*Chemistry of Heterocyclic Compounds, Vol. 41, No. 4, 2005*

# MOLECULAR AND CRYSTAL STRUCTURE OF OCTAMETHYL-1,4-DIOXACYCLOHEXASILANE

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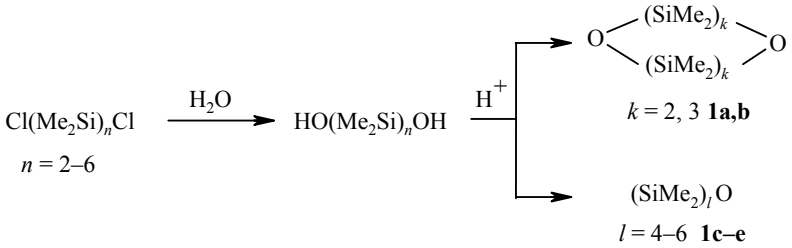
*Using X-ray diffraction, we have observed flattening of the six-membered ring in the octamethyl-1,4-dioxacyclohexasilane molecules. According to the results of a quantum-chemical calculation [B3LYP/6-311+G(d)], this flattening is due to the low barrier to hindered internal rotation about the Si–O bonds.*

**Keywords:** permethylcyclooxysilanes, internal rotation, quantum-chemical calculation, X-ray diffraction study, thermal motion.

Permethylcyclooxasilanes **1** containing two $[(Me_2Si)_kO]_2$ (**1a,b:** $k$ = 2, 3 respectively) or one $(Me_2Si)_lO$ (**1c-e:** $l$ = 4-6 respectively) oxygen atoms are organosilicon structural analogs of organic heterocyclic compounds (dioxane, THF, etc.). Oxacyclosilanes **1** are convenient starting compounds for synthesis of permethylpolyoxasilanes of the form $–[(SiMe_2)_mO]_n–$ ($m$ = 2-4, 6) by a cationic polymerization mechanism with opening of the ring [1-6]. These polymers are of considerable interest since, while retaining the unusual spectral properties typical of polysilanes (absorbing in the UV region, photocurable, etc.), they are quite soluble in conventional organic solvents because of the presence of oxygen bridges between oligosilane moieties in the polymer chain (in contrast to infusible and insoluble polydimethylsilane $–(SiMe_2)_n–$).

The first oxacyclosilane, octamethyl-1,4-dioxacyclohexasilane (**1a**), was obtained in an attempt to synthesize tetramethyldisilanediol by hydrolysis of 1,2-dichlorotetramethyldisilane [7].




Oxacyclosilane **1b** (dodecamethyl-1,5-dioxacyclooctasilane) is synthesized by hydrolysis of the product of reaction between 1,5-dichlorohexamethyltrisilane and sulfuric acid [8]. The general method for synthesis of compound **1** is hydrolysis of the corresponding α,ω-dichloropermethyloligosilanes $Cl(Me_2Si)_nCl$ ($n$ = 2-6) [9]. The oligosilanediols $HO(SiMe_2)_nOH$ formed during the reaction are very unstable compounds that are readily condensed in acid medium (in the absence of an HCl acceptor) according to a mechanism of intermolecular or intramolecular condensation, with formation of oxacyclosilanes **1**.

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 0009-3122/05/4104-0536

Compound **1b** is a liquid with bp 98-100°C (2 torr) [8]; **1c-3** are solids with mp 45, 70, and 161°C respectively [9] which according to X-ray diffraction analysis, DSC, and Raman spectroscopy are plastic crystals; and only oxacyclosilane **1a** is a truly crystalline compound with mp 45°C, the molecular structure of which has been studied by X-ray diffraction at -50°C [10].

The six-membered ring of molecule **1a** has the conformation of a very flattened *chair* with deviation of the oxygen atoms from the plane of the silicon atoms ($\Delta_O$) by 0.07 Å; the Si–O bonds are slightly shortened (1.61 Å on the average) compared with the standard value (1.64 Å). Flattening of the six-membered ring and shortening of the SiO bonds in compound **1a** were connected with increased $d_\pi$–$p_\pi$ conjugation in [11]. Unfortunately, that study had poor accuracy (the uncertainties in the bond lengths were more than 0.01 Å), which did not make it possible to discuss in detail the structural features of the **1a** molecule.

In this work, using a modified technique from [7], we obtained oxacyclosilane **1a** in 72% yield and studied the characteristic features of its molecular and crystal structure in detail.

Low-temperature X-ray diffraction showed that the molecular and crystal structure parameters for compound **1a** at 110 K are close to the corresponding values at -50°C. Molecules of **1a** are located in a special position (center of symmetry). In the crystal, the molecules are packed into stacks with a hydrophobic (Me group) coating that are parallel to the *b* axes. The intermolecular contacts correspond to the usual van der Waals interactions.

The six-membered ring in the **1a** molecule is in fact planar (the mean-square deviation for all the atoms is not more than 0.02 Å), while the Si–O bond lengths are close to the standard value (1.642(1) Å] (Table 1). Since flattening of the ring may be explained by superposition of different conformers, we carried out an analysis of the anisotropic atomic displacement parameters.

As we see from Fig. 1*a*, thermal motion of the oxygen atom is strongly anisotropic, where the largest mean-square atomic displacements (0.117 Å2) are observed in the direction perpendicular to the plane of the six-membered ring. Such atomic thermal vibrations and also the presence in the Fourier difference synthesis of an additional electron density maximum of ~1.5 $e$Å$^{-3}$ near the oxygen atom made it possible to split the position of the oxygen atom into two positions with equal occupancies (Fig. 1*b*) separated by 0.5 Å. In this case, we observe some lengthening of the Si–O bonds (by ~0.02 Å) compared with the **1a** molecule with an unsplit position for the oxygen atom.

Strong correlations between the anisotropic atomic displacement parameters make it impossible to properly refine them. Therefore the two positions of the oxygen atom were refined in an isotropic approximation.

Thus the geometry of the six-membered ring in the **1a** molecule corresponding to the X-ray data (Fig. 1*a*) may be described as the result of superposition of its different conformations. In the crystal, the **1a** molecule may have several conformations existing simultaneously and independently (static disordering) or dynamically interconverting. We can evaluate the ratio of these conformers and the possibilities for dynamic interconversions only on the basis of analysis of their total energies. Therefore we carried out a quantum-chemical study within density functional theory [B3LYP/6-311+G(d) variant] with full optimization of the geometry and taking into account the zero-point vibrational energy.

With the aim of improving the accuracy of the calculated values, in solving the self-consistent field equations we specified a smaller integration step and a higher convergence limit in optimization of the geometry compared with the standard values. The geometric parameters and the total energies of the different conformations of the six-membered ring of the **1a** molecule are given in Table 2.

The calculations with and without symmetry constraints allowed us to observe an energy minimum corresponding to the *chair* conformation expected for a six-membered ring. We also found a minimum corresponding to the planar conformation and characterized by two very low imaginary frequencies, corresponding to its *twist* distortion. A minimum corresponding to the *boat* conformation was not found; optimization of the geometry led to considerable flattening of the six-membered ring. Further calculations showed that this conformation corresponds to a transition state with imaginary frequency -180 cm$^{-1}$.

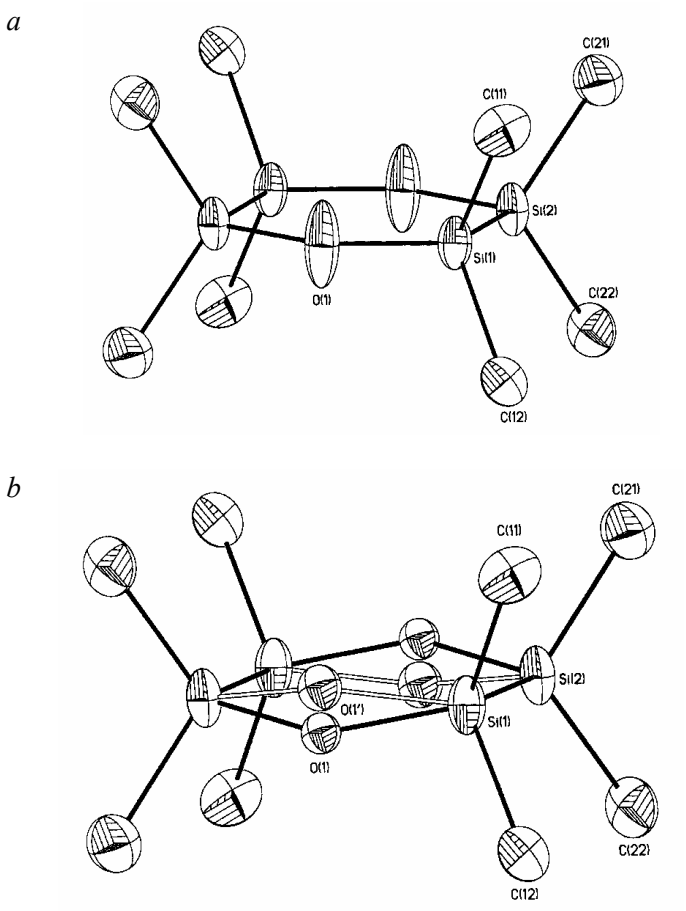


Fig. 1. General view of the **1a** molecule with representation of the atoms by 50% probability anisotropic displacement thermal ellipsoids with disordering of the oxygen atoms (*a*) and without disordering (*b*).

TABLE 1. Bond Lengths (*l*) and Bond Angles (ω) in the **1a** Molecule When Using Models with Disordering of the Oxygen Atoms (*a*) and Without Disordering (*b*)

| Bond | Parameters | | | |
|---|---|---|---|---|
| | *a* | | *b* | |
| | *l*, Å | ω, deg. | *l*, Å | ω, deg. |
| $Si_{(1)}–O_{(1)}$ | 1.654(3) | | 1.642(1) | |
| $Si_{(1')}–O_{(1')}$ | 1.666(2) | | | |
| $Si_{(1)}–Si_{(2)}$ | 2.3646(7) | | 2.3648(6) | |
| Si–C | 1.862(2) | | 1.862(2) | |
| Si–O–Si | | 140.7(2) | | 144.34(9) |
| O–Si–Si | | 107.5(1) | | 107.75(5) |
| O–Si–Si | | 107.8(1) | | 108.3(1) |
| $\Delta_O$*, Å | 0.25 | | 0.05 | |

* Deviation of oxygen atoms from the plane of the silicon atoms.

TABLE 2. Quantum-chemical Calculations* of Conformations for the **1a** Molecule

| Parameter | Conformation | | | |
|---|---|---|---|---|
| | planar ($D_{2h}$) | *chair* ($C_{2V}$) | *chair* ($C_1$) | *boat* ($C_{2h}$) |
| Bond length, Å, Si–O | 1.672 | 1.673 | 1.673 | 1.672 |
| Si–Si | 2.391 | 2.389 | 2.389 | 2.394 |
| Si–C | 1.887 | 1.888 | 1.888 | 1.894 |
| Si–O–Si bond angle, degrees | 148.5 | 146.5 | 146.5 | 148.9 |
| $\Delta_O$, Å | | 0.18 | 0.18 | 0.07 |
| Total energy, kcal/mol | 1021731.48 | 1021731.45 | 1021731.48 | 1021725.62 |
| Zero-point vibrational energy, kcal/mol | 193.19 | 193.24 | 193.19 | 192.66 |
| Imaginary frequencies, $cm^{-1}$ | -18.4, -12.5 | -5.93 | | -180.0 |

* All the calculations were performed using the program Gaussian 98W [18]; in optimization of the geometry and calculations of the frequencies of the vibrational spectrum, the following parameters were specified: INT(GRID = ULTRAFINE) and SCF(CONVER = 9).

The bond lengths and Si–O–Si bond angles in all the conformations of the six-membered ring do not differ much from one another. In this case, the calculated Si–O bond lengths (1.672 Å) and also the value of $\Delta_O$ (0.18 Å) for the *chair* conformation agree well with those established experimentally for the structure of **1a** with split positions of the oxygen atoms (1.666 Å and 0.25 Å on the average).

This allows us to conclude that the model splitting the positions of the oxygen atoms (Fig. 1*b* and Table 1) is more correct, despite the higher value of the *R* factor, and that lengthening of the Si–O bond compared with the standard value (1.64 Å) is not a systematic calculation error. The latter is also confirmed by the results of quantum-chemical studies (MP2/6-31G*) of the silicon analog of tetrahydrofuran $Si_4H_8O$, in which the Si–O bond lengths are 1.679 Å [12].

In the *boat* conformation, some lengthening of the Si–Si bond occurs, which may be explained by repulsion of the methyl groups since the distances between some hydrogen atoms of these groups are shortened to 2.51 Å.

We may consider it to be obvious that in the crystal, inversion of the six-membered ring (similar to inversion of cyclohexane) is impossible due to steric hindrances. Therefore all the conformational transitions probably are mainly due to changes in the positions of the oxygen atoms relative to the plane of the silicon atoms. Analysis of the total energies of the considered conformations suggests that they are all equally probable and can interconvert with practically no barrier. The barriers to such transitions are probably much lower than the zero-point vibrational energy for all the conformations.

We should note that internal hindered rotation of the oxygen atom is a strongly anharmonic process and may not be described sufficiently accurately in the harmonic approximation used in calculations of atomic vibrations by quantum chemistry methods. The maximum difference in the energies for the conformations is comparable to the experimentally obtained barrier to internal hindered rotation of the oxygen atom (0.5 kcal/mol) [13] and the barrier to inversion of the five-membered ring from a local minimum ($C_2$) through a transition state with a planar structure ($C_{2v}$) in the $Si_4H_8O$ molecule (0.51 kcal/mol) [12].

The **1a** molecule is practically as flexible as six-membered cyclic siloxanes [11]. The conformation of the molecule in this case is determined by the nature of the exocyclic substituents on the silicon atoms [14]. For example, replacing some of the methyl groups on the six-membered ring by phenyl groups leads to stabilization

of the *twist* conformation. It is interesting to note that in the germanium analog of compound **1a** with phenyl exocyclic substituents, the six-membered ring has a *chair* conformation in which the oxygen atoms are displaced by 0.61 Å [15].

Thus in the case of octamethyl-1,4-dioxacyclohexasilane, conformational transitions may occur even at a temperature of 110 K, and consequently we experimentally observe an unusual planar structure for the six-membered ring of the molecule and librational shortening of the Si–O bond lengths.

## EXPERIMENTAL

The $^{29}$Si NMR spectrum was recorded on a Bruker WP-200 SY spectrometer (39.76 MHz), internal standard TMS, solvent $CCl_4$. The IR spectrum was taken on a Specord M-82 spectrometer in KBr disks; the UV spectrum was taken on a Specord M-40 spectrophotometer in vaseline oil; the Raman spectrum was taken on a U-1000 spectrometer.

**Octamethyl-1,4-dioxacyclohexasilane (1a).** A solution of 1,2-dichlorotetramethyldisilane (2 g, 10.7 mmol) in ethyl ether (5 ml) was added with vigorous stirring to a mixture of $H_2O$ (5 ml) and acetone (1 ml). The reaction mixture was held for another 2 h. The organic layer was removed, washed with water until it tested neutral, dried over $Na_2SO_4$, and then the solvent was removed under vacuum and the residue was recrystallized from a 4:1 $C_2H_5OH$–$H_2O$ mixture. Yield 1.02 g (72%); mp 44°C (mp 45°C [7]). $^{29}$Si NMR spectrum ($CCl_4$), δ, ppm: 2.96. IR spectrum, ν, cm$^{-1}$: 2954, 2892 (CH), 1405, 1257, 1245, 869, 855 ($CH_3$), 1083, 1030 (SiOSi), 801, 774 (SiC). UV spectrum (*n*-hexane), $\lambda_{max}$, nm: 215, 234. Raman spectrum, Δ, cm$^{-1}$: 2958, 2893 (CH), 1409, 1257, 1245, 869, 855 ($CH_3$), 773, 698, 683, 651 (SiC), 392, 329 (SiSi).

**X-ray Diffraction Study.** Crystals of **1a** ($C_8H_{24}O_2Si_4$), M = 264.63, monoclinic at 100 K, space group $P2_1/c$; $a$ = 7.6141(6), $b$ = 6.4186(6), $c$ = 16.190(1) Å; β = 97.582(3)°; $V$ = 788.7(1) Å$^3$; $Z$ = 2. The measurements were made on a Bruker SMART diffractometer using the SMART control program [16] at 100 K (λ(Mo$K\alpha$) = 0.71072 Å, ω scanning, 2θ < 60°). The three series of frames obtained, corresponding to half a sphere of reciprocal space, were processed using the SAINT Plus program [16] and averaged by the SADABS program [16]. We measured the intensities of 4938 reflections, of which 2191 independent reflections ($R_{int}$ = 0.0232) were used later in deciphering and refining the structure. The structure was solved by the direct method and refined on $F^2$ in the full-matrix anisotropic/isotropic approximation. The hydrogen atoms were determined from Fourier electron density difference syntheses and refined isotropically. The final refinement parameters in the model with disordering of the oxygen atoms were: $wR_2$ = 0.1350 (using all the reflections), $R^1$ = 0.0485 [using 1778 reflections with $I > 2\sigma(I)$], *GOOF* = 1.023. In the model without disordering of the oxygen atoms: $wR_2$ = 0.1241 (using all the reflections), $R_1$ = 0.0455 [using 1778 reflections $I > 2\sigma(I)$], *GOOF* = 1.001. All the calculations were carried out using the SHELXTL PLUS V5.10 software package on a PC [17].

This work was performed with the financial support of the Russian Foundation for Basic Research (projects No. 03-03-32214 and 02-07-90169).

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