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Preparation and structures of novel silamacrocyclic compounds: silacalix[4]quinone and silacalix[4]hydroquinone octamethyl ether†‡

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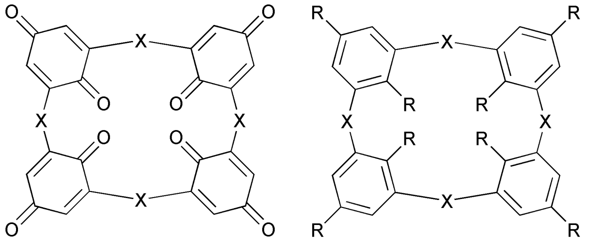
X-Ray crystallographic analysis revealed that novel silamacrocyclic compounds, 2,8,14,20-tetrasilacalix[4]quinone and 2,8,14,20-tetrasilacalix[4]hydroquinone octamethyl ether, adopted 1,3-alternate structures in the solid state.

1,4-Benzoquinone (quinone) is one of the most interesting fundamental π-electron systems because its high electron affinity and photoreactivity.[1–3] Calixquinones[4,5] (*e.g.* **1**) and calixhydroquinones[4–7] (*e.g.* **2** and **3**), which are members of the calixarenes,[8] have received intense interest due to their electrochemical reactivities, conformational behavior in solution, structures in the solid states, and incorporation of metal ions (Chart 1). However, silicon-bridged calixquinones and calixhydroquinones have not been reported.[9,10] We report the first successful syntheses of tetrasilacalix[4]quinone **4** and tetrasilacalix[4]hydroquinone octamethyl ether **5**.

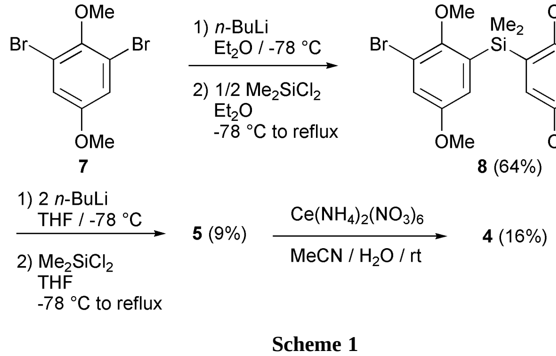
Compounds **4** and **5** were prepared as shown in Scheme 1. Monolithiation of **7** and reaction with Me_2SiCl_2 yielded **8** as colorless crystals in 64% yield. Dilithiation of **8** followed by the addition of Me_2SiCl_2 gave **5** as colorless crystals in 9% yield. Oxidation of **5** by cerium ammonium nitrate[3] gave **4** as orange crystals in 16% yield. The structures of **4** and **5** were characterized by ^1H, ^{13}C, and ^{29}Si NMR and mass spectrometry.§¶ Finally, their structures were unequivocally determined by X-ray crystallography as described below.‖** To the best of our knowledge, **4** is the first example of a heteroatom-bridged calix[4]quinone derivative.



1 ($X = CH_2$)
4 ($X = SiMe_2$)

2 ($X = CH_2$, $R = OH$)
3 ($X = CH_2$, $R = OMe$)
5 ($X = SiMe_2$, $R = OMe$)
6 ($X = SiMe_2$, $R = H$)

Chart 1



Scheme 1

A single crystal of **5** suitable for X-ray crystallographic analysis was obtained from a hexane solution. The crystal lattice of **5** included no solvent molecule. The observed molecular structure of **5** is shown in Fig. 1. Compounds **6**[10] and **3**[7] (Chart 1) have a 1,2-alternate conformation and an acutely pinched cone structure, respectively, in the solid state. However, a 1,3-alternate structure of **5** was revealed using X-ray analysis. The two pairs of opposing benzene rings are nearly parallel. Interatomic distances between Si(1)···Si(3) and Si(2)···Si(4), corresponding to the diameter of an internal 16-membered ring of **5**, were 8.35 Å and 8.30 Å, respectively. The angles of C(arene)–Si–C(arene) in **5** were 111.2–114.9° (av. 112.9°), which are slightly wider than those in **6** (av. 109.7°). The bond lengths of C(arene)–Si in **5** were 1.894–1.918 Å (av. 1.909 Å), which are slightly longer than those in **6** (av. 1.873 Å). The slightly wider C(arene)–Si–C(arene) angles and longer C(arene)–Si bonds in the structure of **5** are indicative of its strained structure.

A single crystal of **4** suitable for X-ray analysis was obtained from a *p*-xylene solution and contained solvent molecules in the lattice at a **4** : *p*-xylene ratio of 2 : 3. Although the corresponding carbon-bridged calix[4]quinone **1** has a partial cone conformation,[4] **4** had a 1,3-alternate structure as shown in Fig. 2. The interatomic distance between Si(1)···Si(2)*, corresponding to the diameter of an internal 16-membered ring of **4**, was 8.17 Å. The closest interatomic distance between C(4)···C(25) was 3.351 Å, which is slightly shorter than the sum of the van der Waals radii (3.4 Å), indicating that hydrophobic interactions between **4** and *p*-xylene would exist. The angles of C(quinone)–Si–C(quinone) in **4** were 108.52 and 108.54°, which are close to the ideal angle in an sp^3 silicon atom (109.5°). Neither an elongation of the covalent bonds nor a significant distortion of the coordination geometry was observed in the structure of **4**, indicative of its strain-free structure.

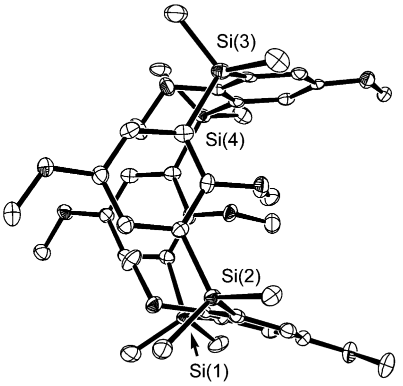


Fig. 1 Molecular structure of **5**.** Hydrogen atoms are omitted for clarity.

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† Dedicated to Prof. Mitsuo Kira on the occasion of his 60th birthday.
‡ Electronic supplementary information (ESI) available: experimental procedures, spectral data and X-ray data of the products. See http://www.rsc.org/suppdata/cc/b3/b307048d/

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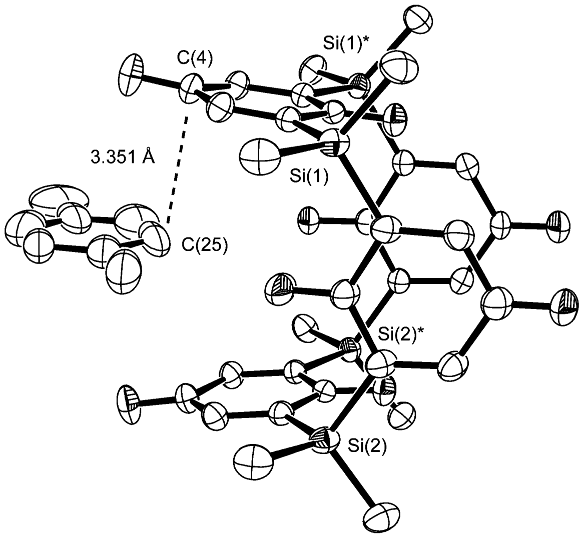

Fig. 2 Molecular structure of **4** with the closest *p*-xylene.‖ Hydrogen atoms and the other *p*-xylene are omitted for clarity.

The conformational behavior of **4** and **5** in solution was investigated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **4** showed one methyl peak and one quinone-ring proton peak in $CDCl_3$ at room temperature. The ^{1}H NMR spectrum of **5** contained two types of methoxy peaks, one methyl peak, and one phenyl peak in $CDCl_3$ at room temperature. We conducted variable-temperature ^{1}H NMR analyses of **4** and **5** in acetone-*d*$_6$, but no splitting of the peaks derived from freezing or changing of the conformation was observed, even at 183 K, not only for **4** but also for the slightly strained molecule **5**. Compounds **4** and **5** would adopt 1,3-alternate structures, or ring inversion of **4** and **5** occurred rapidly on the NMR time scale even at low temperatures. Yoshida *et al.* reported that **6** possesses significant conformational flexibility in solution judging from the X-ray data and PM3 calculations.[10] Thus, it is reasonable that **4** and **5** possess significant conformational flexibility in solution.

Electronic spectra of **4**, **9** and **10** in CH_2Cl_2 are shown in Fig. 3. A band centered at *ca.* 250 nm assignable to a π–π* transition was observed for the silylquinones. The absorption maxima of the π–π* transition was similar to that in **1** (248 nm in $CHCl_3$).[5] The spectrum of **4** showed an apparent hypochromic effect. In the spectra of **4** and **9**, a broad band was observed at *ca.* 300 nm, which would originate from conjugation of the quinone moieties through the silicon groups.

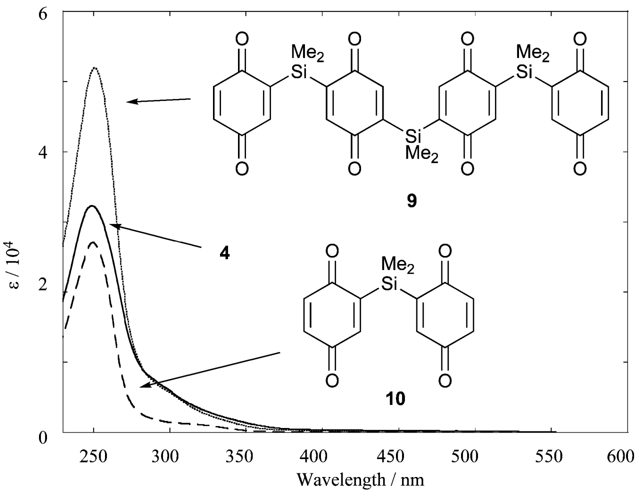

Fig. 3 UV-Vis spectra of **4**, **9**, and **10** in CH_2Cl_2.

In conclusion, we have succeeded in preparing novel silamacrocyclic compounds, tetrasilacalix[4]quinone **4** and tetrasilacalix[4]hydroquinone octamethyl ether **5**. Compound **5** was converted to **4** by cerium ammonium nitrate oxidation. Compound **4** is the first example of a heteroatom-bridged calix[4]tetraquinone. The 1,3-alternate structures of **4** and **5** were revealed by X-ray crystallographic analysis. The UV–Vis spectrum of **4** indicated that a hypochromic effect appeared in the π–π* transition band. Further investigations on the properties of **4** and **5** are in progress.

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Notes and references

§ Spectral data for **4**: orange crystals; mp 163–165 °C (decomp.); ^{1}H NMR ($CDCl_3$, δ) 0.31 (s, 24H), 6.97 (s, 8H); ^{13}C NMR ($CDCl_3$, δ) −4.26, 144.18, 150.12, 185.15, 192.44; ^{29}Si NMR ($CDCl_3$, δ) −11.92; FAB-HRMS *m*/*z* found 657.1269 [M + H$^+$], calcd for $C_{32}H_{33}O_8Si_4$, 657.1253; IR $\nu_{C=O}$ 1648, 1653 cm^{-1}; UV (CH_2Cl_2) $\lambda_{max/nm}$ (ε) 249 (32300).

¶ Spectral data for **5**: colorless crystals; mp 294–294.5 °C; ^{1}H NMR ($CDCl_3$, δ) 0.51 (s, 24H), 2.68 (s, 12H), 3.78 (s, 12H), 7.04 (s, 8H); ^{13}C NMR ($CDCl_3$, δ) −0.57, 55.56, 61.61, 121.82, 132.52, 154.51, 164.05; ^{29}Si NMR ($CDCl_3$, δ) −11.16; MS (70 eV) 777 (M$^+$); Anal. Calcd for $C_{40}H_{56}O_8Si_4$: C, 61.81; H, 7.26%. Found: C, 61.71; H, 7.14%.

‖ Crystal data for **4**: $2(C_{32}H_{32}O_8Si_4)\cdot3(C_8H_{10})$, M = 1632.35, orange prism, monoclinic, Mo-Kα (λ = 0.71073 Å); space group = $C2/m$, a = 24.866(4) Å, b = 13.099(2) Å, c = 16.060(3) Å, β = 122.575(3)°, V = 4407.9(13) Å^3, Z = 2, T = 123 K, D_c = 1.230 g cm^{-3}, GOF = 1.027, R = 0.0570 [$I > 2\sigma(I)$], R = 0.1872 (all data). CCDC 213340. See http://www.rsc.org/suppdata/cc/b3/b307048d/ for crystallographic data in .cif or other electronic format.

** Crystal data for **5**: $C_{40}H_{56}O_8Si_4$; M = 777.21, colorless prism; Mo-Kα (λ = 0.71073 Å); monoclinic; $P2(1)/n$, a = 11.569(11) Å, b = 16.408(16) Å, c = 23.63(2) Å, β = 103.093(17)°, V = 4369(8) Å^3, Z = 4, D_{calc} = 1.182 g cm^{-3}, T = 120 K, GOF = 0.821, R = 0.0525 [$I > 2\sigma(I)$], R = 0.1202 (all data). CCDC 213339. See http://www.rsc.org/suppdata/cc/b3/b307048d/ for crystallographic data in .cif or other electronic format.

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