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Cyclotetrasiloxanetetrols with Methyl Groups at Silicon: Isomers *all-cis*- and *cis-trans-cis*-$[\mathrm{MeSi(O)OH}]_4$

Yulia A. Pozdnyakova,* Alexander A. Korlyukov, Elena G. Kononova, Konstantin A. Lyssenko, Alexander S. Peregudov, and Olga I. Shchegolikhina

A. N. Nesmeyanov Institute of Organoelement Compounds of RAS, Vavilova 28, 119991 Moscow, Russia

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1,3,5,7-Tetramethyl-1,3,5,7-tetrahydroxycyclotetrasiloxane has been synthesized in good yield from tetrapotassium tetramethylcyclotetrasiloxanolate. Methods for isolation of *all-cis*-isomer **I** and *cis-trans-cis*-isomer **II** as the only crystalline product have been developed. Both isomers have been characterized by single-crystal X-ray diffraction analysis (XRD), elemental analysis, NMR (^{1}H, ^{13}C, ^{29}Si), and IR. The stability of these compounds in solutions and the solid state has been investigated.

1. Introduction

Cyclic organosiloxane polyols (COSPOs) of the common formula $[\mathrm{RSi(O)OH}]_n$ are of growing scientific interest due to their promising properties as precursors to the synthesis of stereoregular polysilsesquioxanes of different structures (ladderlike, polyhedral, dendrimer, etc.) and materials based on them.[1−4]

A large number of articles is devoted to the synthesis, properties and application of organosilicon compounds containing silanol groups $\mathrm{Si(OH)}_x$ ($x = 1-3$).[1−9] However, publications on cyclic organosiloxane polyols are not numerous.[4,10−15] The standard method of COSPOs synthesis is hydrolysis of the corresponding organotrichlorosilanes.[4,10−14] Disadvantages of this method, namely, its high sensibility to the set of reaction conditions and evolving of hydrogen chloride promoting condensation of the formed silanol groups, determine uncontrollable process running. This causes low-yield isolation of COSPOs and the possibility to incorporate only bulk organic groups at silicon.[16] Up to date, few COSPOs with the next substituents at silicon have been separated and characterized: Ph (phenyl), *i*-Pr (iso-propyl), FcN (2-(dimethylaminomethyl)ferrocenyl), and 2-naphthyl.[4,10−14]

Undoubtedly, synthesis of COSPOs with small-size organic groups at silicon such as methyl would be an essential step on the way to creation of new organosilicon materials with low-dielectric constants. However, the standard method, i.e. organochlorosilane hydrolysis, does not allow the preparation of these compounds.

Earlier it has been shown[15] that polyhedral alkali metal and/or transition metal oligophenylsiloxanes are the ideal precursors for the synthesis of cyclic oligophenylsiloxane polyols of the common formula $[\mathrm{PhSi(O)OH}]_n$. Removal of metal ions by the reaction between the corresponding oligophenylmetallasiloxane and the dilute hydrogen chloride acid solution in water has been found to be an easy-handling method resulting in high-yield (80−90%) formation of new stereoregular oligophenysiloxane polyols with siloxane cycles of different size: *all-cis*-$[\mathrm{PhSi(O)OH}]_4$, *all-cis*-$[\mathrm{PhSi(O)OH}]_6$, *tris-cis-tris-trans*-$[\mathrm{PhSi(O)OH}]_{12}$.

The developed approach seems to be ideal for the synthesis of the first cyclic siloxane polyol with methyl substituents at silicon. Crystalline tetrapotassium tetramethylcyclotetrasiloxanolate, *all-cis*-$[\mathrm{MeSi(O)OK}]_4\cdot \mathrm{L}_x$ (L = EtOH, $\mathrm{H_2O}$),

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*E-mail: pozdn@ineos.ac.ru.

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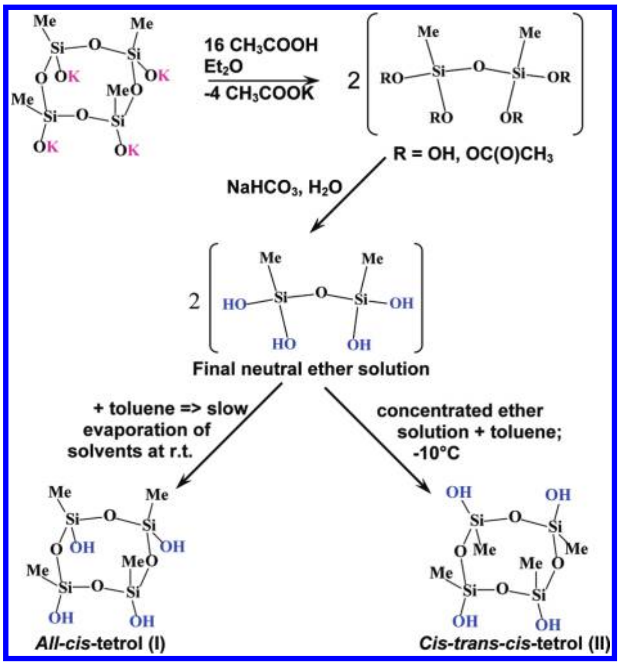
Scheme 1. Formation of *all-cis*-Tetrol **I** and *cis-trans-cis*-Tetrol **II** from *all-cis*-Tetrapotassiumtetramethylcyclotetrasiloxanolate



based on tetra-membered methylsiloxane cycle[17] is chosen as the precursor.

2. Results and Discussion

The reaction used for the synthesis of tetraphenylcyclotetrasiloxane tetrol has been found unacceptable for the synthesis of the methyl analog. This can be easily explained by the strong change of the properties (in particular, solubility) both of the initial and the final compounds with the exchange of phenyl to methyl substituents at silicon.

It has been found that tetramethylcyclotetrasiloxane tetrol can be obtained by the reaction of tetrapotassium tetramethylcyclotetrasiloxanolate with acetic acid (Scheme 1). After the treatment of *all-cis*-$[\mathrm{MeSi(O)OK}]_4 \cdot \mathrm{L}_x$ (L = EtOH, H_2O) with a 4-fold excess of acetic acid dissolved in ether and removal of potassium acetate precipitate, the solution has been neutralized with soda solution in water. The removal of ether from the final neutral solution affords oligomeric material. The use of the solvent with higher vapors pressure (toluene) results in the crystallization of tetramethylcyclotetrasiloxanetetrol in two isomeric forms. Thus, spontaneous evaporation of the solvents (i.e., ether in view of the difference in vapors pressure $p_{\mathrm{Et_2O}}$ = 442 mm/Hg, p_{toluene} = 22.3 mm/Hg) at room temperature (~20 °C) affords the crystallization of *all-cis*-tetramethylcyclotetrasiloxanetetrol **I** as the only type of crystal structure (the yield is up to 29%). The rest of the product is an oligomeric one. In contrast, the quick and deep concentrating of the neutral ether solution (removal of more than 3/4 of the solvent volume) on a rotary evaporator and further cooling up to −10 °C of the mixture toluene or benzene with concentrated ether solution gives rise to the crystallization of *cis-trans-cis*-tetramethylcyclotetrasiloxanetetrol **II** as the only type of crystal structure (the yield is up to 60%). The rest of the product is the oligomer.

Formation of the tetrol with isomerism different from the isomerism of the initial tetrapotassium tetramethylcyclotetrasiloxane indicates that the reaction progresses through the cleavage of the cycle siloxane bond. There are several possibilities of the reaction route: (a) the cleavage of one siloxane bond with the further rotation, (b) the cleavage of several siloxane bonds with the formation of silane and siloxane fragments set ($\mathrm{MeSi(OR)_3}$, $\mathrm{[MeSi(OR)_2]_2O}$, $\mathrm{Me(RO)_2SiOSiMe(OR)OSiMe(OR)_2}$, etc.), (c) the cleavage of two siloxane bonds with the formation of dimethyldihydroxy(or acetoxy)disiloxane $\mathrm{[MeSi(OR)_2]_2O}$. All possible isomers, *all-cis*, *all-trans*, *cis-trans-cis-cis*, *cis-trans-cis*, should present in the reaction products in the first two cases. The formation of only *all-cis*- and *cis-trans-cis*-isomers and absence of *all-trans*- and *cis-trans-cis-cis*-isomers (that we have in practice) seems to be an important argument for the benefit of the third reaction route (Scheme 1).

The separation of the *all-cis*-isomer and absence of any traces of *cis-trans-cis*-isomer (neither in the crystals no in the residue) after a week or more at room temperature agrees with the computations (see the Supporting Information for further details) showing the *all-cis*-isomer being the more stable one. The separation of only the less-stable *cis-trans-cis*-isomer and the absence of any traces of *all-cis*-isomer (neither in the crystals no in the residue) under the severe conditions (intensive concentration, low temperature) allowed us to consider the formation of the corresponding isomer from intermediate dimethyltetrahydroxydisiloxane during the crystallization. Isolation of the more stable *all-cis*-isomer **I** with the yield (29%) lower than the yield of the less-stable *cis-trans-cis*-isomer **II** (60%) could be explained by the difference in their crystallization (or formation, as we suppose) conditions. Room temperature and long time promote the formation of the target individual cyclic tetrol, but mostly the byproduct oligomers. Low temperature decreases but does not prevent the oligomeric byproduct formation. Also the kinetic favorability of the *cis-trans-cis*-isomer that does not form at room temperature at all could be assumed upon these data.

XRD data for *cis-trans-cis*-tetrol **II** have been taken for the crystal of benzene solvate. Identity of the tetrols obtained from benzene and toluene has been confirmed by NMR investigation. According to XRD, the crystal of **I** contains no solvate molecules while **II** is benzene solvate (see Figures 1 and 3). The bond lengths and angles at silicon atoms in **I** are close to these in **II** and similar to the structural parameters of this type compounds[4,11,13] (Table 1). Although there is some tendency of exo-cyclic Si−O bond elongation in comparison to endo ones, both of them vary in the narrow range of 1.619(2)−1.631(2) Å. The conformation of 4-membered ring in two isomers is different and can be described as crown in **I** (the deviation of O(1), O(2), O(3), and O(4) atoms from the plane of silicon atoms is −0.38, 0.46, −0.44, and 0.46 Å) and chair in **II** (the deviation of Si(1) and Si(1A) atoms from the plane of rest atoms is 0.63 Å.).

In addition to the ordered crystal structure of the *all-cis*-isomer, the structure of its other polymorph modification has been studied. The latter is characterized by disorder of molecules relative to the crystallographic *m* plane. The experimental details concerning disordered polymorph are present in the Supporting Information. In crystal packing of **I** molecules are assembled by O−H···O bonds into a double layer (Figure 2) with a hydrophobic coating composed by methyl groups. In contrast, molecules in **II** are interlinked

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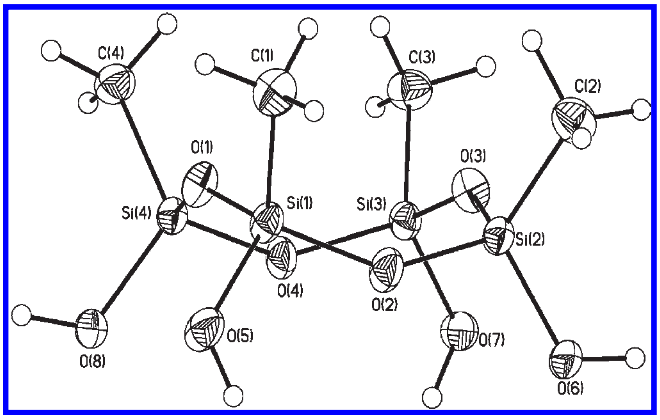

Figure 1. General view of **I** in a representation of atoms by thermal ellipsoid plot ($p = 50\%$).

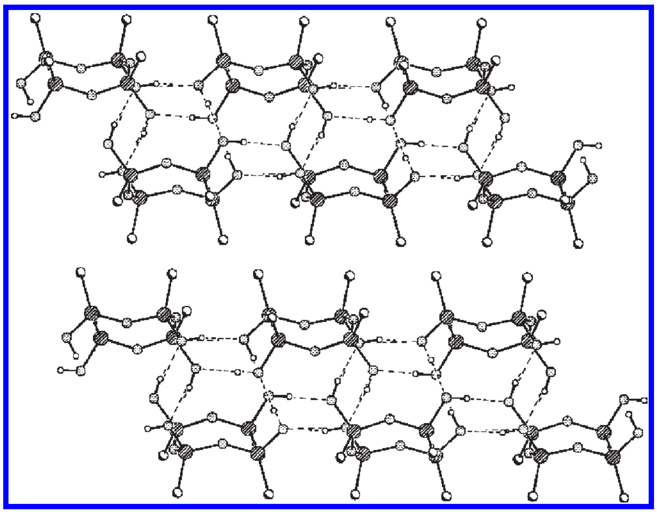

Figure 2. Packing of **I** into double layers.

Table 1. Crystal Data and Structure Refinement Parameters for **I** and **II**

compound	I	II
empirical formula	$C_4H_{16}O_8Si_4$	$C_4H_{16}O_8Si_4 \cdot C_6H_6$
formula weight	304.53	382.64
crystal color, habit	colorless prism	colorless plate
temperature (K)	120(2)	120(2)
crystal system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a (Å)	12.018(3)	7.498(1)
b (Å)	8.490(2)	7.607(1)
c (Å)	14.342(3)	9.381(1)
α (°)	90	100.151(4)
β (°)	111.283(5)	95.335(3)
γ (°)	90	115.309(3)
V (Å^3)	1363.6(6)	467.6(1)
Z (Z')	4(1)	1(0.5)
F(000)		202
D_{calc} (g cm^{-1})	1.483	1.359
linear absorption, μ (cm^{-1})	4.56	3.48
scan type	ω	ω
θ range (°)	2.76−28.99	3.05−29.02
completeness of data set (%)	96	99.0
reflections measured	6845	5263
independent reflections	3487 [0.0190]	2473 [0.0143]
observed reflections [$I > 2\sigma(I)$]	2852	1877
parameters	193	100
final $R(F_{hkl})$: R_1	0.0458	0.0550
wR_2	0.1075	0.1412
GOF	1.175	1.068
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.592/-0.410	0.605/-0.338

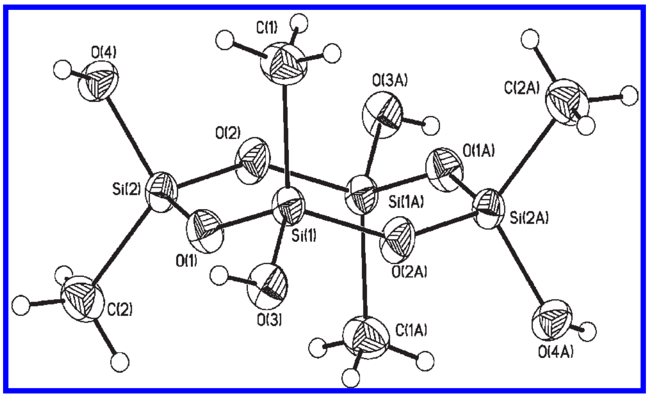

Figure 3. General view of **II** in a representation of atoms by thermal ellipsoid plot ($p = 50\%$). Atoms with the letter A are obtained from the base ones by symmetry operation 1 $-x + 1, -y + 2, -z$.

into corrugated layers by hydrogen bonds (Figure 4). Benzene molecules are situated between the layers. So, the supramolecular organization of two isomers is different. The strength cooperative H-bonds in both crystals may be slightly different due to the disorder of hydroxyl groups in **II**. Indeed, the average distance between donor and acceptor of hydrogen atom in **II** is 2.708(2) Å while the same parameter in **I** is 2.671(2) Å. Thus, we can suppose that in solid state the association of molecules in **II** is somewhat weaker than in **I**.

From the viewpoint of silanols and, especially siloxanepolyols, as a building block, the stability against the self-condensation reaction is a serious problem to be overcome because it decreases with an increase in the number of silanol groups as well as the decrease in the steric hindrance of the substituent.[18] In fact, the amount of silanol groups at each silicon atom and in a whole molecule is the first of fundamental factors determining the stability of silanoles. Other factors are the amount, nature, and steric hindrance of organic substituents at the silicon atom. Silanols and siloxanepolyols with methyl as the smallest organic group at silicon demonstrate the lowest stability in the row of organosilan- and siloxanols. Thus, $Me_2Si(OH)_2$, the most reactive silanol which has been isolated, condenses at room temperature in contact with a trace of alkali from ordinary laboratory glassware, and cannot be obtained without special treatment of the glassware before the synthesis.[19−21] Siloxane diol containing only methyl groups $[MeSi(OH)_2]_2O$ are very susceptible to condensation and has not been reported. In contrast, tetramethylsiloxanediol $[Me_2Si(OH)]_2O$ has been isolated and characterized as stable at room temperature without decomposition (the lifetime is not reported).[22] One more factor could add a further stabilizing effect. This is an intermolecular association of the hydroxyl groups.[19]

The tendency of silanol groups to form of hydrogen bonded coordination associates of different supramolecular architecture, spheric, linear, layered, etc., has been clearly shown by X-ray studies of almost all crystalline silanols and siloxanepolyols isolated up to date. One can find these data in the comprehensive reviews of Lickiss.[5,6] This material is too

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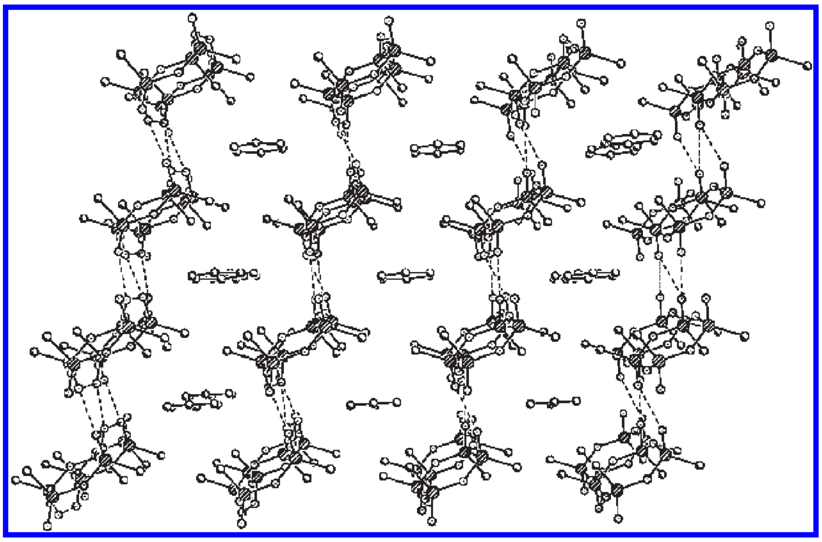

Figure 4. Packing of **II** into corrugated layers.

extensive to be discussed here. We would like to make only some notes. The factors controlling the molecule packing type are practically the same that control the stability of silanols: the number of silanol groups at each silicon atom and in a whole molecule, and the steric hindrance of organic substituent at silicon. The higher the hindrance of the organic group and the less silanol groups in a molecule, the less molecules participate in the associate construction; usually it is a dimer structure. A higher number of silanol groups and lesser organic substituent hindrance afford the formation of layered or double-layered supramolecular architecture. In our experiments, the molecule packing of tetramethylcyclotetrasiloxane tetrols could be considered as an illustration of this tendency. Furthermore, organic group volume and siloxane cycle isomerism have been demonstrated to be the crucial factors in the case of cyclic organosiloxane polyols. Thus, bulky substituents (R = ferrocenyl FcN, or 2,4, 6-triisopropylphenyl Tip) at silicon afford the hydrogen bonding of cyclosiloxane polyol molecules into infinite linear (wirelike) associates.[13,23] Determining the influence of siloxane cycle isomerism has been demonstrated in the case of highly stable isopropyl-substituted cyclotetrasiloxanetetrols [i-PrSi(O)OH]$_4$: the formation of the tetramer of the *all-cis*-isomer, corrugated layers of the *cis-trans-cis*-isomer and sheetlike aggregates of the *cis-cis-trans*-isomer has been reported by Unno et al.[4,11] Also in the hydrogen bond formation the presence of solvent or water associate molecules play significant role. So, the crystal isolation conditions could be mentioned as one of the factor controlling the supramolecular architecture. For example, molecules of hexaphenylcyclohexasiloxanehexol [PhSi(O)OH]$_6$ crystallized from acetone form infinite tubelike packing,[15] while molecules of tetraphenylcyclotetrasiloxanetetrol [PhSi(O)OH]$_4$ crystallized from ether create dimeric structure.[10]

Formation of the net linked by the strong hydrogen bonds can explain the long-life stability in air of the tetramethylcyclotetrasiloxanetetrols obtained in comparison with the less stable dimer cyclotetrasiloxanetetrol containing phenyl groups at silicon.[10] NMR investigation shows that tetramethylcyclotetrasiloxanetetrols keep their structure in the concentrated solution (0.4 m/L, acetone) up to 10 days, in the dilute solution (0.05 m/L, acetone) up to 5 weeks, and in solid state for several years. Figure 5 shows (a) ^{1}H spectrum of the tetrol **II** just isolated, (b) ^{1}H spectrum of the tetrol **II** kept in the dilute acetone solution for 5 weeks, and (c) ^{1}H spectrum of the same tetrol **II** kept in solid state for 4 years, illustrating the stability of tetrols **I** and **II**. It is clear that spectra have not been changed. NMR ^{1}H, ^{13}C, ^{29}Si spectra of the specially prepared mixture of the tetrols **I** and **II** are shown in Figure 6. Different concentration of **I** and **II** tetrols has been used for the clear identification of the signals. ^{1}H and ^{13}C spectra represent the peaks corresponding to **I** and **II** tetrols that collocate very close to each other. Thus, the ^{29}Si spectrum can be used for the certain identification of the tetrols (the difference between the peaks is about 5 ppm).

The obtained IR spectra possess all the spectral features expected for these types of compounds:[24,25] the broad intense band at 3275 cm^{-1} corresponding to the stretching vibrations of Si$-$OH groups, the band of medium intensity at 1273 cm^{-1} assigned to Si$-$CH$_3$ vibrations, and that at about 1080 cm^{-1} characteristic for Si$-$O$-$Si vibrations.

The position, width, and contour of the bands of the Si$-$OH group indicate that they are involved in hydrogen bonding, whose strength is of the same values for both *all-cis*- and *cis-trans-cis*-isomers.

However it should be noted that *all-cis*- and *cis-trans-cis*-isomers demonstrate certain differences in their vibrational spectra that further can be used for their identification. So, the band assigned to Si$-$O$-$Si vibrations (1085 cm^{-1}) is upshiftted in the case of the *cis-trans-cis*-isomer compared to that of *all-cis* one (1077 cm^{-1}). Moreover this band contour differs for *cis*- and *trans*-isomers as well. The ratio of the intensities of the bands corresponding to displacement of Si$-$O$-$Si and that of Si$-$CH$_3$ is also depends on the isomer decreasing from *cis-trans-cis* to the *all-cis* one.

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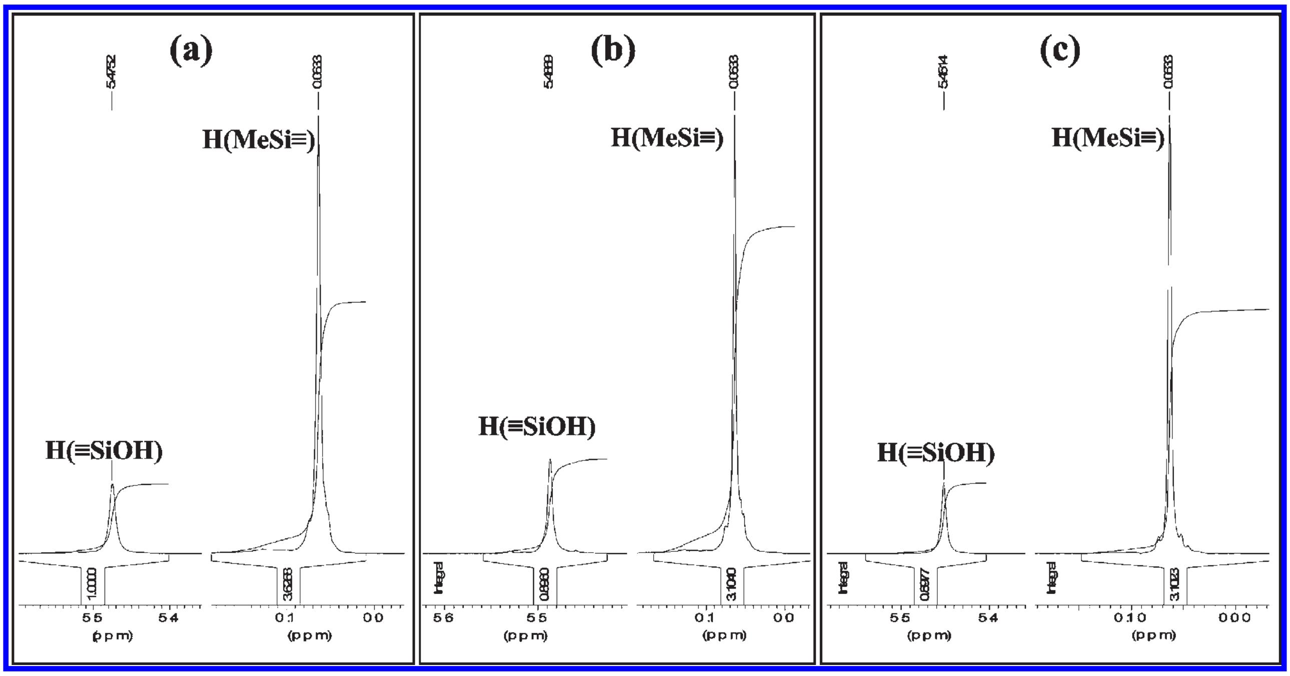

Figure 5. ^{1}H NMR spectra of tetrol **II**: (a) made immediately after the preparation; (b) kept in dilute solution for 5 weeks; (c) kept in solid state for 4 years.

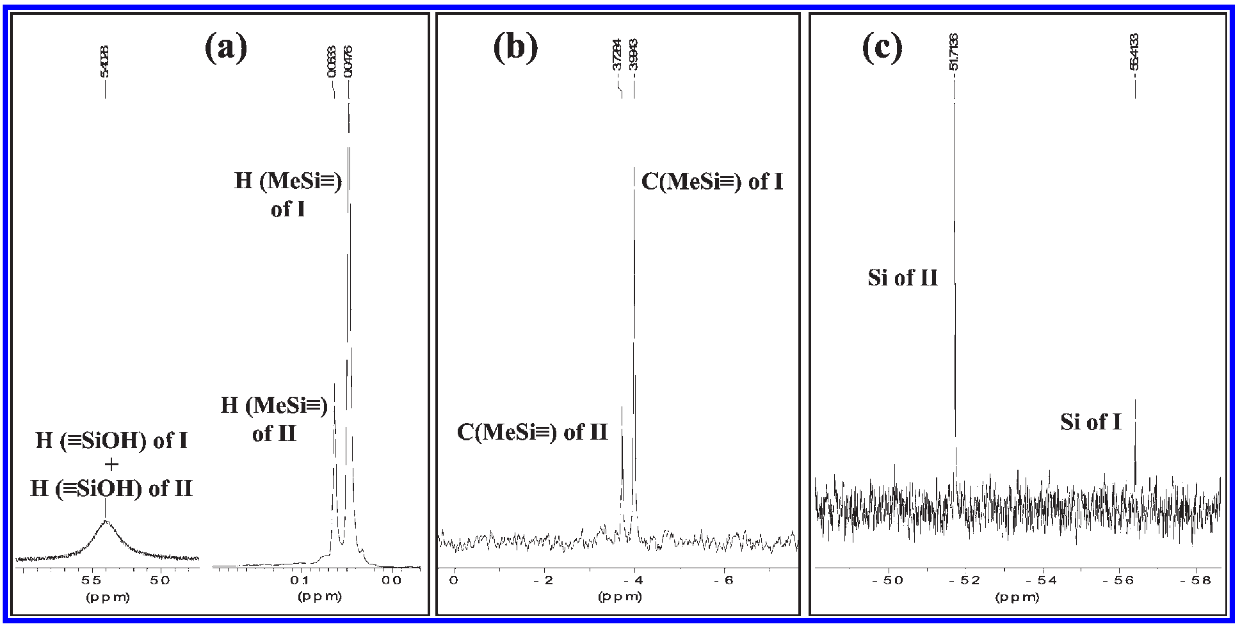

Figure 6. (a) ^{1}H, (b) ^{13}C, (c) ^{29}Si NMR spectra of the mixture of tetrols **I** and **II**. Tetrols **I** and **II** have been used in different concentrations for the purpose. (a) ^{1}H and (b) ^{13}C NMR spectra have been made for the same sample with the higher concentration of **I**. (c) The ^{29}Si NMR spectrum has been made for the other sample with the higher concentration of **II**.

3. Experimental Section

Crystalline tetrapotassium tetramethylcyclotetrasiloxanolate, *all-cis*-$[MeSi(O)OK]_4 \cdot L_x$ (L = EtOH, H_2O), was synthesized by the method described earlier.[17]

The NMR spectra were recorded on a Bruker Avance 400 spectrometer operating at 400.13, 100.61, and 79.49 MHz for ^{1}H, ^{13}C, and ^{29}Si, respectively.

The prepared **I** and **II** tetrols were characterized by IR spectra recorded in the range of 3600−400 cm^{-1} in KBr pellets and as mulls in hexachlorobutadiene using a M-82 Carl Zeiss spectrometer.

X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å, ω-scans with a 0.3° step in ω) at 120 K. Reflection intensities were integrated using SAINT software,[26] and adsorption correction was carried out semiempirically using SADABS program.[27] The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for no-hydrogen atoms. All hydrogen atoms including the disordered hydroxyl atoms were located from the Fourier density synthesis and refined in isotropic

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approximation. Crystal data and structure refinement parameters for **I** and **II** are given in Table 1.

All calculations were performed using the SHELXTL software.[28]

Tetramethylcyclotetrasiloxane-tetrols I and II. The mixture of tetrapotassium tetramethylcyclotetrasiloxanolate (3.7 g, 0.008 m) and acetic acid (5.86 g, 0.097 m) in ether (105 mL) was stirred at room temperature for the half an hour. Then, the precipitation was filtered off and the solution was washed with saturated aqueous sodium bicarbonate solution from the excess of acid. Toluene (or benzene) was added to the final ether solution in amount equal to 1/4 of the ether volume to isolate *all-cis*-tetrol **I**. The result mixture was stored at room temperature. Big transparent bricklike crystals were formed in several days. One of them was investigated by XRD. The molecular formula $[CH_3Si(O)OH]_4$ was determined. The other crystals (0.72 g, 29%) were separated by filtration and dried in vacuum. Anal found, %: C, 15.52; H, 5.09; Si, 36.61. Anal calc for $[CH_3Si(O)OH]_4$, $C_4H_{16}Si_4O_8$, %: C, 15.78; H, 5.30; Si, 36.89. ^1H NMR (400 MHz, acetone-d_6, δ, ppm): 5.43 (s, 1H, OH), 0.048 (s, 3H, Me) with the ratio of integral intensities 1:3. ^{13}C NMR (400 MHz, acetone-d_6, δ, ppm): −4.0 (s, CH_3). ^{29}Si NMR (400 MHz, acetone-d_6, δ, ppm): −56.4.

The next procedure was used to isolate *cis-trans-cis*-tetrol **II**. Most of the ether (~ 3/4) was evaporated on a rotary evaporator from the final neutral ether solution, and toluene (or benzene) was added in an amount equal to the evaporated one. The resulting mixture was stored in a refrigerator overnight. The crystals (very thin plates) were formed in several hours. The crystal from a benzene-containing solution was investigated by XRD. The molecular formula $[CH_3Si(O)OH]_4 \cdot C_6H_6$ was determined. The other crystals (2 g, 60%) were separated by filtration and dried in vacuum. Anal found, %: C, 16.59; H, 5.58; Si, 36.61. Anal calc. for $[CH_3Si(O)OH]_4$, $C_4H_{16}Si_4O_8$, %: C, 16.90; H, 5.35; Si, 36.34. ^1H NMR (400 MHz, acetone-d_6, δ, ppm): 5.48 (s, 1H, OH), 0.063 (s, 3H, Me) with the ratio of integral intensities 1:3. ^{13}C NMR (400 MHz, acetone-d_6, δ, ppm): −3.7 (s, CH_3). ^{29}Si NMR (400 MHz, acetone-d_6, δ, ppm): −51.6.

4. Conclusions

Cyclic siloxane tetrol with methyl group at silicon has been synthesized for the first time with good yield. Its long-life stability in air has been shown. Alkali metal organosiloxanolates have been demonstrated to be perspective precursors for the synthesis of small-size cyclic organosiloxane polyols with small organic substituents at silicon.

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Supporting Information Available: XRD data on the second polymorth modification of the *all-cis*-tetrol isomer. Quantum chemical calculations of *all-cis-* and *cis-trans-cis*-isomers carried out with the use of the hybrid PBE0 functional and 6-311G(d,p) basis set implemented in PC-GAMESS/FIREFLY software partially based on the GAMESS-US source code. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] Sheldrick, G. M. *SHELXTL-97*, version 5.10; Bruker AXS Inc.: Madison, WI, 1997.