Synthesis and spatial structure of novel organosilicon derivatives of *p-tert*-butylthiacalix[4]arene from two-dimensional NMR data

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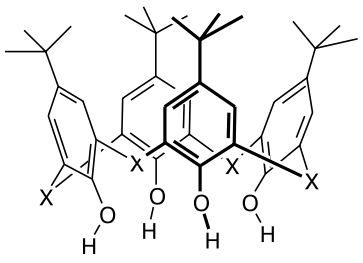
New organosilicon derivatives of *p-tert*-butylthiacalix[4]arene with one or two ring fragments at the macrocycle lower rim were synthesized. The spatial structures of the resulting compounds were established by two-dimensional NMR spectroscopy. On going from the methyl substituents at the silicon atom to phenyl substituents, closure of the second silicon-containing ring is hampered because of steric hindrance in the reaction site.

Key words: *p-tert*-butylthiacalix[4]arene, silylation, cyclophanes, functionalization, organosilicon compounds, two-dimensional NMR spectroscopy.

Calix[*n*]arenes (*n* = 4 (**1**), 6, 8), macrocyclic products of the condensation of *p*-alkylphenols and formaldehyde in an alkaline medium, are widely used as molecular platforms for the preparation of synthetic receptors.[1] Calix[4]arene derivatives are successfully used for the separation of metal cations and in catalytic systems.[2] In recent years, much attention has been paid to derivatives of the thia analog of *p-tert*-butylcalix[4]arene[3] **1**, compound **2**, in which the bridging methylene fragments have been replaced by sulfur atoms.[4]



1, 2

X = CH_2 (**1**), S (**2**)

Functionalized thiacalix[4]arenes proved to be more efficient and selective reagents compared with the corresponding derivatives of the parent calix[4]arene.[5]

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Organosilicon compounds playing an important role in catalytic and biological processes are used in the chemistry of calix[4]arenes[1] and their thia analogs[4,6—8] as intermediates in the syntheses of partial alkylation products of macrocycles. The introduction of silicon-containing groups into the *p-tert*-butylcalix[4]arene molecule was first carried out[5] in relation to construction of one and two ring fragments in the lower rim. Silicon-containing derivatives of thiacalix[4]arene were prepared[9] by treatment of *p-tert*-butylthiacalix[4]arene (**2**) with 1,1,3,3-tetraisopropyl-1,3-dichlorodisiloxane in the presence of imidazole as the base. This resulted in isolation of the product with one silicon-containing *O*,*O*′-bridging fragment at the lower rim of the macrocycle.

In this work, we synthesized new silicon-containing thiacalix[4]arene derivatives **3** and **4** incorporating one or two ring fragments in the lower rim and isolated products **5** and **6** with one cyclic and one acyclic organosilicon fragments. The spatial structures of the resulting compounds were determined by two-dimensional NMR methods.

Results and Discussion

The spatial structure of calix[4]arenes is usually considered[1] in terms of four ideal conformations: *cone*, *partial cone*, 1,2-*alternate*, and 1,3-*alternate*. Using the

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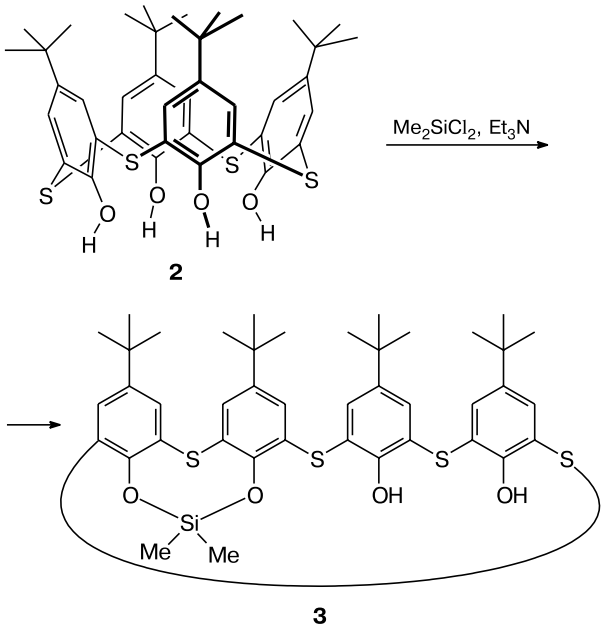
^{1}H NMR signals of the bridging methylene protons in combination with the signals of the substituents located in the upper or lower rim, it is possible, most often, to determine unambiguously the macrocycle conformation and consider the spatial arrangement of substituents. In the case of thiacalix[4]arene derivatives, determination of the conformation becomes much more complicated due to the absence of protons in the bridges connecting the aryl residues of the macrocycle. Therefore, the conformation of the new derivatives of macrocycle **2** was determined using 2D NMR spectroscopy techniques.

The silylation of cyclophane **2** with dichlorodimethylsilane in the presence of triethylamine gives products with either one (**3**) or two (**4**) silicon-containing rings in the lower rim depending on the starting reactant ratio and the reaction time and temperature (Scheme 1). The structures of the compounds were studied by a number of physicochemical methods: NMR (^{1}H, ^{13}C, ^{29}Si; 2D COSY, NOESY, HSQC, HMBC, ^{1}H/^{29}Si-HMBC), IR spectroscopy, and MALDI-TOF mass spectrometry. The assignment of signals in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of new organosilicon thiacalix[4]arenes was a challenge. This was accomplished using homonuclear ^{1}H—^{1}H 2D NMR (COSY and NOESY) and heteronuclear ^{1}H—^{13}C 2D NMR techniques (HSQC and HMBC).

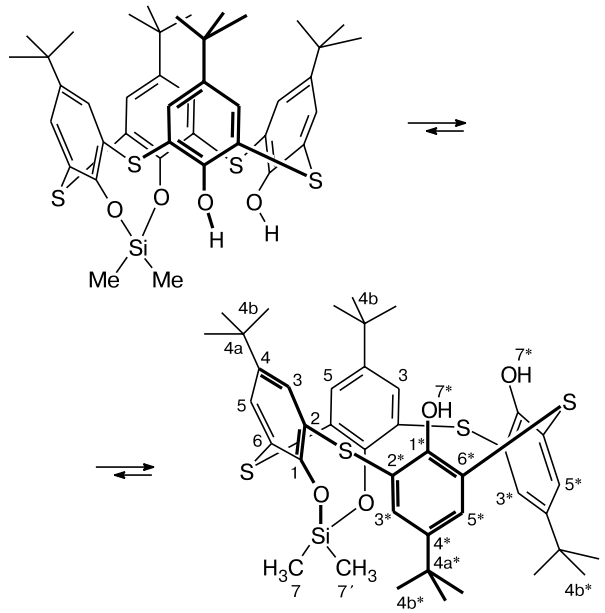
Scheme 1



Product **3** with one silicon-containing ring was obtained in 50% yield on refluxing equimolar amounts of macrocycle **2** and dichlorodimethylsilane for 16 h in toluene. In the ^{1}H NMR spectrum of thiacalix[4]arene **3**, the *tert*-butyl group protons, H(4b) and H(4b*), are responsible for two singlets and the aromatic protons account for two AB-spin system ($^4J_{H(3),H(5)}$ = 2.6 Hz, $^4J_{H(3*),H(5*)}$ = 2.4 Hz). The spectrum also exhibits a singlet at δ 6.89 corresponding to the H(7*) protons of two hydroxy groups. The signals of two Me groups at the same silicon atom differ substantially in the chemical shifts (δ 0.03 for H(7′) and δ 0.73 for H(7)). The C(7′)H$_3$ group at δ 0.03 is located in the deshielding region of the calix[4]arene aromatic rings. The number and multiplicity of the proton signals in the ^{1}H NMR spectrum of cyclophane **3** attest to the formation of 1,2-disubstituted *p-tert*-butylcalix[4]arene.

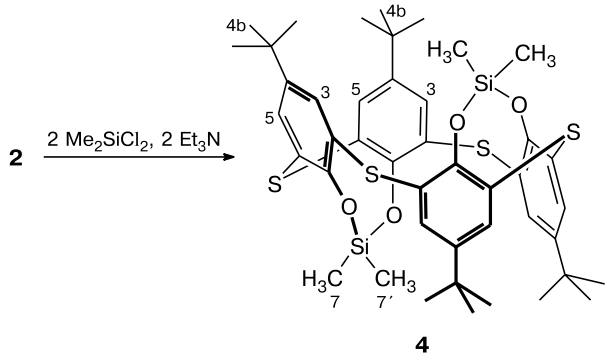
Analysis of the NOESY spectrum of compound **3** has shown that exchange between the *cone* and 1,2-*alternate* conformations takes place in the solution. In the NOESY spectrum of macrocycle **3** most of cross-peaks correspond to the *cone* conformation (H(7′), H(7*)/H(7); H(4b*)/H(3), H(5); H(4b)/H(3*); H(3*)/H(3)); however, correlations between the proton signals corresponding to the 1,2-*alternate* conformation (H(7)/H(3*), H(7)/H(5*), H(3)/H(7*)) are also present. This implies fast rotation of the hydroxyl-containing aryl fragments with respect to the macrocycle plane (Scheme 2).

Scheme 2



Silylation for 12 h at ~20 °C in the presence of triethylamine at the molar ratio **2** : Me_2SiCl_2 = 1 : 2 results in thiacalix[4]arene **4** (yield 4%) poorly soluble in organic solvents (Scheme 3). When the reaction time increases to 48 h, the yield of compound **4** increases to 19%. When the reaction is carried out in boiling toluene, macrocycles **3** and **4** are formed in 40 and 4% yields, respectively.

Scheme 3



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In the ^{1}H NMR spectrum of compound **4**, the signals of the H(4b) protons of the *tert*-butyl groups occur as a singlet, while the aromatic protons form an AB-spin system ($^4J_{H(3),H(5)}$ = 2.6 Hz), indicating a symmetrical structure of thiacalix[4]arene **4**. The ^{29}Si NMR spectrum shows one signal at δ −10.8. According to analysis of the ^{1}H/^{29}Si-HMBC 2D spectrum, the ^{1}H NMR signals at δ −1.56 (H(7′)) and δ 0.64 (H(7)) refer to the protons of the Me groups at silicon. The difference between the chemical shifts is due to the fact that one of these is located closely to the π-system of the calixarene aromatic rings and occurs in the deshielding region. The ^{13}C NMR signals were interpreted by means of the HMBC 2D NMR method. The NOESY spectrum of macrocycle **4** exhibits intense cross-peaks between the H(7′) and H(4b), H(3), H(5) proton signals, which attests in favor of the 1,2-*alternate* conformation in the case of thiacalix[4]arene.

Compounds **3** and **4** are poorly soluble in organic solvents, which hampers their further functionalization. To increase the solubility of the organosilicon thiacalix[4]arene, we used dichlorodiphenylsilane as the silylating reagent. In the study of the reaction of cyclophane **2** with dichlorodiphenylsilane, the reaction time and temperature and the reactant ratio were also varied. For the molar ratio **2** : Ph_2SiCl_2 = 1 : 2 in the presence of triethylamine, the starting macrocycle **2** was recovered quantitatively both at room temperature and in boiling toluene.

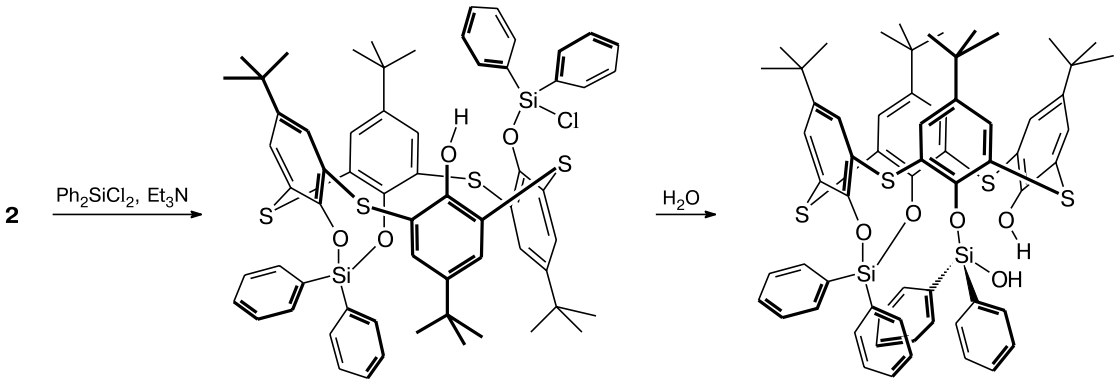
With the use of a tenfold excess of dichlorodiphenylsilane, compound **5** was obtained in 80—90% yield (Scheme 4). Macrocycle **5** is readily soluble in chloroform or dichloromethane, but is almost insoluble in alkanes.

The ^{1}H NMR spectrum of macrocycle **5** contains four singlets corresponding to the H(4b), H(4b′), H(4b*), and H(4b$^+$) protons of the *tert*-butyl groups. All eight aryl protons of the calixarene macrocycle differ by chemical shifts. The spectrum also shows signals for the protons of four Ph substituents at the silicon atoms and the singlet for the hydroxyl proton at the arene fragment of the macrocycle (δ 6.2). In the ^{29}Si NMR spectrum, two signals are observed, at δ −35.9 and −13.5. Analysis of the ^{1}H/^{29}Si HMBC spectra showed that the former corresponds to the ring silicon atom and the latter refers to the acyclic silicon atom.

The NOESY spectrum of compound **5** exhibits intense cross-peaks between the protons of the aromatic groups at the silicon atom and the protons of the opposing *tert*-butyl and aromatic substituents in the macrocycle. The H(4b) protons are located closely (distance >4.5 Å) to the H(8$^+$) and H(9$^+$) protons; H(4b′) are close to H(8$^+$), H(9$^+$), H(8^{++}), H(9^{++}), and H(10^{++}); H(4b*) are close to H(9) and H(10); and the H(4b$^+$) protons are close to H(8), H(9), and H(10). In addition, correlations were noted for the signals of aromatic protons of neighboring arene fragments in the calixarene ring, H(5) and H(3′), H(5*) and H(3$^+$), and the OH* and H(5′) proton signals. A set of such nuclear Overhauser effects (NOE) is possible only provided that thiacalix[4]arene **5** has the 1,2-*alternate* conformation.

However, the ^{1}H—^{1}H 2D NMR spectrum contains also cross-peaks between the OH*-group proton signal

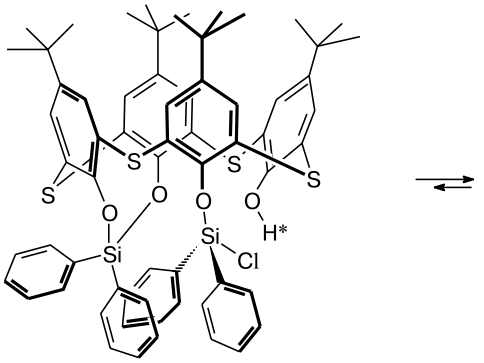
Scheme 4



5 **6**

and the H(8), H(8^+), and H(8^{++}) proton signals and also between the H(4b) and H(3^+), H(8^+) and H(9) proton signals. This is indicative of both the ability of the "non-cross-linked" arene fragments to rotate around the thiacalix[4]arene ring and of flattening of the structure. Apparently, rotation of the aryl fragment containing the hydroxy group with respect to the macrocycle plane occurs simultaneously with flattening of the cyclophane structure. Hence, rotation of the Bu^t group at the C(4^+) atom through the macrocycle plane becomes possible (Scheme 5).

Scheme 5



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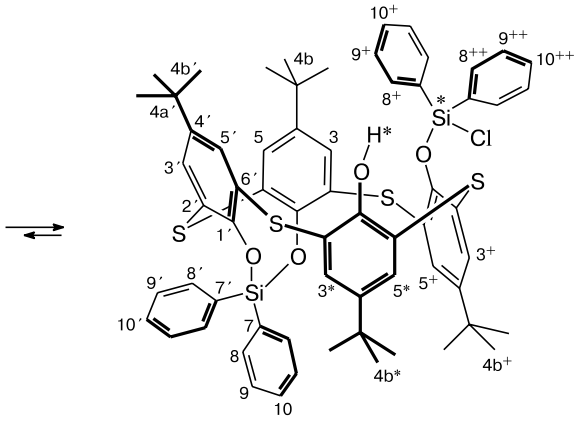
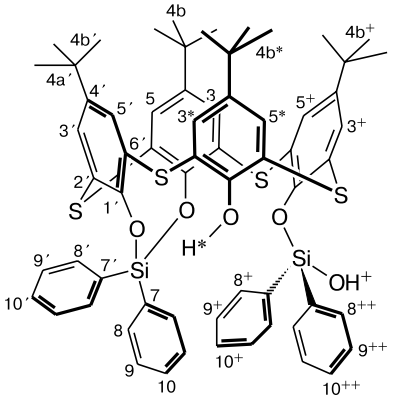


On going from Me to aryl substituent at the silicon atom, the second ring at the thiacalixarene lower rim is no longer closed. Carrying out the reaction for 2 weeks in refluxing toluene did not induce closure of the second eight-membered ring either.

When the refluxing time of the reaction mixture was increased and a 20-fold excess of dichlorodiphenylsilane was used, thiacalix[4]arene **5** was also formed in 86% yield. The product with two ring fragments at the *p-tert*-butylthiacalix[4]arene lower rim was not found. Probably, this is due to the greater bulk of Ph substituents compared to methyl groups, *i.e.*, the second eight-membered ring is not closed for steric reasons.

Compound **5** was quantitatively hydrolyzed to macrocycle **6** (see Scheme 4). The ^{1}H NMR spectrum of thiacalix[4]arene **6** shows a broad singlet at δ 3.2. Using ^{1}H/^{29}Si-HMBC 2D NMR spectroscopy, it was shown that this proton signal corresponds to the hydroxy group at the acyclic silicon atom. The ^{29}Si NMR signal at δ −36.7 was shown to correspond to the ring silicon atom and the signal at δ −32.6 is due to the acyclic silicon atom.

In the case of compound **6**, the NOESY experiment showed a strong NOE for the opposing *tert*-butyl protons (H(4b´) and H(4b), H(4b´) and H(4b*), H($4b^+$) and H(4b*)) and the aromatic protons of the substituents at silicon. This means that thiacalix[4]arene **6** exists in the *flattened cone* conformation.



6

Study of compound **6** by NOESY 2D spectroscopy demonstrated that thiacalix[4]arenes **6** and **5** exist in different conformations. Probably, during hydrolysis of chloro derivative **5**, the "non-cross-linked" aryl fragments of the macrocycle rotate around the thiacalix[4]arene ring to give first the *partial cone* conformation and then the *cone* conformation. Due to the formation of hydrogen bonds by the hydroxy groups and pronounced flattening of the cyclophane structure, the steric repulsion between the bulky phenyl fragments decreases, and the *flattened cone* conformation becomes thermodynamically more favorable.

The molecular weights of cyclophanes **3—6** determined by MALDI-TOF mass spectrometry correspond to the assumed structures.

Thus, we prepared novel organosilicon *p-tert*-butylthiacalix[4]arenes and determined their spatial structure by 2D NMR techniques.

Experimental

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 (^{1}H) and 125.77 MHz (^{13}C)). Pulse z-gradients were used for COSY, HSQC, and HMBC experiments. The spectra were recorded in $CDCl_3$ using Me_4Si as the internal standard. 2D experiments were carried out with

proton instrumentation operating at 4 MHz in both dimensions. The NOESY spectrum was obtained in the TPPI mode, with 512 scans over time interval t_1 for the second frequency dimension, 32 accumulations, and the time delay between the repetitions $d_1 = 2.0$ s. The mixing time parameter τ_m was chosen equal to 0.8 s. Mass spectra were recorded on MALDI-TOF Dynamo Finnigan and Kratos Compact MALDI-II mass spectrometers (with 1,8,9-trihydroxyanthracene or 4-nitroaniline matrices). IR spectra were recorded in KBr pellets on a Bruker Vector 2-2 FT IR spectrometer with a resolution of 1 cm^{-1} with 64 accumulated scans in the range of 400—4000 cm^{-1}. The reactions were monitored by ^1H NMR spectroscopy and TLC (Silufol UV-254 plates, visualization by iodine vapor).

5,11,17,23-Tetra-*tert*-butyl-27,28-dihydroxy-25,26-dimethylsilylenedioxy-2,8,14,20-tetrathiacalix[4]arene (3). A mixture of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-2,8,14,20-tetrathiacalix[4]arene (**2**)[3] (1 g, 1.39 mmol), dichlorodimethylsilane (0.17 mL, 1.39 mmol), and triethylamine (0.39 mL, 2.78 mmol) in anhydrous toluene (20 mL) was refluxed for 16 h under argon. The precipitate was filtered off, and the solvent and the excess of reactants were evaporated from the filtrate *in vacuo*. The solid residue was extracted with dry hexane (3×10 mL). The solvent was evaporated *in vacuo* and the residue was recrystallized from octane to give 0.55 g (50%) of the colorless solid compound **3**. Found (%): C, 64.74; H, 6.85; S, 16.44. $C_{42}H_{52}O_4S_4Si$. Calculated (%): C, 64.91; H, 6.74; S, 16.50. IR, ν/cm^{-1}: 800, 880 ($SiMe_2$); 938, 1099 ($Si(OR)_2$). ^1H NMR ($CDCl_3$), δ: 0.03 (s, 3 H, Si—C(7)H_3); 0.73 (s, 3 H, Si—C(7′)H_3); 1.17 (s, 18 H, C(4b*)H_3); 1.25 (s, 18 H, C(4b)H_3); 6.89 (s, 2 H, OH(7*)); 7.34 (d, 2 H, C(3*)H, $^4J_{H,H}$ = 2.4 Hz); 7.42 (d, 2 H, C(5*)H, $^4J_{H,H}$ = 2.4 Hz); 7.53 (d, 2 H, C(5)H, $^4J_{H,H}$ = 2.6 Hz); 7.67 (d, 2 H, C(3)H, $^4J_{H,H}$ = 2.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 0.9 (s, 1 C, C(7)); 5.5 (s, 1 C, C(7′)); 31.2 (s, 12 C, C(4b), C(4b′)); 34.2 (s, 4 C, C(4a), C(4a*)); 119.6 (s, 2 C, C(6*)); 121.3 (s, 2 C, C(2*)); 122.9 (s, 2 C, C(6)); 124.3 (s, 2 C, C(2)); 131.5 (s, 2 C, C(3*)); 132.2 (s, 2 C, C(5*)); 134.2 (s, 2 C, C(5)); 135.4 (s, 2 C, C(3)); 144.7 (s, 2 C, C(4*)); 145.1 (s, 2 C, C(4)); 154.9 (s, 2 C, C(1*), C(1)). ^{29}Si NMR ($CDCl_3$), δ: −5.9 (s, 1 Si, $SiMe_2$). ^1H—^1H NOESY NMR (NOE): H(7)/H(7*), H(7)/H(7′), H(7)/H(3*) > H(7)/H(5*), H(7*)/H(5*), H(7*)/H(3), H(7*)/H(4b*), H(4b*)/H(3*), H(4b*)/H(5*), H(4b)/H(3), H(4b)/H(5), H(4b)/H(3*) > H(4b*)/H(5), H(3*)/H(3), H(3*)/H(5*), H(3)/H(5). MS MALDI-TOF, *m/z*: 777 $[M + H]^+$.

5,11,17,23-Tetra-*tert*-butyl-25,26;27,28-bis(dimethylsilylenedioxy)-2,8,14,20-tetrathiacalix[4]arene (4). A mixture of macrocycle **2**[3] (1 g, 1.39 mmol), dichlorodimethylsilane (0.34 mL, 2.78 mmol), and triethylamine (0.77 mL, 5.56 mmol) in dry toluene (20 mL) was refluxed for 48 h under argon. The precipitate was filtered off and refluxed for 1 h in dry toluene (60 mL), and the insoluble part was filtered off. On cooling the filtrate, crystals precipitated, which were recrystallized from a chloroform—hexane mixture. The precipitate was filtered off and dried *in vacuo* at 25 °C. The product yield was 0.23 g (40%), m.p. 390 °C. Found (%): C, 63.37; H, 6.79; S, 15.26. $C_{44}H_{56}O_4S_4Si_2$. Calculated (%): C, 63.42; H, 6.77; S, 15.39. IR, ν/cm^{-1}: 800, 880 ($SiMe_2$); 938, 1099 ($Si(OR)_2$). ^1H NMR ($CDCl_3$), δ: −1.56 (s, 6 H, Si—C(7)H_3); 0.64 (s, 6 H, Si—C(7′)H_3); 1.27 (s, 36 H, C(4b)H_3); 7.41 (d, 4 H, C(3)H, $^4J_{H,H}$ = 2.6 Hz); 7.54 (d, 4 H, C(5)H, $^4J_{H,H}$ = 2.6 Hz). ^{13}C NMR ($CDCl_3$), δ: −2.7 (s, 2 C, Si—C(7)H_3); 7.5 (s, 2 C, Si—C(7′)H_3); 31.3 (s, 12 C, C(4b)H_3); 34.2 (s, 4 C, C(4a)); 123.3 (s, 4 C, C(6)); 123.7 (s, 4 C, C(2)); 129.2 (s, 4 C, C(3)); 132.4 (s, 4 C, C(5)); 144.9 (s, 4 C, C(4)); 153.9 (s, 4 C, C(1)). ^{29}Si NMR ($CDCl_3$), δ: −10.76 (s, 2 Si, $SiMe_2$). ^1H—^1H NOESY 2D NMR (NOE): H(7)/H(7′), H(7)/H(4b), H(7)/H(5) > H(7)/H(3). MS MALDI-TOF, *m/z*: 833 $[M + H]^+$.

5,11,17,23-Tetra-*tert*-butyl-28-hydroxy-25,26-diphenylsilylenedioxy-27-diphenylchlorosiloxy-2,8,14,20-tetrathiacalix[4]arene (5). A mixture of macrocycle **2**[3] (1 g, 1.39 mmol), dichlorodiphenylsilane (2.31 mL, 0.0113 mol), and triethylamine (0.77 mL, 5.56 mmol) in dry toluene (50 mL) was stirred under argon for 12 h at ~20 °C. The precipitate was filtered off, and the solvent and the excess of reactants were evaporated from the filtrate *in vacuo*. Recrystallization of the solid residue from a dichloromethane—hexane mixture gave 1.34 g (86%) of compound **5**. Found (%): C, 68.59; H, 5.75; S, 11.46. $C_{64}H_{65}ClO_4S_4Si_2$. Calculated (%): C, 68.75; H, 5.86; S, 11.47. ^1H NMR ($CDCl_3$), δ: 0.86 (s, 9 H, C(4b$^+$)H_3); 1.03 (s, 9 H, C(4b′)H_3); 1.22 (s, 9 H, C(4b*)H_3); 1.30 (s, 9 H, C(4b)H_3); 6.16 (s, 1 H, OH); 6.53 (t, 2 H, C(9)H, $^3J_{H,H}$ = 7.5 Hz); 6.66 (d, 2 H, C(8)H, $^3J_{H,H}$ = 7.5 Hz); 6.90 (d, 2 H, C(8$^+$)H, $^3J_{H,H}$ = 7.5); 6.95 (t, 1 H, C(10)H, $^3J_{H,H}$ = 7.6 Hz); 7.02 (d, 1 H, C(3*)H, $^4J_{H,H}$ = 2.3 Hz); 7.10 (d, 1 H, C(5$^+$)H, $^4J_{H,H}$ = 2.5 Hz); 7.18 (d, 1 H, C(3$^+$)H, $^4J_{H,H}$ = 2.5 Hz); 7.20 (t, 2 H, C(9$^+$)H, $^3J_{H,H}$ = 7.5 Hz); 7.23 (d, 2 H, C(8^{++})H, $^3J_{H,H}$ = 7.6 Hz); 7.25 (t, 2 H, C(9^{++})H, $^3J_{H,H}$ = 7.6 Hz); 7.28 (d, 1 H, C(5*)H, $^4J_{H,H}$ = 2.5 Hz); 7.31 (t, 2 H, C(9′)H, $^3J_{H,H}$ = 7.6 Hz); 7.36 (t, 1 H, C(10′)H, $^3J_{H,H}$ = 7.6 Hz); 7.39 (t, 1 H, C(10$^+$)H, $^3J_{H,H}$ = 7.6 Hz); 7.44 (t, 1 H, C(10^{++})H, $^3J_{H,H}$ = 7.6 Hz); 7.45 (d, 1 H, C(5)H, $^4J_{H,H}$ = 2.5 Hz); 7.55 (d, 1 H, C(3)H, $^4J_{H,H}$ = 2.5 Hz); 7.62 (d, 2 H, C(8′)H, $^3J_{H,H}$ = 7.6 Hz); 7.70 (d, 1 H, C(5′)H, $^4J_{H,H}$ = 2.5 Hz); 7.88 (d, 1 H, C(3′)H, $^4J_{H,H}$ = 2.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 30.67 (s, 3 C, C(4b$^+$)); 30.84 (s, 3 C, C(4b′)); 31.3 (s, 3 C, C(4b)); 31.4 (s, 3 C, C(4b)); 125.7 (s, 1 C, C(3)); 126.9 (s, 2 C, C(9)); 127.6 (s, 1 C, C(5$^+$)); 127.7 (s, 2 C, C(9′)); 127.8 (s, 2 C, C(9^{++})); 128.1 (s, 2 C, C(9$^+$)); 128.7 (s, 1 C, C(5)); 129.0 (s, 1 C, C(10)); 129.1 (s, 1 C, C(10′)); 130.8 (s, 1 C, C(10$^+$)); 131.3 (s, 1 C, C(10^{++})); 131.7 (s, 1 C, C(3$^+$)); 132.5 (s, 2 C, C(8′)); 133.9 (s, 1 C, C(3)); 133.9 (s, 1 C, C(5)); 134.4 (s, 2 C, C(8$^+$)); 134.3 (s, 2 C, C(8)); 134.8 (s, 1 C, C(3′)); 135.6 (s, 4 C, C(8^{++})); 137.4 (s, 1 C, C(5′)). ^{29}Si ($CDCl_3$), δ: −35.9 (s, 1 Si, Si); −13.5 (s, 1 Si, Si*). ^1H—^1H NOESY 2D NMR (NOE): H*/H(5′), H*/H(8), H*/H(8$^+$), H*/H(8^{++}), H(9)/H(3$^+$), H(8)/H(8′); H(8$^+$)/H(3), H(9$^+$)/H(3′), H(5′)/H(3′), H(5)/H(3$^+$), H(5*)/H(3*), H(5$^+$)/H(3$^+$), H(4b)/H(3), H(4b)/H(5), H(4b)/H(3$^+$), H(4b)/H(8$^+$), H(4b$^+$)/H(5), H(4b$^+$)/H(3$^+$), H(4b$^+$)/H(8), H(4b$^+$)/H(9), H(4b$^+$)/H(10), H(4b*)/H(5*), H(4b*)/H(3*), H(4b*)/H(3$^+$), H(4b*)/H(9), H(4b*)/H(10), H(4b′)/H(3′), H(4b′)/H(5′), H(4b′)/H(8^{++}), H(4b′)/H(9^{++}), H(4b′)/H(10^{++}), H(4b′)/H(9$^+$), H(4b′)/H(10$^+$), H(9)/H(8), H(9)/H(10), H(8$^+$)/H(9), H(9$^+$)/H(10$^+$), H(9^{++})/H(10^{++}). MS MALDI-TOF, *m/z*: 1118 $[M + H]^+$.

5,11,17,23-Tetra-*tert*-butyl-28-hydroxy-27-hydroxydiphenylsiloxy-25,26-diphenylsilylenedioxy-2,8,14,20-tetrathiacalix[4]arene (6). A solution of compound **5** (1.34 g, 1.20 mmol) in chloroform containing traces of water was stirred for 12 h. The solvent was evaporated *in vacuo*. Recrystallization of the solid residue from dichloromethane—hexane mixture gave 1.32 g (100%) of compound **6**. Found (%): C, 69.88; H, 5.99; S, 11.62. $C_{64}H_{66}O_5S_4Si_2$. Calculated (%): C, 69.91; H, 6.05; S, 11.66.

IR, ν/cm^{-1}: 936 (Si—OH, Si(OAr)$_2$); 1096 ((OAr)$_2$); 1124, 1430 (SiPh). ^{1}H NMR ($CDCl_3$), δ: 0.47 (s, 9 H, C(4b$^+$)H$_3$); 1.061 (s, 9 H, C(4b´)H$_3$); 1.25 (s, 9 H, C(4b*)H$_3$); 1.35 (s, 9 H, C(4b)H$_3$); 3.22 (br.s, 1 H, OH$^+$); 5.86 (s, 1 H, OH*); 6.13 (d, 1 H, C(5$^+$)H, $^4J_{H,H}$ = 2.5 Hz); 6.35 (d, 1 H, C(3$^+$)H, $^4J_{H,H}$ = 2.5 Hz); 7.13 (t, 2 H, C(9)H, $^3J_{H,H}$ = 7.5 Hz); 7.18 (t, 1 H, C(10)H, $^3J_{H,H}$ = 7.5 Hz); 7.21 (t, 2 H, C(9´)H, $^3J_{H,H}$ = 7.4 Hz); 7.23 (t, 1 H, C(10´)H, $^3J_{H,H}$ = 7.4 Hz); 7.30 (t, 2 H, C(9^{++})H, $^3J_{H,H}$ = 7.6 Hz); 7.34 (d, 1 H, C(5´)H, $^4J_{H,H}$ = 2.5 Hz); 7.39 (t, 1 H, C(10^{++})H, $^3J_{H,H}$ = 7.6 Hz); 7.42 (t, 2 H, C(9$^+$)H, $^3J_{H,H}$ = 7.6 Hz); 7.45 (d, 1 H, C(5*)H, $^4J_{H,H}$ = 2.4 Hz); 7.48 (t, 1 H, C(10$^+$)H, $^3J_{H,H}$ = 7.6 Hz); 7.51 (d, 1 H, C(5)H, $^4J_{H,H}$ = 2.6 Hz); 7.60 (d, 2 H, C(8´)H, $^3J_{H,H}$ = 7.4 Hz); 7.63 (d, 1 H, C(3*)H, $^4J_{H,H}$ = 2.4 Hz); 7.67 (d, 2 H, C(8^{++})H, $^3J_{H,H}$ = 7.6 Hz); 7.84 (d, 1 H, C(3)H, $^4J_{H,H}$ = 2.6 Hz); 8.02 (d, 2 H, C(8$^+$)H, $^3J_{H,H}$ = 7.6 Hz); 8.47 (d, 2 H, C(8´)H, $^3J_{H,H}$ = 7.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 30.8 (s, 3 C, C(4b$^+$)); 31.0 (s, 3 C, C(4b´)); 31.4 (s, 6 C, C(4b), C(4b*)); 127.0 (s, 1 C, C(10^{++})); 127.6 (s, 2 C, C(10)); 127.7 (s, 2 C, C(9´)); 127.8 (s, 2 C, C(9^{++})); 128.5 (s, 2 C, C(9)); 129.3 (s, 1 C, C(5$^+$)); 129.4 (s, 1 C, C(10´)); 129.8 (s, 1 C, C(3$^+$)); 130.2 (s, 1 C, C(10$^+$)); 130.3 (s, 2 C, C(9$^+$)); 132.6 (s, 2 C, C(8´)); 133.3 (s, 2 C, C(5*), C(5)); 133.8 (s, 1 C, C(3*)); 134.7 (s, 2 C, C(8)); 135.0 (s, 2 C, C(8^{++})); 135.1 (s, 2 C, C(8$^+$)); 138.0 (s, 1 C, C(3)). ^{29}Si NMR ($CDCl_3$), δ: −36.7 (s, Si); −32.6 (s, Si$^+$—OH). ^{1}H—^{1}H NOESY 2D NMR (NOE): H(4b$^+$)/H*, H(4b$^+$)/H(3´), H(4b$^+$)/H(5´), H(4b$^+$)/H(5*), H(4b$^+$)/H(5), H(4b$^+$)/H(3$^+$), H(4b$^+$)/H(3), H(4b$^+$)/H(5$^+$), H(4b$^+$)/H(4b), H(4b$^+$)/H(4b´), H(4b´)/H(4b*), H(4b´)/H(3*), H(4b´)/H(3´), H(4b´)/H(5´), H(4b´)/H(9´), H(4b´)/H(3$^+$), H(4b*)/H(3*), H(4b*)/H(5*), H(4b*)/H(5´), H(4b*)/H(3$^+$), H(4b)/H(3), H(4b)/H(5), H(4b)/H(5$^+$), H(4b)/H(3´), H(5$^+$)/H(3), H(3$^+$)/H(5*), H(5´)/H(3*), H(3´)/H(5), H*/H(8), H*/H(9), H(9)/H(8), H(9)/H(8$^+$), H(9)/H(8^{++}), H(9)/H(9$^+$), H(9´)/H(8´), H(9$^+$)/H(8$^+$), H(9^{++})/H(8^{++}), H(8)/H(8´), H(8)/H(8^{++}), H(9)/H(8^{++}). MS MALDI-TOF, *m/z*: 1122 [M + Na]$^+$.

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