

The Crystal Structure of 2,2,5,5,7,7,10,10,-Octamethyl-2,5,7,10-tetrasil-1,6-dioxa-3,8-cyclodecadiyne

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1,6-Cyclodecadiyne *I*, in size, between the carbocyclic 1,7-cyclododecadiyne¹ and 1,5-cyclooctadiyne², was recently prepared.³ Closely related to *I* is the dioxa analogue 1,6-dioxa-3,8-cyclodecadiyne *2*, first prepared by Lespieau,⁴ but poorly characterized and in low yield. Later Sondheimer *et al.*⁵ repeated the synthesis and confirmed Lespieau's structural assignment by X-ray space group determination: *I* is present in chair form only in the crystals. A silicon analogue to the parent compound *I*, 3,3,5,5,8,8,10,10-octamethyl-10-tetrasil-1,6-cyclodecadiyne *3* has recently been synthesized.⁶ Its molecular structure was determined by X-ray crystallographic methods,⁷ whereby the chair as well as the boat conformer were shown to be present in the same crystal in the ratio 1:2.

In this paper, we present the results of the structure determination of the combined oxo- and sila-analogue to *2* and *3*, 2,2,5,5,7,7,10,10-octamethyl-2,5,7,10-tetrasil-1,6,dioxa-3,8-cyclodecadiyne, *4*. This compound was formed by hydrolysis and dimerisation of 2,5-dichloro-2,5-dimethyl-2,5-disila-3-hexyne⁸ and isolated as a byproduct in the syntheses of cyclic α silaalkynes. It is readily sublimable and forms coarse, transparent crystals of m.p. 117.0–117.5°C (closed cap.). Spectroscopic analyses are compatible with structure *4* [MS: 312 (M^+); ¹H-NMR (300 MHz, DCCl₃ (standard): 0.24 ppm (CH₃); UV (pentane): 215, 207, 202 nm].

The crystals of C₁₂H₂₄O₂Si₄, *4*, are triclinic, space group *P*1, cell dimensions ($t = -135^\circ$) $a = 6.229(1)$ Å, $b = 8.224(1)$ Å, $c = 9.481(1)$ Å, $\alpha =$

$93.08(1)^\circ$, $\beta = 104.88(1)^\circ$, $\gamma = 92.75(1)^\circ$, $Z = 1$, $D_x = 1.110$ g cm⁻³.

X-ray data were collected on a Nicolet P3/F diffractometer, MoK α -radiation, $\sin\theta/\lambda$ (max) = 0.8 Å⁻¹, $\theta/2\theta$ scan mode, scan speed 3°/min (2θ), $t = -135^\circ$ C, specimen size 0.12 × 0.20 × 0.32 mm, 3005 observed reflections ($I > 2.5\sigma(I)$). The structure was solved by direct methods⁹ and re-

Table 1. Final coordinates with estimated standard deviations.

Atom	x	y	z
Si1	.64112(4)	-.10721(3)	.74358(3)
Si2	.83613(4)	.25455(3)	.81107(3)
O	.7350(1)	.0779(1)	.7275(1)
C1	.8101(2)	-.1812(1)	.9103(1)
C2	1.0485(2)	.2171(1)	.9789(1)
C3	.6647(2)	-.2366(1)	.5832(1)
C4	.3489(2)	-.1068(2)	.7566(2)
C5	.6135(2)	.3677(1)	.8611(1)
C6	.9693(2)	.3680(2)	-.6889(1)
H31	.812(3)	-.238(2)	.582(2)
H32	.588(3)	-.189(2)	.498(2)
H33	.621(3)	-.340(3)	.586(2)
H41	.332(3)	-.044(2)	.837(2)
H42	.303(3)	-.207(2)	.767(2)
H43	.256(3)	-.069(2)	.671(2)
H51	.545(3)	.302(2)	.919(2)
H52	.512(2)	.399(2)	.775(2)
H53	.671(3)	.466(2)	.913(2)
H61	1.079(3)	.306(2)	.667(2)
H62	1.036(3)	.467(2)	.731(2)
H63	.871(3)	.384(2)	.599(2)

Table 2. Structural data with estimated standard deviations calculated from the variance-covariance matrix.

Bond lengths (Å)									
Si1	O	1.633(1)	Si2	O	1.634(1)				
Si1	C1	1.837(1)	Si2	C2	1.840(1)				
Si1	C3	1.850(1)	Si2	C5	1.842(1)				
Si1	C4	1.856(1)	Si2	C6	1.853(1)				
C1	C2	1.215(1)							
Bond angles (°)									
O	Si1	C1	107.6(1)	O	Si2	C2	108.0(1)		
O	Si1	C3	108.0(1)	O	Si2	C6	108.1(1)		
O	Si1	C4	110.2(1)	O	Si2	C5	110.4(1)		
C1	Si1	C3	109.1(1)	C2	Si2	C6	109.2(1)		
C1	Si1	C4	110.3(1)	C2	Si2	C5	109.1(1)		
C3	Si1	C4	111.5(1)	C5	Si2	C6	112.0(1)		
Si1	C1	C2	173.8(1)	Si2	C2	C1	175.1(1)		
Si1	O	Si2	146.5(1)						
Torsion angles (°)									
C1	Si1	O	Si2	-41.1(1)	C2	Si2	O	Si1	44.9(1)
C3	Si1	O	Si2	-158.8(1)	C6	Si2	O	Si1	163.0(1)
C4	Si1	O	Si2	79.1(1)	C5	Si2	O	Si1	-74.2(1)

finied by full matrix least squares calculations.¹⁰ In order to avoid effects from the asymmetry in bonding electrons, only reflections with $\sin\theta/\lambda > 0.4 \text{ \AA}^{-1}$ were included in the final calculations, refining the Si, O, and C atoms with anisotropic thermal parameters and H with isotropic temperature factors. Weights were calculated from the standard deviation in intensities, taken as $\sigma(I) = [C_T + (0.02C_N)^2]^{1/2}$ where C_T is the total number of counts and C_N the net count. The final R values for 2618 reflections were $R = 0.032$, $R_w = 0.030$ and $S = [\sum w\Delta^2/(n-m)]^{1/2} = 1.23$. Fractional coordinates with estimated standard deviations are given in Table 1. Structural data are presented in Table 2. An ORTEP plot of the molecule is shown in Fig. 1 with the numbering of the atoms. Tables of observed and calculated structure factors and of thermal parameters are available from the authors. The conformation of the molecule is of the chair type. The Si-C \equiv bond length, 1.839(1) Å, and the C \equiv C bond length, 1.215(1) Å, are both as found for the methylene analogue, 3, 1.842(2) Å and 1.216(3) Å, respectively.⁷ The large Si-O-Si angle of 146.5(1)°, the Si-O bond length of 1.634(1) Å and the Si-C(methyl) bond length of 1.852(1) Å are well within the range of corresponding values ob-

served in methyldisiloxanes.¹¹ The Si-C \equiv C-Si arrangement is not quite linear, the mean Si-C \equiv C angle being 175.5°. The effect of this is to bring the acetylenic carbon atoms further apart across the ring; the Si1-Si2 separation is 3.13 Å, whereas that of C1-C2 is 3.47 Å.

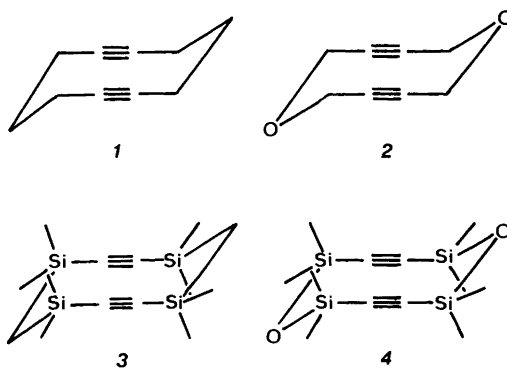


Fig. 1. ORTEP plot of the molecule 4.

References

1. a. Cram, D. J. and Allinger, N. L. *J. Amer. Chem. Soc.* 78 (1956) 2518; b. Stephens, R. D. *J. Org. Chem.* 38 (1973) 2260.
2. a. Kloster-Jensen, E. and Wirz, J. *Helv. Chim. Acta* 58 (1975) 162; b. *Angew. Chem.* 85 (1973) 723; *Angew. Chem. Int. Ed. Engl.* 12 (1973) 671.
3. Gleiter, R. G., Karcher, M. and Schäfer, W. *Tetrahedron Lett.* 26 (1985) 1635.
4. Lespieau, R. *C.R. Acad. Sci. C* 188 (1929) 502.
5. Sondheimer, F., Gaoni, Y. and Bregman, J. *Tetrahedron Lett.* L26 (1960) 25.
6. Kloster-Jensen, E. and Eliassen, G. Å. *Angew. Chem.* 97 (1985) 587; *Angew. Chem. Int. Ed. Engl.* 24 (1985) 565.
7. Eliassen, G. Å., Kloster-Jensen, E. and Rømming, C. *Acta Chem. Scand. B.* In press.
8. a. Komarov, N. V., Maroshim, Y. V., Lebedeva, A. D. and Astaf'eva, L. N. *Izvestiya Akad. Nauk. S.S.S.R.* (1963) 97; b. *Brit. Pat.* 740, 991, Nov. 23, 1955. c. Kloster-Jensen, E. *Unpublished work.*
9. Gilmore, C. J. *J. Appl. Crystallogr.* 17 (1984) 42.
10. Groth, P. *Acta Chem. Scand.* 27 (1973) 1837.
11. Barrow, M. J., Ebsworth, E. A. V. and Harding, M. M. *Acta Crystallogr. B* 35 (1979) 2093.

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