3)	7·21(5)
H(41)	3·43(5)	−1·22(5)	9·83(4)
H(42)	4·04(5)	0·02(5)	9·72(5)
H(43)	5·03(5)	−1·46(6)	9·93(4)
H(7)	4·10(3)	1·72(3)	3·97(4)

TABLE 2

Temperature factors * (× 10^4 Å^2), U_{ij} for heavy atoms with standard deviations

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Si(1)	366(4)	602(5)	503(5)	70(7)	66(8)	379(7)
Si(2)	495(5)	657(6)	632(6)	59(8)	331(9)	662(9)
O	474(12)	826(18)	785(17)	171(23)	437(27)	741(24)
C(1)	460(18)	1433(45)	606(23)	−238(47)	−315(53)	368(32)
C(2)	670(24)	759(27)	922(33)	357(42)	−158(49)	525(45)
C(3)	928(32)	699(28)	1359(41)	−1(46)	446(53)	1419(60)
C(4)	872(31)	1553(51)	625(29)	322(63)	444(61)	860(48)
C(5)	415(14)	496(16)	470(17)	−42(25)	26(28)	429(24)
C(6)	378(13)	469(16)	444(16)	−38(23)	−15(25)	348(23)
C(7)	421(15)	508(17)	496(18)	59(25)	164(27)	392(26)

* In the form: $\exp - 2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13})$.

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[1] W. Fink, unpublished work.

[2] D. Sayre, *Acta Cryst.*, 1952, **5**, 60; W. Cochran, *Acta Cryst.*, 1952, **5**, 65; W. H. Zachariasen, *Acta Cryst.*, 1952, **5**, 68; H. Hauptman and J. Karle, 'Solution of the Phase Problem, I: The Centrosymmetric Crystal,' A.C.A. Monograph, No. 3, 1953.

[3] D. W. J. Cruickshank, D. E. Pilling, A. Bujosa, F. M. Lovell, and M. R. Truter, 'Computing Methods and the Phase Problem in X-Ray Crystal Analysis,' Pergamon Press, Oxford, 1961, p. 32.

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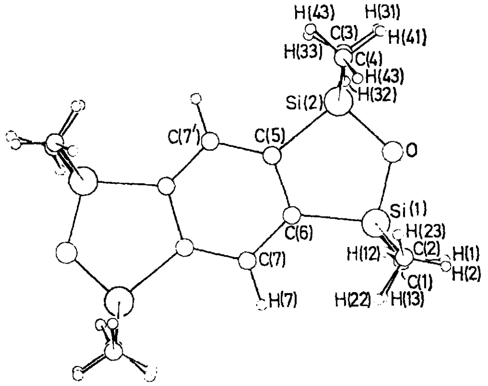
The molecule has a crystallographic centre of symmetry and (Table 1 and Figure) approximates quite closely to the symmetry *mmm* (D_{2h}).

TABLE 3

Bond lengths (Å) and angles (°), with standard deviations

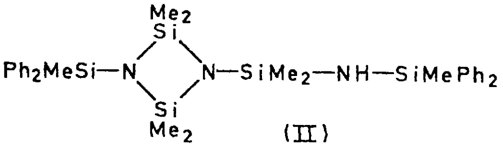
(*a*) Lengths	
Si(1)–O	1·643(3)
Si(2)–O	1·650(3)
Mean Si–O	1·647
Si(1)–C(1)	1·844(5)
Si(1)–C(2)	1·850(5)
Si(2)–C(3)	1·852(6)
Si(2)–C(4)	1·847(6)
Mean Si–C(sp^3)	1·848
Si(1)–C(6)	1·884(3)
Si(2)–C(5)	1·880(3)
Mean Si–C(sp^2)	1·882
C(7′)–C(5)	1·401(5)
C(5)–C(6)	1·411(5)
C(6)–C(7)	1·399(5)
Mean C–C	1·404

(*b*) Angles	
Six-membered ring	
C(7′)–C(5)–C(6)	119·2(3)
C(5)–C(6)–C(7)	119·5(3)
C(6)–C(7)–C(5′)	121·3(3)
Five-membered ring	
Si(1)–O–Si(2)	118·2(2)
O–Si(1)–C(6)	98·7(2)
Si(1)–C(6)–C(5)	112·2(2)
C(6)–C(5)–Si(2)	111·9(2)
C(5)–Si(2)–O	98·9(2)
Other angles	
C(1)–Si(1)–C(2)	110·5(2)
C(1)–Si(1)–C(6)	112·3(2)
C(2)–Si(1)–C(6)	112·8(2)
C(1)–Si(1)–O	111·4(2)
C(2)–Si(1)–O	110·6(2)
C(3)–Si(2)–C(4)	109·6(3)
C(3)–Si(2)–C(5)	114·2(2)
C(4)–Si(2)–C(5)	113·3(2)
C(3)–Si(2)–O	109·5(2)
C(4)–Si(2)–O	110·8(2)
Si(1)–C(6)–C(7)	128·3(3)
Si(2)–C(5)–C(7′)	128·9(3)

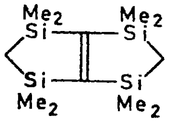


The molecule projected on the least-squares plane of the benzenoid ring, showing the atoms labelling

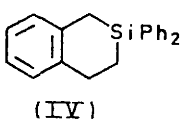
The Si–C(sp^2) bond length [1·882(3) Å], is longer than the Si–C(sp^3) length [1·848(6) Å]. However, the methyl-group carbon atoms have much higher temperature factors than the other carbon atoms so that a correction to the bond lengths by allowing for thermal motion should lengthen the Si–C(sp^3) bond more than the Si–C(sp_4^2) bond. Similar bond-length differences are also observed in (II)[4] and (III)[5] in which the



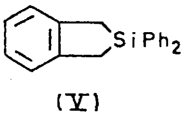
(II)



(III)



(IV)



(V)

C(sp^3) atoms undergo more thermal motion than the C(sp^2) atoms. In (IV)[6] and (V),[7] however, the C(sp^3) carbons are constrained by ring formation and have about the same temperature factors as the C(sp^2) carbons: in these two compounds Si–C(sp^3) (1·885 Å) is longer than Si–C(sp^2) (1·873 (Å).

Our Si–C(sp^2) bond length [1·882(3) Å] is in reasonably good agreement with those in Ph_4Si[8] [1·872(7)], (II)[4] [1·879(10)], (IV)[6] [1·871(3)], and (V)[7] [1·876(4) Å], but it is considerably longer than that in $PhSiH_3$[9] [1·843(5) Å]. The Si–C(sp^3) bond lengths in $MeSiH_3$[10] and Me_2SiH_2[11] [1·867(1) and 1·871 Å] are longer than ours [1·848(6) Å] which should increase with a thermal motion correction although probably not to the corrected value of 1·92 Å in $(SiMe_2)_6$.[12]

The six-membered ring is planar, maximum deviation from the least-squares plane being 0·0024 Å; the five membered ring has non-zero ring-torsion angles and is therefore not planar. These torsion angles [O–Si(2) 1·97(12), Si(2)–C(5) −1·08(19), C(5)–C(6) −0·01(5), C(6)–Si(1) 1·10(20), Si(1)–O −1·97(12)°] are small, so that the deviations from planarity are not great. They show that the ring is very slightly distorted from C_{2v} (*mm*2) symmetry to the envelope form with $C_s(m)$ symmetry in which the oxygen atom is displaced from the plane of the other four atoms.

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[*] For detail see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

[4] G. Chiocciola and J. J. Daly, *J. Chem. Soc.* (*A*), 1968, 1659.

[5] H. G. v. Schnering, E. Krahě, and G. Fritz, *Z. anorg. Chem.*, 1969, **365**, 113.

[6] J. P. Vidal, J. Lapasset, and J. Falgueirettes, *Acta Cryst.*, 1972, *B*, **28**, 3137.

[7] J. P. Vidal and J. Falgueirettes, *Acta Cryst.*, 1973, *B*, **29**, 263.

[8] C. Glidewell and G. M. Sheldrick, *J. Chem. Soc.* (*A*), 1971, 3127.

[9] F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, 1956, **25**, 1218.

[10] R. W. Kilb and L. Pierce, *J. Chem. Phys.*, 1957, **27**, 108.

[11] L. Pierce, *J. Chem. Phys.*, 1959, **31**, 547.

[12] H. L. Carrell and J. Donohue, *Acta Cryst.*, 1972, *B*, **28**, 1566.