1,2-Dimethyl-1,2-diphenyldisilane-1,2-diol and its K, Na, and Fe^{II} derivatives. Molecular structure of the all-*trans*-isomer, 2,3,5,6-tetramethyl-2,3,5,6-tetraphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane

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Hydrolysis of 1,2-dimethyl-1,2-diphenyl-1,2-dichlorodisilane yields 1,2-dimethyl-1,2-diphenyldisilane-1,2-diol, which undergoes dimerization into stereoisomeric 2,3,5,6-tetramethyl-2,3,5,6-tetraphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexanes under the action of H_2SO_4. Pure all-*trans*-isomer has been isolated and characterized by ^1H NMR and IR spectroscopy and X-ray analysis. The reaction of sodium disilanediolate with $FeBr_2$ results in the formation of 1,2-dimethyl-1,2-diphenyl-4-ferra(II)-3,5-dioxa-1,2-disilacyclopentane.

Key words: organodisilanes, silanoles, silanolates, cyclosiloxanes, ferrosiloxanes; molecular structure.

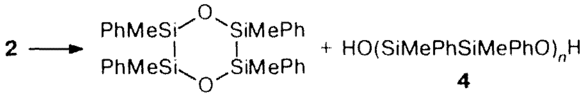
The stability of silanoles depends on the number of hydroxyl groups and the number of substituents at the silicon atom.[1] Tetramethyldisilane-1,2-diol $HOSiMe_2SiMe_2OH$ is known to undergo fast dimerization into octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane.[2] Two isopropyl groups have a pronounced stabilizing effect: 1,2-diisopropyl-1,2-dimethyldisilane-1,2-diol was isolated and characterized.[3] In this work, the data on synthesis and several reactions of 1,2-dimethyl-1,2-diphenyldisilane-1,2-diol are reported.

Results and Discussion

Hydrolysis of 1,2-dimethyl-1,2-diphenyl-1,2-dichlorodisilane **1**[4] with equivalent amount of aqueous solution of NaOH results in the formation of disilanediol **2**, a yellow liquid with a camphor odor.

$$\underset{\mathbf{1}}{\text{(Cl)PhMeSiSiMePh(Cl)}} \xrightarrow[\text{NaOH}]{\text{Et}_2\text{O, H}_2\text{O}} \underset{\mathbf{2}}{\text{(HO)PhMeSiSiMePh(OH)}}$$

The content of the main product **2** in the residue after removal of the solvent is 96% according to determination of the active hydrogen using the Chugaev—Zerewitinoff reaction. It follows from the IR spectroscopy data that the molecules of disilanediol **2** form associates at the expence of intermolecular hydrogen bonds. A broad intense absorption band at ~3300 cm^{-1} (SiO—H), characteristic of associated hydroxyl compounds, is present in the spectrum. Compound **2** condenses slowly at room temperature in the absence of catalysts. Addition of 2—3 drops of diluted sulfuric acid to the ether solution of disilanediol **2** causes its fast dimerization into cycle **3** and condensation to oligomers **4**. The absorption band of OH groups (with intensity ~1/10 relative to the initial value) still persists in the IR spectrum of the products after heating the ether solution of **2** for 15 h. This band is due likely to the presence of oligodisilaneoxane-α,ω-diols **4**. According to ^1H NMR spectra (Fig. 1), the yields of cyclic compounds **3** and oligomeric compounds **4** are 55 and 45%, respectively.



3 **4**

A chromatogram of separation of the condensation products of disilanediol **2** by high performance liquid chromatography (HPLC) technique is shown in Fig. 2, *a*. It is seen that the reaction mixture contains three main products and not less than five by-products. However, it is impossible to state that we succeeded in separation of

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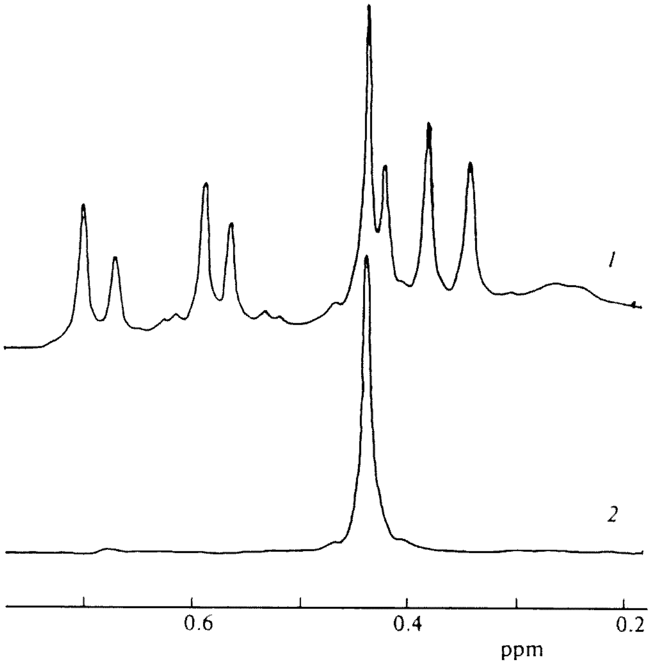


Fig. 1. ^{1}H NMR spectra of condensation products of disilanediol (*1*) and racemate of stereoisomers *RR*-3 and *SS*-3 (*2*).

all possible stereoisomeric cyclic compounds **3**, since oligomers and large cycles can also elute with the solvent. One of the isomers was isolated in chromatographically pure form (see Fig. 2, *b*) by recrystallization of **3** from heptane. The absorption band in the IR spectrum of this compound, corresponding to asymmetric stretching vibration of the Si—O bond, is split into a doublet with frequencies of 1026 and 1015 cm^{-1}. Two absorption bands of medium intensity at 575 and 390 cm^{-1} are due likely to the stretching vibration of the Si—Si bond. The Si—Me fragments are characterized by absorption bands at 2935, 2905, 2880, 1238, and 770 cm^{-1}, and the Si—Ph fragments are characterized by absorption bands at 1415, 1100, 728, 707, 690, and 465 cm^{-1}.

An analysis of ^{1}H NMR spectroscopy data allows one to conclude that all five possible stereoisomeric 2,3,5,6-tetramethyl-2,3,5,6-tetraphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexanes **3** were obtained in the hydrolysis of **1** and subsequent condensation of **2**. The starting dichloride **1** and the resulting disilanediol **2** are the mixtures of *meso*- and *R,S*-isomers; the latter partially condenses by the time of recording the ^{1}H NMR spectrum. Since we failed to determine the exact ratio of *meso*- and *R,S*-isomers in compound **2**, the ratio of *meso*- and *R,S*-isomers found for dichloride **1** from ^{1}H NMR spectroscopy data was used in further calculations. It is 2 : 1 (or 1 : 2), since it is not known which of the methyl proton signals is assigned to *meso*-, and which to *R*- (or *S*-)-isomer.

Tetrasiladioxacyclohexanes **3** are present in the mixture as stereoisomers (Scheme 1). According to the type of the cycle formation from *R,S*-, and *meso*-**2**, one can denote them as *MR*-**3** (*MS*-**3**), *RR*-**3** (*SS*-**3**), *RS*-**3**, *trans-MM*-**3**, and *cis-MM*-**3**. The *MR*-**3**—*MS*-**3** and *RR*-**3**—*SS*-**3** pairs must have the same NMR characteristics. Thus, five stereoisomers differing in their NMR spectra can be present in the mixture. All four methyl groups in the *MR*-**3**(*MS*-**3**) isomer have a different environment, and each of them appears as a separate peak. All methyl protons in four other isomers are equivalent, and each of these cycles produces one signal in the region of methyl protons. Therefore, theoretically, the spectrum can contain not more than eight signals corresponding to the proton resonances of methyl groups. Actually, eight singlet signals are observed in the ^{1}H NMR spectrum of the mixture after hydrolysis and condensation. Apart from the indicated narrow signals in the region of 0—0.6 ppm, broad bands, corresponding to the methyl protons of oligodisilaneoxanes, are present in the spectrum.

Assuming that the initial configuration of **2** has no effect on the stereoselectivity of its cyclodimerization, the composition of the mixture **3** formed was calculated

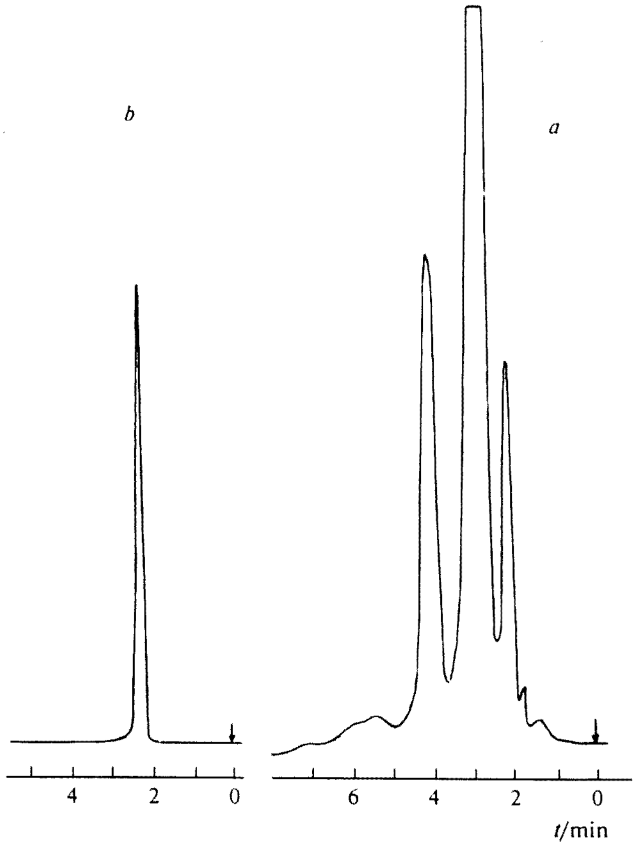
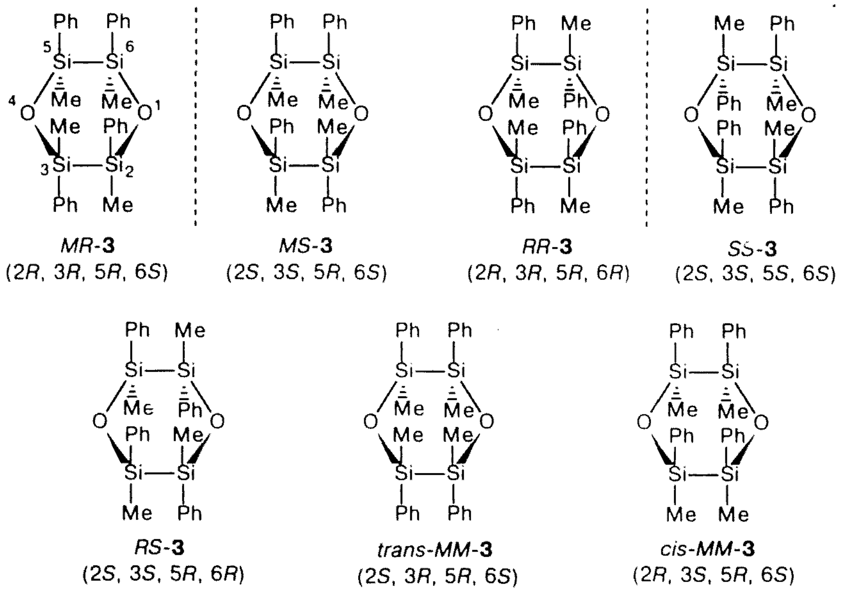


Fig. 2. HPLC analysis of condensation products of disilanediol **2** (*a*) and racemate of stereoisomers *RR*-**3** and *SS*-**3** isolated by recrystallization (*b*).

Scheme 1



MR-**3** (2*R*, 3*R*, 5*R*, 6*S*)
MS-**3** (2*S*, 3*S*, 5*R*, 6*S*)
RR-**3** (2*R*, 3*R*, 5*R*, 6*R*)
SS-**3** (2*S*, 3*S*, 5*S*, 6*S*)
RS-**3** (2*S*, 3*S*, 5*R*, 6*R*)
trans-*MM*-**3** (2*S*, 3*R*, 5*R*, 6*S*)
cis-*MM*-**3** (2*R*, 3*S*, 5*R*, 6*S*)

from the statistical probability of participation of the *R*-, *S*-, and *meso*-forms in its formation (Table 1). The isomer whose methyl protons have a chemical shift of 0.43 ppm (see Fig. 1, spectrum *2*) was isolated from the condensation products by recrystallization. According to the X-ray analysis data, in the crystalline state it is an all-*trans*-isomer representing a racemate of *RR*-**3**- and *SS*-**3**-forms. Determination of the configuration of this isomer by the X-ray analysis allows one to assign the NMR peaks of the mixture of cyclic compounds **3** to the corresponding isomers, to establish the content of diastereomers in compounds **1** and **2**, as well as to refine the chemical shifts of the latter. Thus, the methyl protons in *meso*-**1** resonate at 0.84 ppm while those in *R*- and *S*-isomers resonate at 0.78 ppm. The calculated composition of **3** is in agreement with the experimental one only for the mixture containing 33% of each *meso*-, *R*-, and *S*-stereoisomers. In addition, it follows from comparison of calculated and experimental data (see Table 1) that *trans*-condensation resulting in the formation of **3** is approximately 1.5 times more probable than *cis*-condensation.

Table 1. Composition of isomers **3**

Isomer	Composition (mol.%)			δ, Me
	Calculation[a]		Experiment[b]	
	66% *meso*, 33% *R* and *S*	33% *meso*, 66% *R* and *S*		
MR-3+*MS*-3	44	44	46	0.33, 0.41, 0.58, 0.69
RR-3+*SS*-3	5	22	24	0.43
RS-3	5	22	15	0.37
trans-*MM*-3	22	5	9	0.56
cis-*MM*-3	22	5	6	0.67

[a] Composition calculated for the ratio 2. [b] The composition was determined from ^{1}H NMR data.

A treatment of disilanediol **2** with metallic potassium or sodium hydride results in disilanediolates of alkali metals. Addition of **2** to a potassium dispersion in benzene results in the formation of potassium 1,2-dimethyl-1,2-diphenyldisilane-1,2-diolate (**5a**) in 68% yield.

$$\mathbf{2} + 2\,\mathrm{K} \xrightarrow{C_6H_6} \underset{\mathbf{5a}}{(\mathrm{KO})\mathrm{PhMeSiSiMePh}(\mathrm{OK})} + \mathrm{H_2}$$

Partial condensation of compound **2** likely proceeds in the course of reaction, since the content of the main substance after removal of the solvent is 76%. Disodium derivative **5b** is obtained from disilanediol and sodium hydride in higher yield (73%) and higher purity.

$$\mathbf{2} + 2\,\mathrm{NaH} \xrightarrow{C_6H_6} \underset{\mathbf{5b}}{(\mathrm{NaO})\mathrm{PhMeSiSiMePh}(\mathrm{ONa})} + 2\,\mathrm{H_2}$$

Disilanediolates **5a,b** are light-weight, light-yellow powders soluble in ether and benzene and deliquescing in the air due to hydrolysis. The replacement of hydrogen atoms by alkali metal atoms causes a pronounced change in the nature of the IR spectra. A broad intense band at 975 cm^{-1}, which points to the presence of the Si—O—M (M = Na, K) fragments, appears in the region of the Si—O bond vibrations; the band at 3300 cm^{-1} (SiO—H) disappears.

Sodium disilanediolate **5b** reacts with iron(II) bromide in THf resulting in 1,2-dimethyl-1,2-diphenyl-4-ferra(II)-3,5-dioxa-1,2-disilacyclopentane, $[(\mathrm{PhMeSiSiMePhOFeO})]\cdot\mathrm{NaBr}]_2$, (**6**) a brown noncrystallizing solid substance, which is extremely sensitive to oxygen and moisture. Its brown color rapidly changes to red in contact with air. It follows from the elemental analysis data and determination of the molecular mass that compound **6** exists as a complex with one molecule of NaBr; the compound is a dimer in benzene solution. According to ^{1}H NMR spectroscopy, the methyl (and, hence, phenyl) groups of the five-membered ring of **6** can have both *cis*- and *trans*-positions with an ~1 : 1 ratio of isomers.

Tetramethylethylenediamine (TMEDA) reacts with **6** in benzene displacing sodium bromide (which precipitates quantitatively) to give a complex $[(\mathrm{PhMeSiSiMePhOFeO})]\cdot\mathrm{TMEDA}]$ (**7**). Its formation is accompanied by an appreciable change in the IR spectrum as compared to that in the region of vibrations of the Si—O—Fe bonds. The broad band at 870—930 cm^{-1} disappears. An intense peak appears at 965 cm^{-1} with two shoulders at 940 and 925 cm^{-1}. The two most intense bands at 1060 and 1015 cm^{-1} become less intense. The positions of the bands, characterizing the Si—Ph and Si—Me groups, change insignificantly. Compound 7 is also as sensitive to oxygen and moisture as 6.

Heating of compound **6** in an evacuated ampule (2 h) showed that its thermal decomposition begins at 150 °C and is accompanied by a partial loss of benzene solubility. A pronounced decrease in the intensity of the absorption band at 860 cm^{-1} is observed in the IR spectrum. Heating at 200 °C causes a sharp decrease in the intensity of this band and a simultaneous increase in the intensity and broadening of the bands in the range from 1000 to 1080 cm^{-1} (SiOSi). The products of thermal decomposition are virtually insoluble in benzene. The dependences of the specific magnetization of compound **6** before and after heating (2 h at 250 °C) are shown in Fig. 3. It is seen that the compound was paramagnetic before heating. The heat treatment turns it into a weak ferromagnetic with a minor contribution of the paramagnetic component.

The X-ray study of the crystalline all-*trans*-isomer (Fig. 4) showed that its six-membered cycle, containing four silicon and two oxygen atoms, has a sofa conformation. Therein lies the distinction between two enantiomeric molecules *RR*-**3**—*SS*-**3** and the investigated compounds of the same type ($\mathrm{Me_8Si_4O_2}$,[5] $\mathrm{Me_{12}Si_6}$,[6] $\mathrm{Me_6Si_6Ph_6}$,[7,8] $\mathrm{Ph_{12}Si_6\cdot 7C_6H_6}$,[9] $\mathrm{Ph_8Ge_4O_2}$,[10] $\mathrm{Ph_{12}Ge_6\cdot 7C_6H_6}$,[11] and $\mathrm{Ph_{12}Ge_6\cdot 7PhMe}$[12]), whose six-membered cycles have a distorted chair conformation. The values of torsion angles Si(1)—Si(2)—O(2)—Si(3), Si(2)—O(2)—Si(3)—O(4), O(2)—Si(3)—Si(4)—O(1), Si(3)—Si(4)—O(1)—Si(1), Si(4)—O(1)—Si(1)—Si(2), and O(1)—Si(1)—Si(2)—O(2) in *RR*-**3**—*SS*-**3** are −8.9°, −11.6°, 18.2°, 0.9°, −21.2°, and 24.4°, respectively. The alternating positions of methyl and phenyl groups is undeniably more favorable from the viewpoint of steric repulsion between them. However, other molecular configurations are also realized for compounds in question in the crystalline state. For instance, compound $\mathrm{Me_6Si_6Ph_6}$ has both all-*trans*-(*tttttt*)[7]- and partial *cis*-(*ttttcc*)[8]- configurations of substituents at the Si atoms.

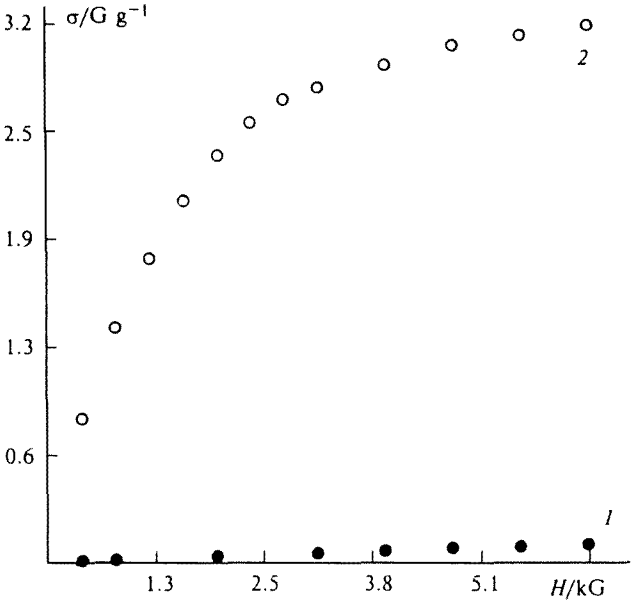


Fig. 3. Dependences of the specific magnetization σ of compound **6** (*1*) and the products of its thermal decomposition (*2*) on the magnetic field strength *H*.

Average distances Si—Si (2.362 Å), Si—C(Ph) (1.868 Å), and Si—C(Me) (1.866 Å) in enantiomers *RR*-**3**—*SS*-**3** (Table 2) are comparable to analogous distances in $\mathrm{Me_8Si_4O_2}$ (Si—Si 2.35 Å, Si—C(Me) 1.88 Å),[5] $\mathrm{Me_{12}Si_6}$ (Si—Si 2.338 Å, Si—C(Me) 1.888 Å),[6] *tttttt*—$\mathrm{Me_6Si_6Ph_6}$ (Si—Si 2.359 Å, Si—C(Ph) 1.893 Å, Si—C(Me) 1.8[illegible]2 Å),[7] *ttttcc* $\mathrm{Me_6Si_6Ph_6}$ (Si—Si 2.351 (2.366) Å, Si—C(Ph) 1.893 (1.888) Å, Si—C(Me) 1.890 (1.888) Å; the values for the second independent molecule are given in parentheses) and in $\mathrm{Ph_{12}Si_6\cdot 7C_6H_6}$ (Si—Si 2.394 Å, Si—C(Ph) 1.879 Å).[9] The Si—O distances in *RR*-**3**—*SS*-**3** lie in the interval from 1.640(2) to 1.647(2) Å, which is somewhat longer than analogous distances in $\mathrm{Me_8Si_4O_2}$ (the average value is 1.61 Å)[5] and significantly shorter than the Ge—O distances in $\mathrm{Ph_8Ge_4O_2}$ (1.781, 1.786 Å)[10] with allowance for the distinction in the tetrahedral covalent radii of Si and Ge (r_{Si} = 1.17 Å, r_{Ge} = 1.22 Å)[13].

The Si—O and Ge—O distances in these molecules are somewhat lengthened as compared to the sum of the covalent radii of Si(Ge) and O, (r_{O} = 0.66 Å), whereas the Si—Si and Ge—Ge (2.448 Å)[10] distances nearly coincide with the sum of covalent radii.[13] This points to the fact that steric effects of the substituents at the Si(Ge) atoms affect primarily the geometry of the Si(Ge)—O bond and the conformation of the cycles.

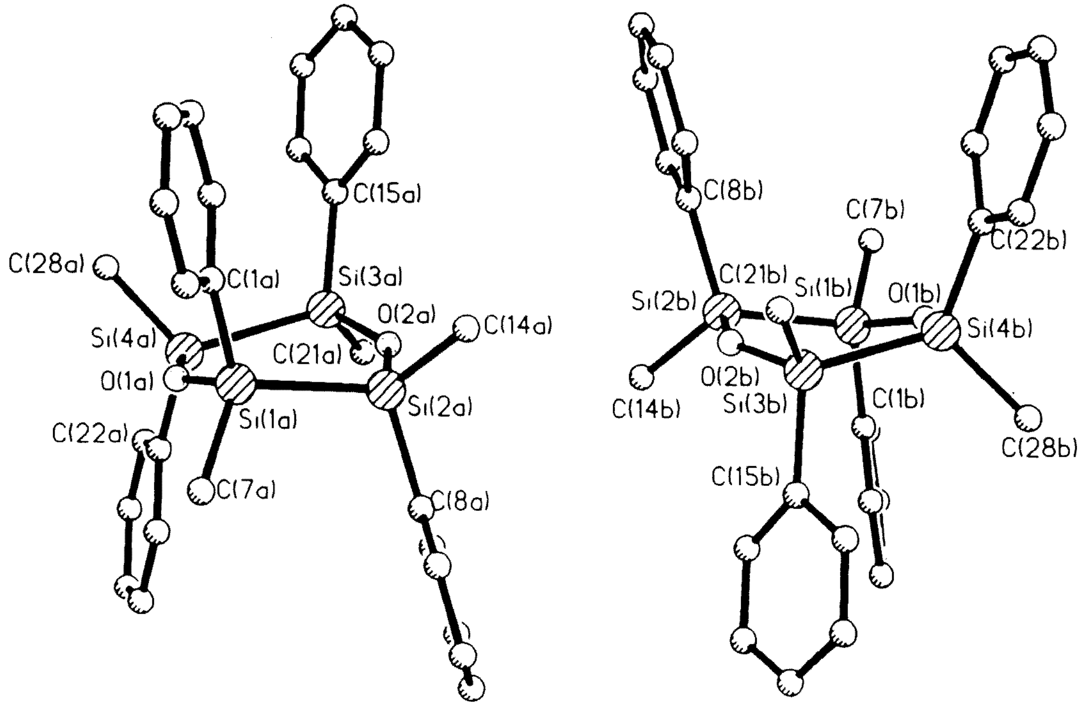


Fig. 4. General view of the centrosymmetrical pair of molecules **3** with *RR*- and *SS*-configurations.

This is also confirmed by the relatively small deviations of the bond angle values at the Si atoms 106.6(1)—113.0(2)° (the average is 109.5°) from the ideal tetrahedral angle in enantiomeric molecules *RR*-**3**—*SS*-**3**.

Experimental

IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer (dispersions in vaseline oil). ^{1}H NMR spectra were recorded on a Tesla BS-567 A spectrometer (100 MHz) in $CDCl_3$, with $CHCl_3$ (δ 7.25) and $(Me_3Si)_2O$ (δ 0.055) as inner standard

HPLC analysis was performed on a Milikhrom-1A chromatograph (a stainless steel 64×2 mm column; with Separon-SGX 5 μm as adsorbent; a heptane : THF, 200 : 1 mixture as eluent, 200 μL min^{-1}; UV detector, λ = 240 nm).

Magnetochemical measurements were carried out on a Bruker B-E 15 Faraday balance at 25 °C.

Iron content in compound **4** was determined by titration with a solution of $Hg_2(NO_3)_2$ in the presence of ammonium rhodanide [14]

Reactions with potassium and sodium hydride were carried out under an argon atmosphere, and those with $FeBr_2$ were carried out in evacuated ampules. Specimens for recording IR and NMR spectra were prepared in a dry argon box. Iron(II) bromide was obtained by the known procedure.[15]

1,2-Dimethyl-1,2-diphenyl-1,2-dichlorodisilane (1) was synthesized by partial phenylation of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane under the action of PhMgCl.[4] Two fractions with b.p. 183—186 °C (2 Torr) and 186—189 °C (2 Torr) were isolated by distillation *in vacuo*. The second fraction has been crystallized in storage whereas the first fraction remained liquid. According to ^{1}H NMR spectra, the first fraction consists of equal amounts of *meso*- and *R,S*-forms while the second fraction (just used in this work) contains 33% of *meso*- and 66% of *R, S*-forms.

1,2-Dimethyl-1,2-diphenyldisilane-1,2-diol (2). A solution of 1,2-dimethyl-1,2-diphenyl-1,2-dichlorodisilane **1** (12.85 g, 0.041 mol) in ether (50 mL) was added dropwise for 0.5 h to a 0.96 *M* solution of NaOH (90 mL) with stirring and cooling with ice water. The mixture was stirred for 15 min, the organic layer was separated, and the aqueous layer was extracted three times with ether. The ethereal solution was dried with Na_2CO_3, and the solvent was removed *in vacuo*. Disilanediol **2** (10.40 g, 92%) was obtained as a transparent viscous liquid, n_D^{20} 1.5741, d_4^{20} 1.2496, MR_D 72.49 (calc. 73.61). IR, ν/cm^{-1}: 3300 (OH), 3050, 3030, 3000, 1575, 1475, 1420, 1295, 1100, 730, 695, 470 (PhSi), 2885, 1243, 835, 770 (MeSi), 1050, 1015, 590 (SiOSi), 390 (SiSi). ^{1}H NMR ($CDCl_3$), δ: 0.40 (s, Me, *R,S*-isomers); 0.47 (s, Me, *meso*-isomer); 7.3—7.6 (m, Ph).

2,3,5,6-Tetramethyl-2,3,5,6-tetraphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane (3). To a solution of disilanediol **2** (2.11 g, 0.0077 mol) in ether (50 mL), 3 drops of 15% H_2SO_4 were added and the mixture was heated with reflux condenser for 20 h. Ether was removed *in vacuo*. A mixture of stereoisomeric cyclosiloxanes **3** (1.86 g, 94.3%) was obtained as a resin-like mass. IR, ν/cm^{-1}: 3050, 3025, 3000, 2935, 2905, 2880 (CH), 1575, 1473, 1415, 1100, 725, 705, 690, 465 (PhSi), 1240, 795, 765, (MeSi), 1060, 1025, 1012, 590 (SiOSi), 415, 390 (SiSi). ^{1}H NMR, δ: 0.3—0.7 (8s, Me); 7.3—7.6 (m, Ph). The racemic mixture of *RR*-**3** and *SS*-**3** stereoisomers (0.3 g, 15.2%) was isolated by recrystallization from heptane as needle-shaped crystals, m.p. 145—147 °C. IR, ν/cm^{-1}: 1415, 1100, 990, 728, 707, 690, 465 (PhSi), 1238, 797, 770 (MeSi), 1026, 1015, 575 (SiOSi), 390 (SiSi). ^{1}H NMR ($CDCl_3$), δ: 0.43 (s, 12 H, Me); 7.30—7.57 (m, 20 H, Ph). Found (%): C, 66.00; H, 6.89; Si, 21.30. $C_{28}H_{32}O_2Si_4$. Calculated (%): C, 65.57; H, 6.29; Si, 21.90.

Sodium 1,2-dimethyl-1,2-diphenyldisilane-1,2-diolate (5b). A solution of disilanediol **2** (4.36 g, 0.016 mol) in benzene

Table 2. Bond lengths (*d*) and bond angles (ω) in molecule **3**

Bond	*d*/Å	Bond	*d*/Å
Si(1)—Si(2)	2.359(1)	C(5)—C(6)	1.375(7)
Si(1)—O(1)	1.647(2)	C(8)—C(9)	1.390(5)
Si(1)—C(1)	1.866(3)	C(8)—C(13)	1.390(5)
Si(1)—C(7)	1.866(4)	C(9)—C(10)	1.383(6)
Si(2)—O(2)	1.642(2)	C(10)—C(11)	1.360(6)
Si(2)—C(8)	1.868(3)	C(11)—C(12)	1.359(6)
Si(2)—C(14)	1.864(4)	C(12)—C(13)	1.375(6)
Si(3)—Si(4)	2.364(1)	C(15)—C(16)	1.386(4)
Si(3)—O(2)	1.645(2)	C(15)—C(20)	1.391(5)
Si(3)—C(15)	1.873(3)	C(16)—C(17)	1.390(5)
Si(3)—C(21)	1.867(4)	C(17)—C(18)	1.360(6)
Si(4)—O(1)	1.640(2)	C(18)—C(19)	1.374(6)
Si(4)—C(22)	1.865(3)	C(19)—C(20)	1.369(5)
Si(4)—C(28)	1.867(4)	C(22)—C(23)	1.371(5)
C(1)—C(2)	1.374(5)	C(22)—C(27)	1.400(5)
C(1)—C(6)	1.389(5)	C(23)—C(24)	1.377(5)
C(2)—C(3)	1.396(6)	C(24)—C(25)	1.375(6)
C(3)—C(4)	1.357(7)	C(25)—C(26)	1.354(6)
C(4)—C(5)	1.350(7)	C(26)—C(27)	1.369(6)

Angle	ω/deg	Angle	ω/deg
Si(2)-Si(1)-O(1)	106.6(1)	C(1)-C(2)-C(3)	122.6(4)
Si(2)-Si(1)-C(1)	112.0(1)	C(2)-C(3)-C(4)	119.1(4)
O(1)-Si(1)-C(1)	108.3(1)	C(3)-C(4)-C(5)	119.8(4)
Si(2)-Si(1)-C(7)	111.7(1)	C(4)-C(5)-C(6)	121.2(4)
O(1)-Si(1)-C(7)	108.4(2)	C(1)-C(6)-C(5)	121.4(4)
C(1)-Si(1)-C(7)	109.6(2)	Si(2)-C(8)-C(9)	123.3(3)
Si(1)-Si(2)-O(2)	107.6(1)	Si(2)-C(8)-C(13)	120.8(3)
Si(1)-Si(2)-C(8)	109.9(1)	C(9)-C(8)-C(13)	115.9(3)
O(2)-Si(2)-C(8)	108.1(1)	C(8)-C(9)-C(10)	121.5(4)
Si(1)-Si(2)-C(14)	113.0(2)	C(9)-C(10)-C(11)	120.6(4)
O(2)-Si(2)-C(14)	109.2(2)	C(10)-C(11)-C(12)	119.4(4)
C(8)-Si(2)-C(14)	108.9(2)	C(11)-C(12)-C(13)	120.4(4)
Si(4)-Si(3)-O(2)	107.5(1)	C(8)-C(13)-C(12)	122.2(4)
Si(4)-Si(3)-C(15)	110.8(1)	Si(3)-C(15)-C(16)	123.5(2)
O(2)-Si(3)-C(15)	108.0(1)	Si(3)-C(15)-C(20)	120.2(2)
Si(4)-Si(3)-C(21)	112.0(1)	C(16)-C(15)-C(20)	116.2(3)
O(2)-Si(3)-C(21)	109.2(2)	C(15)-C(16)-C(17)	121.8(3)
C(15)-Si(3)-C(21)	109.2(2)	C(16)-C(17)-C(18)	120.0(3)
Si(3)-Si(4)-O(1)	107.6(1)	C(17)-C(18)-C(19)	119.6(3)
Si(3)-Si(4)-C(22)	110.3(1)	C(18)-C(19)-C(20)	120.2(4)
O(1)-Si(4)-C(22)	107.7(1)	C(15)-C(20)-C(19)	122.2(3)
Si(3)-Si(4)-C(28)	112.3(1)	Si(4)-C(22)-C(23)	123.4(2)
O(1)-Si(4)-C(28)	109.4(2)	Si(4)-C(22)-C(27)	120.9(3)
C(22)-Si(4)-C(28)	109.5(2)	C(23)-C(22)-C(27)	115.6(3)
Si(1)-O(1)-Si(4)	142.0(1)	C(22)-C(23)-C(24)	122.9(3)
Si(2)-O(2)-Si(3)	141.9(1)	C(23)-C(24)-C(25)	119.6(3)
Si(1)-C(1)-C(2)	122.4(3)	C(24)-C(25)-C(26)	119.2(4)
Si(1)-C(1)-C(6)	121.6(3)	C(25)-C(26)-C(27)	120.8(4)
C(2)-C(1)-C(6)	116.0(3)	C(22)-C(27)-C(26)	121.8(4)

(20 mL) was added dropwise with stirring to a dispersion of NaH (2.08 g, 0.087 mol) in benzene (20 mL). Intense gas evolution was observed over a period of 2 h. The mixture was stirred for an additional 4 h, the transparent solution was decanted, and benzene was removed *in vacuo*. Sodium disilanediolate (3.72 g, 73%) was obtained as a light-weight, light-yellow powder deliquescing in the air. The content of the main substance according to the acid-base titration data is 96.4%. IR, ν/cm^{-1}: 1415, 1100, 725, 690, 470 (PhSi), 1240, 755 (MeSi), 1005, 975 (SiONa).

1,2-Dimethyl-1,2-diphenyl-3,5-dioxa-1,2-disila-4-ferra(II)-cyclopentane (6). A solution of sodium disilanediolate **5b** (2.05 g, 6.4 mmol) in THF (20 mL) and a solution of $FeBr_2$ (1.40 g, 6.4 mmol) in THF (10 mL) were degassed and mixed. After 20 h, the NaBr precipitate was centrifuged, THF was removed *in vacuo*. A distilled benzene (20 mL) was added to the residue, the solution was decanted, and benzene was removed *in vacuo*. Compound **6** (2.69 g, 97%) was obtained as a brown powder. Addition of heptane to a benzene solution followed by cooling to 0 °C results in precipitation of **6** as a fine noncrystalline brown powder, M — 860 (cryoscopy in benzene); calculated for the dimer with two NaBr molecules — 862.4. Found (%): C, 40.53; H, 4.04; Fe, 12.56; Si, 12.64. $C_{28}H_{32}Br_2Fe_2Na_2O_4Si_4$. Calculated (%): C, 39.00; H, 3.74; Fe, 12.95; Si, 13.03. IR spectrum contains absorption bands characteristic of the PhMeSiO fragment and a broad band of medium intensity in the range from 870 to 930 cm^{-1} (Si—OFe). ^{1}H NMR ($CDCl_3$), δ: 0.24, 0.39 (12 H, Me); 7.2—7.7 (m, 20 H, Ph).

Complex of 1,2-dimethyl-1,2-diphenyl-3,5-dioxa-1,2-disila-4-ferra(II)cyclopentane with tetramethylethylenediamine (7). A solution of compound **6** (1.46 g, 1.7 mmol) in benzene (10 mL) and a solution of tetramethylethylenediamine (0.46 g, 4.0 mmol) in benzene (5 mL) were degassed and mixed. The NaBr precipitate (0.32 g, 91%) was centrifuged, and the volatile products were removed *in vacuo*. Compound **7** (0.86 g, 59%) was obtained. Found (%): C, 55.00; H, 7.32. $C_{20}H_{32}FeN_2O_2Si_2$. Calculated (%): C, 54.04; H, 7.26. IR, ν/cm^{-1}: 1270, 1235, 790, 765 (Me), 1090, 720, 695, 460 (Ph—Si), 965, 940, 925 (SiOFe, FeN).

X-Ray study was carried out on a Siemens P3/PC diffractometer (Mo-Kα, graphite monochromator, 2θ/θ-scan in the interval $2 < 2\theta < 66°$). The crystals of *RR*-**3**—*SS*-**3** are monoclinic, a = 14.257 (3) Å, b = 10.753 (3) Å, c = 19.140 (4) Å, β = 93.10 (2)°, V = 2930 (2) Å^3, d_{calc} = 1.163 g cm^{-3}, μ(Mo-Kα) = 2.19 cm^{-1}, Z = 4, space group $P2_1/c$ (all data reported at 20 °C). Of the total 6138 measured independent reflections, 2727 with $F > 6\sigma\ (F)$ were used to solve and refine the molecule. The structure was solved by direct methods and refined by a block-diagonal least-squares method anisotropically for all non-hydrogen atoms. The H atoms in the phenyl rings were found from the difference synthesis of the electron density and refined with isotropic thermal parameters. The H atoms of the methyl groups are in the geometrically calculated positions (U_{iso} = 0.08 Å^2) and refined using the riding model with arbitrary isotropic thermal parameters. The following weight scheme was used in the refining: $W^{-1} = \sigma^2\ (F) + 0.0008F^2$. The final values of the reliability factors are R = 0.041, R_w = 0.052, S = 1.41. All calculations were carried out on a personal computer using the SHELXTL PLUS [16] programs. Geometric parameters, atomic coordinates, and their thermal parameters are listed in Tables 2 and 3, respectively.

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Table 3. Atomic coordinates (×10⁴) and their isotropic equivalent thermal parameters (×10³) in the molecule **3**

Atom	x	y	z	U_{eq}/Å^2	Atom	x	y	z	U_{eq}/Å^2
Si(1)	2715(1)	654(1)	3199(1)	58(1)	C(22)	723(2)	2904(3)	2027(2)	49(1)
Si(2)	3866(1)	2209(1)	3092(1)	55(1)	C(23)	1011(2)	2203(3)	1480(2)	62(1)
Si(3)	2317(1)	4199(1)	3265(1)	53(1)	C(24)	695(3)	2406(4)	797(2)	76(1)
Si(4)	1175(1)	2676(1)	2951(1)	54(1)	C(25)	69(3)	3353(4)	644(2)	74(1)
O(1)	1693(2)	1315(2)	3001(1)	67(1)	C(26)	−226(3)	4071(4)	1170(2)	81(2)
O(2)	3356(2)	3560(2)	3196(1)	60(1)	C(27)	89(3)	3860(4)	1848(2)	75(1)
C(1)	2701(2)	39(3)	4110(2)	55(1)	C(28)	172(3)	2695(4)	3539(2)	91(2)
C(2)	2403(3)	740(4)	4656(2)	78(2)	H(2)	230(2)	153(3)	458(2)	8(1)
C(3)	2362(3)	271(5)	5334(2)	87(2)	H(3)	219(3)	83(3)	567(2)	10(1)
C(4)	2641(3)	−916(5)	5466(2)	93(2)	H(4)	259(3)	−125(4)	596(2)	11(1)
C(5)	2930(4)	−1634(5)	4940(3)	105(2)	H(5)	306(3)	−244(4)	503(3)	14(2)
C(6)	2958(3)	−1178(4)	4270(2)	80(2)	H(6)	317(2)	−171(3)	391(2)	10(1)
C(7)	2876(3)	−656(4)	2578(2)	90(2)	H(9)	377(2)	369(3)	182(1)	6(1)
C(8)	4321(2)	2166(3)	2159(2)	55(1)	H(10)	427(2)	361(3)	73(2)	7(1)
C(9)	4108(3)	3066(3)	1690(2)	71(1)	H(11)	523(2)	192(3)	38(2)	10(1)
C(10)	4444(3)	2989(4)	1027(2)	84(2)	H(12)	561(2)	44(3)	124(2)	10(1)
C(11)	4990(3)	2014(5)	848(2)	80(2)	H(13)	509(3)	56(3)	237(2)	11(1)
C(12)	5215(3)	1121(4)	1330(2)	83(2)	H(16)	344(2)	393(3)	462(2)	8(1)
C(13)	4888(3)	1194(4)	1991(2)	74(1)	H(17)	328(2)	452(3)	580(2)	9(1)
C(14)	4873(3)	2052(5)	3749(2)	90(2)	H(18)	191(2)	574(3)	602(2)	8(1)
C(15)	2220(2)	4698(3)	4196(2)	53(1)	H(19)	84(2)	622(3)	520(2)	9(1)
C(16)	2866(2)	4372(3)	4732(2)	58(1)	H(20)	101(2)	565(3)	403(2)	9(1)
C(17)	2767(3)	4756(4)	5417(2)	67(1)	H(23)	141(2)	162(3)	157(1)	6(1)
C(18)	2017(3)	5461(4)	5578(2)	72(1)	H(24)	96(2)	194(3)	39(2)	9(1)
C(19)	1351(3)	5772(4)	5061(2)	83(2)	H(25)	−14(2)	345(3)	14(2)	8(1)
C(20)	1460(3)	5410(4)	4385(2)	75(1)	H(26)	−65(3)	469(4)	109(2)	11(1)
C(21)	2215(3)	5593(3)	2684(2)	81(2)	H(27)	−13(1)	427(1)	218(1)	8(1)

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