Preparation, Structures, and Theoretical Calculations of Novel Silacalixarene Derivatives: Silacalix[4]quinone and Silacalix[4]hydroquinone Octamethyl Ether

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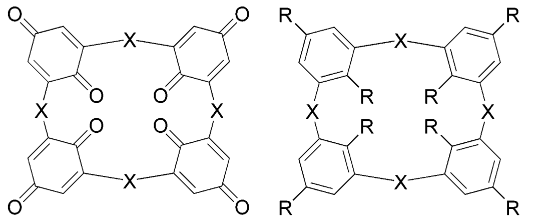
A novel silicon-bridged calix[4]arene derivative, 2,8,14,20-tetrasilacalix[4]hydroquinone octamethyl ether (**6**), has been successfully prepared. Cerium ammonium nitrate oxidation of **6** gave the first heteroatom-bridged calixquinone derivative, 2,8,14,20-tetrasilacalix[4]-quinone (**5**). The structures of **5** and **6** were determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy and mass spectroscopy. X-ray crystallographic analysis confirmed the structures of **5** and **6**. X-ray crystal structures revealed that **5** and **6** adopted 1,3-alternate conformations. The conformations of **5** and **6** were also studied by theoretical calculations. The optimized 1,3-alternate conformer of **5** is at least 4.9 kcal/mol more stable than the other conformers at the B3LYP/6-31G(d) level. This finding is in agreement with the solid-state structure. In contrast, the optimized 1,3-alternate conformer of **6** is 1.3 kcal/mol less stable than the corresponding 1,2-alternate conformer. The result suggests that **6** has significant conformational flexibility.

Introduction

Much attention has been focused on calixarenes due to their ability to form complexes with metal ions and a number of organic molecules.[1] Although there have been numerous reports on calixarenes with various arene units, very few studies on the replacement of all arene units by 1,4-benzoquinones (quinones) or hydroquinones have been reported.[2] Quinone is one of the most interesting fundamental π-electron systems because it possesses properties such as high electron affinity and photoreactivity.[3−5] Calixquinones[6−8] (such as **1**) and calixhydroquinones[9,10] (such as **2** and **3**), which are members of the calixarenes, have received much interest due to their electrochemical reactivity, conformational behavior in solution, structures in the solid states, and ability to incorporate metal ions (Chart 1).[2] The synthesis of **1** was accomplished by Rosik in 1986.[6] In 1989 Morita et al. reported a multistep synthesis of

Chart 1



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

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

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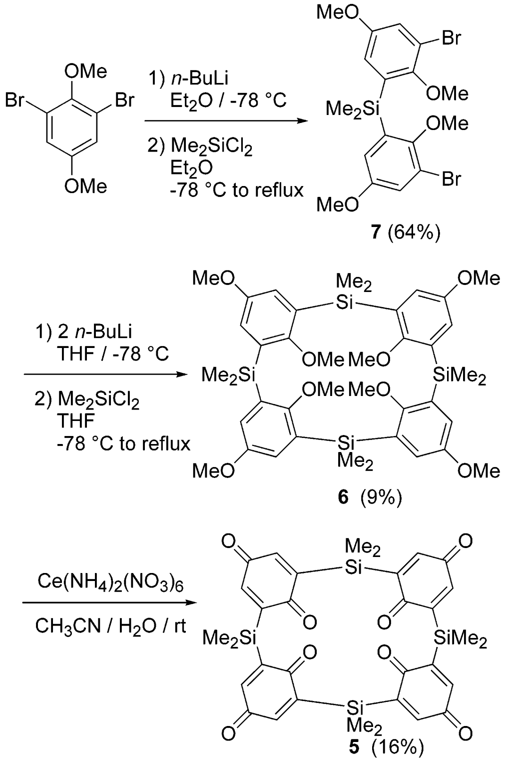
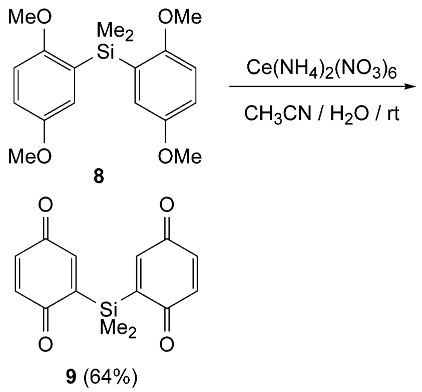
10.1021/om0499310 CCC: $27.50

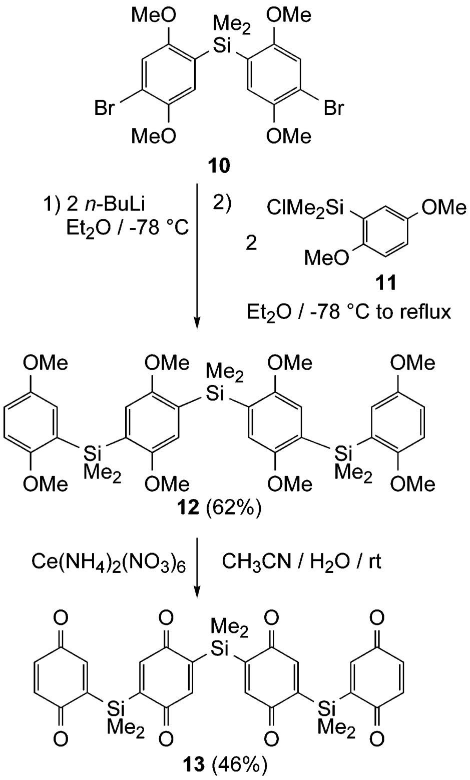
Scheme 1



Scheme 2



Scheme 3



1 and provided conclusive X-ray crystallographic data for its structure.[7a] In 1992 Reddy et al. reported the synthesis and properties of calix[5]quinone and calix[6]quinone.[8a] In 2001 Kim et al. reported the synthesis and characterization of the self-assembly of organic nanotube arrays formed by calix[4]hydroquinone (**2**), which are electrochemically reduced from **1**.[9] A number of silicon-bridged macrocycles (such as **4**) were reported;[11−14] however, silicon-bridged calix[*n*]quinones and calix[*n*]hydroquinones have not been reported so far. The introduction of a silicon atom as the bridge provides an additional opportunity to tune the ring size, conformation, binding properties, and electronic properties of the macrocycle. Herein we report the first successful synthesis of 2,8,14,20-tetrasilacalix[4]quinone (**5**).[15] Compound **5** was obtained by the oxidation of a novel silicon-bridged calix[4]arene derivative, 2,8,14,20-tetrasilacalix[4]arene octamethyl ether (**6**), with cerium ammonium nitrate (CAN).[15,16] To the best of our knowledge, **5** is the first example of a heteroatom-bridged calix[4]tetraquinone derivative. The structures of **5** and **6** in the solid state were established by X-ray crystallography. In addition, the relative stability of the conformational isomers of **5** and **6** was investigated by quantum chemical calculations.

Results and Discussion

Preparation. Compounds **5** and **6** were prepared from the multistep route shown in Scheme 1. Monolithiation of 2,6-dibromo-1,4-dimethoxybenzene and reaction with Me_2SiCl_2 yielded colorless crystals of **7** in 64% yield. Dilithiation of **7** followed by the addition of Me_2SiCl_2 produced colorless crystals of **6** in 9% yield. Oxidation of **6** using CAN yielded orange crystals of **5** in 16% yield. Compounds **5** and **6** were isolated by gel permeation chromatography (GPC). The structures of **5** and **6** were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and mass spectrometry. Finally, their structures were determined unequivocally by X-ray crystallography.

As shown in Schemes 2 and 3, acyclic silicon-bridged quinone dimer and tetramer (**9** and **13**) were also

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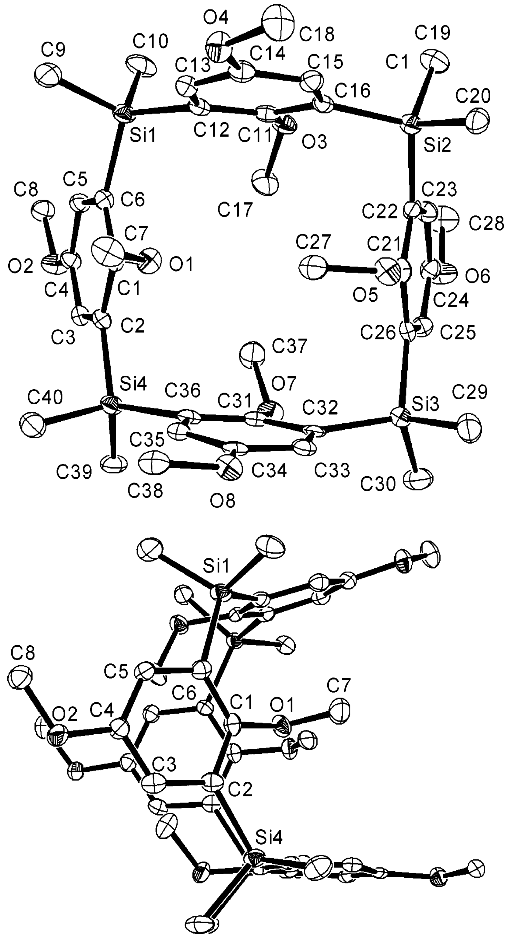

Figure 1. ORTEP drawings of **6** with thermal ellipsoids drawn at the 50% probability level; upper, top view; lower, side view. Hydrogen atoms are omitted for clarity.

prepared by CAN oxidation of the corresponding 1,4-dimethoxybenzene derivatives **8** and **12**, respectively.[17] The structures of **9** and **13** were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR and mass spectrometry. The molecular structure of **9** was determined using X-ray crystallography.

X-ray Crystallographic Analysis. Gutsche suggested the four common conformations of the calix[4]arene derivative: the cone, partial cone, 1,2-alternate, and 1,3-alternate conformations.[18] To reveal the molecular structures of **5** and **6** in the solid state, X-ray crystallographic analysis was performed.

A single crystal of **6**, suitable for X-ray crystallographic analysis, was obtained by recrystallization from hexane. The crystal lattice of **6** did not incorporate a solvent molecule. The observed molecular structure of **6** is shown in Figure 1. Crystal data and structure refinement for **6** are summarized in Table 1. Selected bond lengths and angles for **6** are summarized in Table 2. Silacalix[4]arene **4**[14] and octamethoxycalix[4]arene **3**[10] (Chart 1) have a 1,2-alternate conformation and an acutely pinched cone structure in the solid state, respectively. However, a 1,3-alternate structure of **6** was revealed using X-ray analysis. The interatomic distances between Si(1)- - -Si(3) and Si(2)- - -Si(4), corresponding to the internal diameter of the 16-membered ring of **6**, were 8.35 and 8.30 Å, respectively. The angles of C(arene)−Si−C(arene) in **6** were 111.2−114.9° (av 112.9°), which are slightly wider than those in **4** (av 109.7°). The bond lengths of C(arene)−Si in **6** were 1.894−1.918 Å (av 1.909 Å), which are slightly longer than those in **4** (av 1.873 Å). The slightly wider C(arene)−Si−C(arene) angles and longer C(arene)−Si bonds in the structure of **6** are indicative of its strained structure.

A single crystal of **5**, suitable for X-ray analysis, was obtained by recrystallization from *p*-xylene. This crystal was found to contain solvent molecules in the lattice with a **5**:*p*-xylene ratio of 2:3. A suitable single crystal of **5**, which did not contain solvent molecules, could not be obtained from THF, Et$_2$O, or CHCl$_3$ solutions. The solid-state structure of **9** was also determined for use as a reference. A single crystal of **9**, suitable for X-ray crystallographic analysis, was obtained by recrystallization from hexane, and the crystal lattice did not incorporate solvent molecules. The observed molecular structures of **5** and **9** are shown in Figures 2 and 3, respectively. Crystal data and structure refinement for **5** and **9** are summarized in Table 1. Selected bond lengths and angles for **5** and **9** are summarized in Tables 3 and 4, respectively.

Morita et al.[7a] reported that **1** has a partial cone conformation. The molecule has four quinone rings, two of which are a pair of opposing quinone rings oriented parallel to each other. The other pair of opposing quinone rings, however, has a dihedral angle of 49.7° between the rings with the corresponding carbonyl groups oriented in opposite directions. The molecular structure of **5** was clearly different from that of **1**. Thus, **5** was determined to have a 1,3-alternate structure, as shown in Figure 2. The interatomic distance between Si(1)- - -Si(2)*, corresponding to the internal diameter of the 16-membered ring of **5**, was 8.17 Å. The interatomic distances between one O atom and the opposing O atom were 5.37−6.82 Å. The smallest interatomic distance was determined to be between C(4)- - -C(25) as 3.351 Å, slightly shorter the sum of the van der Waals radii (3.4 Å), indicating that hydrophobic interactions between **5** and *p*-xylene exist. The angles of C(quinone)−Si−C(quinone) in **5** were 108.52° and 108.54°, close to the corresponding angle in **9** (107.11°). The bond lengths of C(quinone)−Si in **5** were 1.874−1.892 Å (av 1.885 Å), which are similar to that of **9** (av 1.889 Å). Neither an elongation of the covalent bonds nor a significant distortion of the coordination geometry was observed in the structure of **5**, confirming its strain-free structure.

NMR Spectroscopy. Mascal et al. reported that octamethoxycalix[4]arene **3** is a mixture of the cone and partial cone conformations in CDCl$_3$.[10] The molecular structure of calix[4]quinone **1** in the solid state appears to have a partial cone conformation. However, the methylene and quinone-ring protons gave two singlet peaks, which would be assignable to a 1,3-alternate conformation, in pyridine-d_6 solution at 243 K. Yoshida et al. previously determined the 1,2-alternate conformation of silacalix[4]arene **4** using X-ray crystallography, and the conformer was not observable in solution even with low-temperature ^{1}H NMR analyses (188 K).[14a] The

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Table 1. Crystal Data and Structure Refinement for 5, 6, and 9

	2(**5**)·3(*p*-xylene)	**6**	**9**
formula	$C_{88}H_{94}O_{16}Si_8$	$C_{40}H_{56}O_8Si_4$	$C_{14}H_{12}O_4Si$
fw	1632.35	777.21	272.33
temp (K)	123(2)	123(2)	123(2)
cryst descript	orange plate	colorless plate	orange needle
cryst size (mm^3)	0.40 × 0.15 × 0.13	0.30 × 0.20 × 0.15	0.30 × 0.30 × 0.20
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*m*	*P*2(1)/*n*	*P*2(1)/*n*
a (Å)	24.866(4)	11.569(11)	6.7860(9)
b (Å)	13.099(2)	16.408(16)	11.7022(15)
c (Å)	16.060(3)	23.63(2)	17.048(2)
α (deg)	90	90	90
β (deg)	122.575(3)	103.093(17)	99.913(2)
γ (deg)	90	90	90
V (Å^3)	4407.9(13)	4369(8)	1333.6(3)
Z	2	4	4
ρ_{calcd} (Mg/m^3)	1.23	1.182	1.356
abs coeff (mm^{-1})	0.185	0.183	0.183
F(000)	1724	1664	568
θ range for data collection (deg)	1.50 to 28.00	1.52 to 25.00	2.12 to 26.99
index range	$-31 \leq h \leq 32$	$-13 \leq h \leq 13$	$-7 \leq h \leq 8$
	$-14 \leq k \leq 17$	$-9 \leq k \leq 19$	$-14 \leq k \leq 14$
	$-20 \leq l \leq 18$	$-28 \leq l \leq 27$	$-20 \leq l \leq 21$
no. of reflns collected	13 196	21 757	7716
no. of indep reflns	5135	7676	2862
R(int)	0.0346	0.1125	0.0229
no. of reflns with $I > 2\sigma(I)$	3185	4197	2240
no. of data/restraints/params	5135/0/290	7676/0/485	2862/0/174
goodness-of-fit on F^2	1.027	0.821	1.007
final R indices $[I > 2\sigma(I)]^a$	R1 = 0.0570	R1 = 0.0525	R1 = 0.0335
	wR2 = 0.1710	wR2 = 0.1073	wR2 = 0.0883
R indices (all data)	R1 = 0.0946	R1 = 0.1043	R1 = 0.0451
	wR2 = 0.1872	wR2 = 0.1202	wR2 = 0.0916
largest diff peak and hole (e Å^{-3})	0.601 and −0.426	0.421 and −0.358	0.454 and −0.203

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

X-ray data and the PM3 calculations established that **4** has significant conformational flexibility in solution.

In the present study, the conformational behavior of **5** and **6** in solution was investigated by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **5** showed one methyl peak and one quinone-ring proton peak in $CDCl_3$ at room temperature. The ^{1}H NMR spectrum of **6** contained two types of methoxy peaks, one methyl peak, and one phenyl peak in $CDCl_3$ at room temperature. Variable-temperature ^{1}H NMR analyses of **5** and **6** in acetone-d_6 were conducted; however no peak splitting derived from freezing or conformational changes was observed, even at 183 K. This finding held true not only for **5** but also for the slightly strained molecule **6**. Either compounds **5** and **6** adopted a 1,3-alternate conformation, or ring inversion of **5** and **6** occurred rapidly on the NMR time scale, even at low temperatures.

Theoretical Calculations. To investigate the conformational isomerism in calixarenes, theoretical calculation studies on the structures of calixarenes have been conducted.[14,19] For example, significant conformational flexibility of silacalixarene **4** in solution has been revealed by PM3 calculations.[14a] In the present study, density functional theory (DFT) calculations on the conformations of **5** and **6** were performed. DFT calculations of **5** and **6** were carried out at the B3LYP/6-31G(d) level. The computed structures of **5** and **6** are shown in Figures 4 and 5, respectively. Relative energies of conformers of **5** and **6** are listed in Table 5.

Four stable conformers of **5** have been found by the calculation as shown in Figure 4. The most stable conformer of **5** is a 1,3-alternate structure, which is in agreement with experimental results (Table 5). The order of stability of the four conformations is 1,3-alternate > partial cone > cone > 1,2-alternate. The 1,3-alternate conformer is at least 4.9 kcal/mol more stable than other conformers at the B3LYP/6-31G(d) level. The stability of the 1,3-alternate conformer probably stems from minimization of the Coulomb repulsion between neighboring quinone rings. The energy levels of the four conformers are within 8.9 kcal/mol.

Four stable conformers have also been obtained for **6** as shown in Figure 5. The order of stability of the four conformations of **6** is 1,2-alternate > 1,3-alternate > partial cone > cone. The 1,3-alternate conformer, which was observed by X-ray crystallographic analysis, is only 1.3 kcal/mol less stable than the 1,2-alternate conformer. The energy levels of the four conformers are within 3.8 kcal/mol. The calculations suggest that **6** possesses significant conformational flexibility.

Conclusions

Multistep preparation of a novel silicon-bridged calixarene, 2,8,14,20-tetrasilacalix[4]hydroquinone octamethyl ether (**6**), has been accomplished. This compound was oxidized to 2,8,14,20-tetrasilacalix[4]quinone (**5**) by CAN. Compound **5** is the first example of a heteroatom-bridged calix[4]tetraquinone. Acyclic silicon-bridged quinone dimer and tetramer (**9** and **13**) were also

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Table 2. Selected Bond Lengths [Å] and Angles [deg] for 5

C(1)−O(1)	1.224(3)	C(13)−C(14)	1.489(3)
C(1)−C(2)	1.492(4)	C(14)−C(15)	1.340(4)
C(1)−C(6)	1.498(4)	C(14)−Si(2)	1.892(3)
C(2)−C(3)	1.339(4)	C(15)−C(16)	1.469(4)
C(2)−Si(1)	1.885(3)	C(16)−O(6)	1.225(5)
C(3)−C(4)	1.472(4)	C(17)−Si(2)	1.870(3)
C(4)−O(2)	1.229(4)	C(18)−Si(2)	1.848(3)
C(4)−C(5)	1.475(4)	C(19)−C(20)	1.376(9)
C(5)−C(6)	1.347(4)	C(19)−C(22)	1.530(11)
C(6)−Si(2)	1.874(3)	C(20)−C(21)	1.431(12)
C(7)−Si(1)	1.863(3)	C(23)−C(28)	1.327(14)
C(8)−Si(1)	1.859(3)	C(23)−C(24)	1.357(15)
C(9)−O(3)	1.228(5)	C(23)−C(29)	1.556(15)
C(9)−C(10)	1.494(4)	C(24)−C(25)	1.374(17)
C(10)−C(11)	1.343(4)	C(25)−C(26)	1.432(16)
C(10)−Si(1)	1.889(3)	C(26)−C(27)	1.368(11)
C(11)−C(12)	1.478(4)	C(26)−C(30)	1.524(15)
C(12)−O(4)	1.234(5)	C(27)−C(28)	1.416(14)
C(13)−O(5)	1.237(5)		

O(1)−C(1)−C(2)	119.6(2)	C(14)−C(15)−C(16)	123.0(3)
O(1)−C(1)−C(6)	119.7(2)	O(6)−C(16)−C(15)	121.33(17)
C(2)−C(1)−C(6)	120.7(2)	C(15)−C(16)−C(15)*	117.3(3)
C(3)−C(2)−C(1)	117.8(2)	C(20)−C(19)−C(22)	120.5(8)
C(3)−C(2)−Si(1)	124.3(2)	C(19)−C(20)−C(21)	120.4(8)
C(1)−C(2)−Si(1)	117.91(19)	C(28)−C(23)−C(24)	121.7(15)
C(2)−C(3)−C(4)	123.1(3)	C(28)−C(23)−C(29)	119.4(11)
O(2)−C(4)−C(3)	121.2(3)	C(24)−C(23)−C(29)	118.9(12)
O(2)−C(4)−C(5)	120.8(3)	C(23)−C(24)−C(25)	120.0(14)
C(3)−C(4)−C(5)	118.0(3)	C(24)−C(25)−C(26)	120.6(11)
C(6)−C(5)−C(4)	122.0(3)	C(27)−C(26)−C(25)	116.8(13)
C(5)−C(6)−C(1)	118.3(2)	C(27)−C(26)−C(30)	122.6(11)
C(5)−C(6)−Si(2)	123.9(2)	C(25)−C(26)−C(30)	120.6(10)
C(1)−C(6)−Si(2)	117.70(19)	C(26)−C(27)−C(28)	120.9(11)
O(3)−C(9)−C(10)	119.21(18)	C(23)−C(28)−C(27)	120.0(11)
C(10)*−C(9)−C(10)	121.6(4)	C(8)−Si(1)−C(7)	111.11(16)
C(11)−C(10)−C(9)	117.5(3)	C(8)−Si(1)−C(2)	108.33(14)
C(11)−C(10)−Si(1)	124.5(2)	C(7)−Si(1)−C(2)	109.82(13)
C(9)−C(10)−Si(1)	118.0(2)	C(8)−Si(1)−C(10)	109.97(15)
C(10)−C(11)−C(12)	122.7(3)	C(7)−Si(1)−C(10)	109.03(14)
O(4)−C(12)−C(11)	121.09(19)	C(2)−Si(1)−C(10)	108.54(12)
C(11)−C(12)−C(11)*	117.8(4)	C(18)−Si(2)−C(17)	110.89(15)
O(5)−C(13)−C(14)	119.62(17)	C(18)−Si(2)−C(6)	110.32(13)
C(14)*−C(13)−C(14)	120.8(3)	C(17)−Si(2)−C(6)	109.52(14)
C(15)−C(14)−C(13)	117.9(3)	C(18)−Si(2)−C(14)	109.10(13)
C(15)−C(14)−Si(2)	123.8(2)	C(17)−Si(2)−C(14)	108.45(14)
C(13)−C(14)−Si(2)	118.3(2)	C(6)−Si(2)−C(14)	108.52(12)

prepared by CAN oxidation. The structures of **5** and **6** were elucidated as 1,3-alternate conformers by X-ray crystallographic analysis. Variable-temperature ^{1}H NMR analyses of **5** and **6** suggested that either **5** and **6** adopted 1,3-alternate conformation, or ring inversion of **5** and **6** occurred rapidly on the NMR time scale, even at low temperatures. Theoretical calculations of the conformational isomers of **5** and **6** showed that a 1,3-alternate conformer of **5** and a 1,2-alternate conformer of **6** were the most stable conformers. The 1,3-alternate conformer of **5** is at least 4.9 kcal/mol more stable than the other conformers, and the energy levels of the four conformers are within 8.9 kcal/mol. On the other hand, the 1,3-alternate conformer of **6** is only 1.3 kcal/mol less stable than the 1,2-alternate conformer, and the energy levels of the four conformers of **6** are within 3.8 kcal/mol. Thus, the presented calculations suggest that **5** adopts the 1,3-alternate conformer and **6** has significant conformational flexibility in solution.

Experimental Section

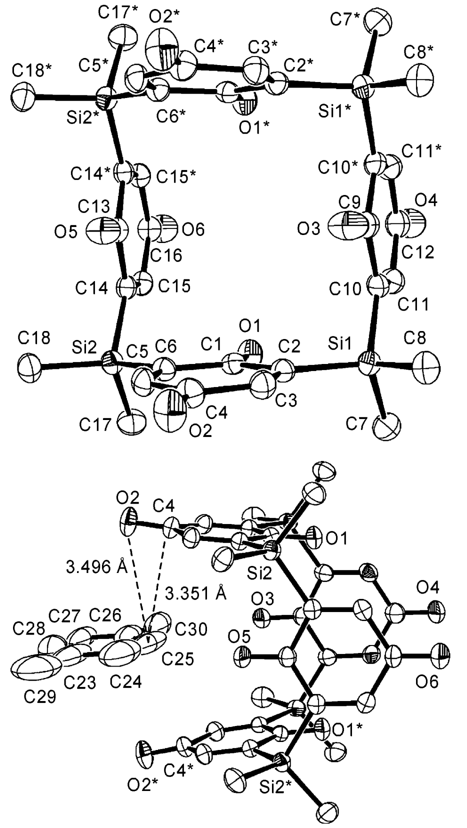

Figure 2. ORTEP drawings of **5** with thermal ellipsoids drawn at the 50% probability level; upper, top view; lower, side view. Hydrogen atoms are omitted for clarity.

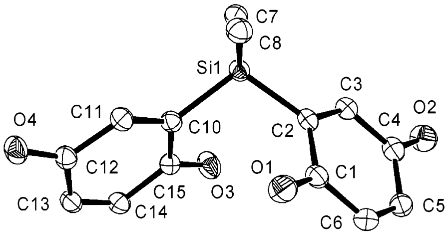

Figure 3. ORTEP drawing of **9** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

General Methods. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian INOVA 300 FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. Mass spectra were recorded on Shimadzu GCMS-QP5050A and HITACHI M-2500 mass spectrometers. High-resolution mass spectra were obtained on HITACHI M-2500 and JEOL MS700 mass spectrometers. Electronic absorption spectra were recorded on a Milton Roy Spectronic 3000 Array spectrometer. Gel permeation chromatography (GPC) was conducted on a LC908-C60 recycling high-pressure liquid chromatograph (Japan Analytical Instruments, Co. Ltd.) with JAIGEL-1H (40 mm × 600 mm), JAIGEL-2H (40 mm × 600 mm), and JAIGEL-2.5H (40 mm × 600 mm) columns using chloroform as the mobile phase.

Materials. *n*-BuLi (1.55 N in hexane), Et_2O, Me_2SiCl_2, hexane, CH_2Cl_2, sodium chloride, anhydrous magnesium sulfate, $CDCl_3$, THF, $CHCl_3$, cerium ammonium nitrate (CAN), CH_3CN, TMEDA, EtOH, 1,4-dimethoxybenzene, and acetone-d_6 were obtained from standard commercial sources. Benzyltrimethylammonium tribromide,[20] 2,6-dibromo-4-methoxyphenol,[21] 2,6-dibromo-1,4-dimethoxybenzene,[21] and 2,5-dibromo-1,4-dimethoxybenzene[22] were prepared as described in the Supporting Information.

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[20] Kajigaeshi, S.; Kakinami, T.; Tokiyama, H.; Hirakawa, T.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2667.

[21] Kajigaeshi, S.; Kakinami, T.; Tokiyama, H.; Hirakawa, T.; Okamoto, T. *Chem. Lett.* **1987**, 627.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 6

C(1)−C(6)	1.402(5)	C(21)−C(22)	1.412(5)
C(1)−C(2)	1.417(5)	C(21)−C(26)	1.418(5)
C(1)−O(1)	1.419(4)	C(21)−O(5)	1.420(4)
C(2)−C(3)	1.416(5)	C(22)−C(23)	1.422(5)
C(2)−Si(4)	1.918(4)	C(22)−Si(2)	1.907(4)
C(3)−C(4)	1.390(5)	C(23)−C(24)	1.399(5)
C(4)−O(2)	1.387(4)	C(24)−O(6)	1.392(4)
C(4)−C(5)	1.398(5)	C(24)−C(25)	1.400(5)
C(5)−C(6)	1.418(5)	C(25)−C(26)	1.408(5)
C(6)−Si(1)	1.914(4)	C(26)−Si(3)	1.912(4)
C(7)−O(1)	1.428(4)	C(27)−O(5)	1.466(4)
C(8)−O(2)	1.441(4)	C(28)−O(6)	1.434(4)
C(9)−Si(1)	1.878(4)	C(29)−Si(3)	1.883(4)
C(10)−Si(1)	1.882(4)	C(30)−Si(3)	1.876(4)
C(11)−O(3)	1.407(4)	C(31)−C(36)	1.416(5)
C(11)−C(16)	1.415(5)	C(31)−O(7)	1.416(4)
C(11)−C(12)	1.422(5)	C(31)−C(32)	1.423(5)
C(12)−C(13)	1.414(5)	C(32)−C(33)	1.411(5)
C(12)−Si(1)	1.911(4)	C(32)−Si(3)	1.894(4)
C(13)−C(14)	1.405(5)	C(33)−C(34)	1.403(5)
C(14)−O(4)	1.397(4)	C(34)−O(8)	1.396(4)
C(14)−C(15)	1.398(5)	C(34)−C(35)	1.398(4)
C(15)−C(16)	1.424(5)	C(35)−C(36)	1.424(5)
C(16)−Si(2)	1.907(4)	C(36)−Si(4)	1.911(4)
C(17)−O(3)	1.439(4)	C(37)−O(7)	1.436(4)
C(18)−O(4)	1.445(4)	C(38)−O(8)	1.444(4)
C(19)−Si(2)	1.895(4)	C(39)−Si(4)	1.878(4)
C(20)−Si(2)	1.881(4)	C(40)−Si(4)	1.885(4)

C(6)−C(1)−C(2)	123.2(3)	O(7)−C(31)−C(32)	113.9(3)
C(6)−C(1)−O(1)	120.1(3)	C(33)−C(32)−C(31)	117.1(3)
C(2)−C(1)−O(1)	116.3(3)	C(33)−C(32)−Si(3)	121.2(3)
C(3)−C(2)−C(1)	116.1(3)	C(31)−C(32)−Si(3)	121.3(3)
C(3)−C(2)−Si(4)	118.6(2)	C(34)−C(33)−C(32)	121.6(3)
C(1)−C(2)−Si(4)	125.3(3)	O(8)−C(34)−C(35)	124.3(3)
C(4)−C(3)−C(2)	122.6(3)	O(8)−C(34)−C(33)	116.2(3)
O(2)−C(4)−C(3)	116.8(3)	C(35)−C(34)−C(33)	119.5(3)
O(2)−C(4)−C(5)	123.8(3)	C(34)−C(35)−C(36)	122.1(3)
C(3)−C(4)−C(5)	119.3(3)	C(31)−C(36)−C(35)	116.3(3)
C(4)−C(5)−C(6)	121.0(3)	C(31)−C(36)−Si(4)	127.3(3)
C(1)−C(6)−C(5)	117.7(3)	C(35)−C(36)−Si(4)	116.2(3)
C(1)−C(6)−Si(1)	127.5(3)	C(1)−O(1)−C(7)	116.0(3)
C(5)−C(6)−Si(1)	114.7(2)	C(4)−O(2)−C(8)	118.0(3)
O(3)−C(11)−C(16)	114.5(3)	C(11)−O(3)−C(17)	117.3(2)
O(3)−C(11)−C(12)	122.4(3)	C(14)−O(4)−C(18)	116.4(3)
C(16)−C(11)−C(12)	122.8(3)	C(21)−O(5)−C(27)	115.1(2)
C(13)−C(12)−C(11)	116.1(3)	C(24)−O(6)−C(28)	117.6(3)
C(13)−C(12)−Si(1)	116.5(3)	C(31)−O(7)−C(37)	118.8(3)
C(11)−C(12)−Si(1)	127.3(3)	C(34)−O(8)−C(38)	116.7(3)
C(14)−C(13)−C(12)	122.7(3)	C(9)−Si(1)−C(10)	107.06(18)
O(4)−C(14)−C(15)	126.0(3)	C(9)−Si(1)−C(12)	109.34(16)
O(4)−C(14)−C(13)	114.3(3)	C(10)−Si(1)−C(12)	108.90(16)
C(15)−C(14)−C(13)	119.8(3)	C(9)−Si(1)−C(6)	108.51(15)
C(14)−C(15)−C(16)	120.1(3)	C(10)−Si(1)−C(6)	108.58(15)
C(11)−C(16)−C(15)	118.4(3)	C(12)−Si(1)−C(6)	114.22(15)
C(11)−C(16)−Si(2)	120.3(3)	C(20)−Si(2)−C(19)	108.30(18)
C(15)−C(16)−Si(2)	121.1(2)	C(20)−Si(2)−C(22)	108.66(16)
C(22)−C(21)−C(26)	122.9(3)	C(19)−Si(2)−C(22)	109.23(16)
C(22)−C(21)−O(5)	119.0(3)	C(20)−Si(2)−C(16)	109.20(16)
C(26)−C(21)−O(5)	118.1(3)	C(19)−Si(2)−C(16)	110.15(16)
C(21)−C(22)−C(23)	117.8(3)	C(22)−Si(2)−C(16)	111.23(15)
C(21)−C(22)−Si(2)	123.6(2)	C(30)−Si(3)−C(29)	107.77(18)
C(23)−C(22)−Si(2)	118.6(2)	C(30)−Si(3)−C(32)	111.39(17)
C(24)−C(23)−C(22)	120.7(3)	C(29)−Si(3)−C(32)	108.35(17)
O(6)−C(24)−C(23)	123.9(3)	C(30)−Si(3)−C(26)	109.19(17)
O(6)−C(24)−C(25)	116.3(3)	C(29)−Si(3)−C(26)	108.89(17)
C(23)−C(24)−C(25)	119.7(3)	C(32)−Si(3)−C(26)	111.16(15)
C(24)−C(25)−C(26)	122.2(3)	C(39)−Si(4)−C(40)	106.21(17)
C(25)−C(26)−C(21)	116.8(3)	C(39)−Si(4)−C(36)	109.43(16)
C(25)−C(26)−Si(3)	119.5(2)	C(40)−Si(4)−C(36)	109.14(17)
C(21)−C(26)−Si(3)	123.6(3)	C(39)−Si(4)−C(2)	109.24(17)
C(36)−C(31)−O(7)	122.8(3)	C(40)−Si(4)−C(2)	107.53(17)
C(36)−C(31)−C(32)	123.2(3)	C(36)−Si(4)−C(2)	114.92(15)

Table 4. Selected Bond Lengths [Å] and Angles [deg] for 9

C(1)−O(1)	1.2272(18)	C(8)−Si(1)	1.8546(15)
C(1)−C(6)	1.480(2)	C(9)−O(3)	1.2203(18)
C(1)−C(2)	1.484(2)	C(9)−C(14)	1.481(2)
C(2)−C(3)	1.346(2)	C(9)−C(10)	1.492(2)
C(2)−Si(1)	1.8914(15)	C(10)−C(11)	1.338(2)
C(3)−C(4)	1.475(2)	C(10)−Si(1)	1.8871(15)
C(4)−O(2)	1.2259(19)	C(11)−C(12)	1.483(2)
C(4)−C(5)	1.470(2)	C(12)−O(4)	1.2267(17)
C(5)−C(6)	1.334(2)	C(12)−C(13)	1.470(2)
C(7)−Si(1)	1.8515(17)	C(13)−C(14)	1.331(2)

O(1)−C(1)−C(6)	120.16(15)	C(11)−C(10)−C(9)	117.97(13)
O(1)−C(1)−C(2)	120.34(14)	C(11)−C(10)−Si(1)	122.84(11)
C(6)−C(1)−C(2)	119.50(13)	C(9)−C(10)−Si(1)	119.16(10)
C(3)−C(2)−C(1)	118.09(14)	C(10)−C(11)−C(12)	123.35(14)
C(3)−C(2)−Si(1)	123.29(12)	O(4)−C(12)−C(13)	121.74(13)
C(1)−C(2)−Si(1)	118.56(10)	O(4)−C(12)−C(11)	120.94(14)
C(2)−C(3)−C(4)	122.61(15)	C(13)−C(12)−C(11)	117.29(13)
O(2)−C(4)−C(5)	120.92(14)	C(14)−C(13)−C(12)	120.79(14)
O(2)−C(4)−C(3)	120.95(16)	C(13)−C(14)−C(9)	121.36(14)
C(5)−C(4)−C(3)	118.12(14)	C(7)−Si(1)−C(8)	111.72(7)
C(6)−C(5)−C(4)	120.69(14)	C(7)−Si(1)−C(10)	109.39(7)
C(5)−C(6)−C(1)	120.82(15)	C(8)−Si(1)−C(10)	107.92(7)
O(3)−C(9)−C(14)	120.40(14)	C(7)−Si(1)−C(2)	109.02(7)
O(3)−C(9)−C(10)	120.67(13)	C(8)−Si(1)−C(2)	111.55(7)
C(14)−C(9)−C(10)	118.92(13)	C(10)−Si(1)−C(2)	107.11(6)

Preparation of Bis(3-bromo-2,5-dimethoxyphenyl)dimethylsilane (7). A hexane solution (48.0 mL) of *n*-BuLi (1.55 N, 74.4 mmol) was added to an Et_2O (500 mL) solution of 2,6-dibromo-1,4-dimethoxybenzene (21.6 g, 73.0 mmol) at −78 °C. The mixture was stirred at −78 °C for 2 h. Then, an Et_2O (10 mL) solution of Me_2SiCl_2 (4.71 g, 36.5 mmol) was added to the solution at −78 °C. The mixture was stirred at room temperature overnight and under reflux for 1 h and subsequently hydrolyzed with water. The organic layer was separated off, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure. Bulb-to-bulb distillation [180−220 °C (bath temperature)/0.8 mmHg] yielded **7** (11.4 g, 23.3 mmol, 64%). **7**: colorless crystals; mp 84−84.5 °C; ^{1}H NMR ($CDCl_3$, δ) 0.58 (s, 6H), 3.47 (s, 6H), 3.74 (s, 6H), 6.92 (d, J = 2.7 Hz, 2H), 7.08 (d, J = 2.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, δ) −1.47, 55.66, 61.13, 116.48, 119.61, 120.52, 134.16, 155.26, 155.82; ^{29}Si NMR ($CDCl_3$, δ) −8.56; MS (70 eV) *m*/*z* 488 (M^+). Anal. Calcd for $C_{18}H_{22}Br_2O_4Si$: C, 44.10; H, 4.52. Found: C, 44.10; H, 4.71.

Preparation of 2,8,14,20-Tetrasilacalix[4]hydroquinone Octamethyl Ether (6). A hexane (3.1 mL) solution of *n*-BuLi (1.55 N, 4.81 mmol) was added to a THF (200 mL) solution of **7** (1.12 g, 2.29 mmol) at −78 °C. The mixture was stirred at −78 °C for 2 h. Me_2SiCl_2 (0.28 mL, 2.31 mmol) was subsequently added to the solution at −78 °C. After stirring at −78 °C for 1 h, then at room temperature overnight, and finally under reflux for 1 h, the mixture was hydrolyzed with water. The organic layer was separated off, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure and separated using a recycling GPC system ($CHCl_3$ as an eluent) to yield **6** (81.0 mg, 0.104 mmol, 9.1%). **6**: 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) *m*/*z* 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.

Preparation of 2,8,14,20-Tetrasilacalix[4]quinone (5). A mixture of **6** (81.0 mg, 0.104 mmol), CAN (3.68 g, 6.72 mmol), CH_3CN (50 mL), and H_2O (35 mL) was stirred at room temperature for 2 days. The mixture was hydrolyzed with

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(22) Nishiyama, H.; Isaka, K.; Itoh, K.; Ohno, K.; Nagase, H.; Matsumoto, K. Yoshiwara, H. *J. Org. Chem.* **1992**, *57*, 407.

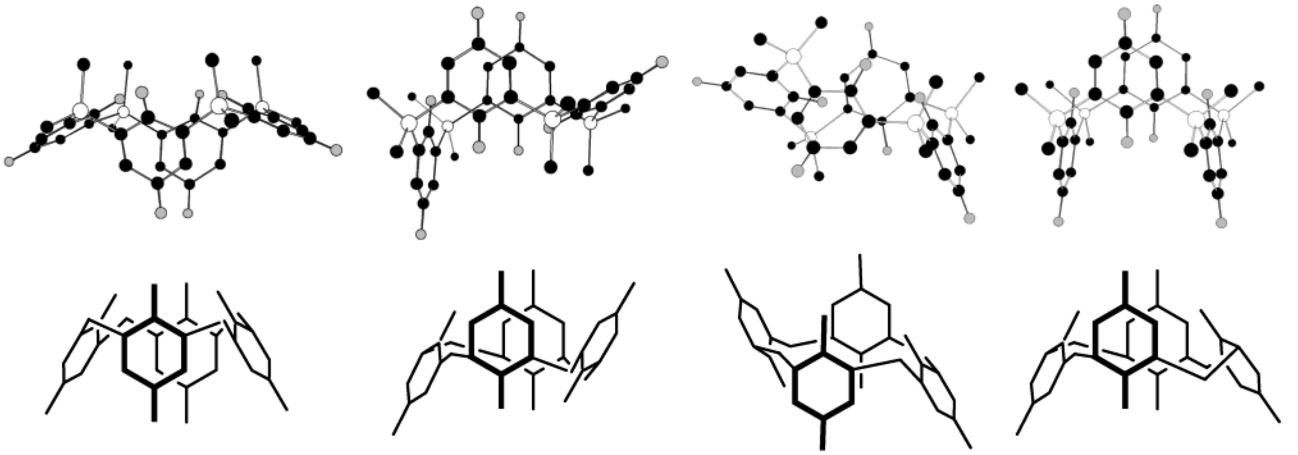
cone partial cone 1,2-alternate 1,3-alternate

Figure 4. Possible conformers of tetrasilacalix[4]quinone **5** optimized at the B3LYP/6-31G(d) level.

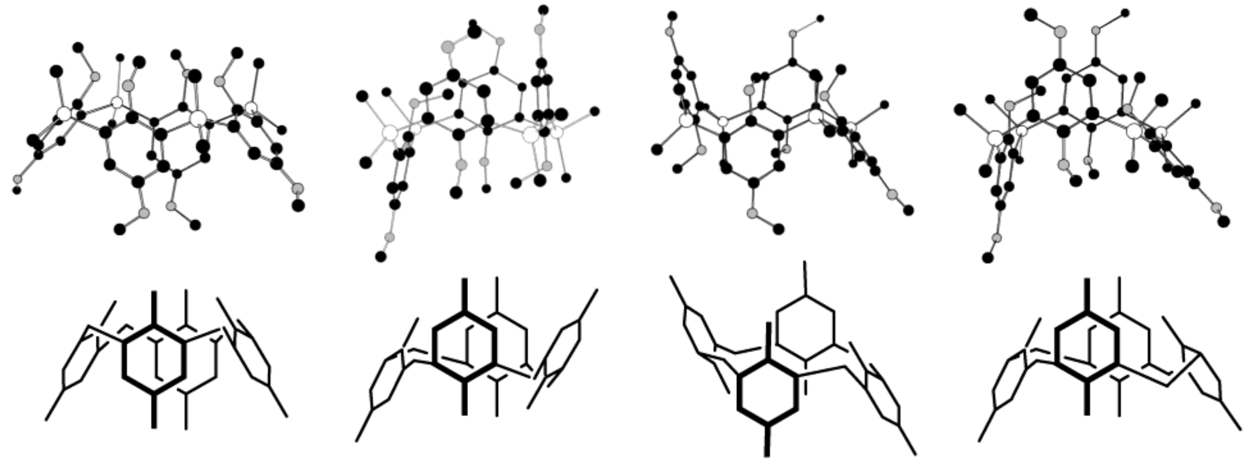
cone partial cone 1,2-alternate 1,3-alternate

Figure 5. Possible conformers of tetrasilacalix[4]hydroquinone octamethyl ether **6** optimized at the B3LYP/6-31G(d) level.

Table 5. Relative Energies of Conformers of 5 and 6 Estimated by Theoretical Calculations[a,b]

conformation	5	6
cone	8.2	2.5
partial cone	4.9	0.2
1,2-alternate	8.9	−1.3
1,3-alternate	0.0	0.0

[a] In kcal/mol. [b] B3LYP/6-31G(d) level.

water. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The organic layer and the extracts were combined, washed with water and brine, dried over magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure and separated using a recycling GPC system ($CHCl_3$ as an eluent) to yield **5** (10.7 mg, 1.62×10^{-5} mol, 16%). **5**: orange crystals; mp 163−165 °C (dec); ^1H NMR ($CDCl_3$, δ) 0.29 (s, 24H), 6.95 (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; MS (70 eV) *m/z* 656 (M^+); IR $\nu_{C=O}$ 1648, 1653 cm^{-1}; UV (CH_2Cl_2) λ_{max}/nm (ϵ) 249 (32300); FAB-HRMS *m/z* found 657.1269 [M + H^+], calcd for $C_{32}H_{33}O_8Si_4$, 657.1253. Anal. Calcd for $C_{32}H_{32}O_8Si_4$: C, 58.51; H, 4.91. Found: C, 58.45; H, 5.20.

Preparation of Bis(2,5-dimethoxyphenyl)dimethylsilane (8). A hexane (195 mL) solution of *n*-BuLi (1.51 N, 292 mmol) was added to a mixture of 1,4-dimethoxybenzene (40.4 g, 292 mmol), TMEDA (35.4 g, 305 mmol), and Et_2O (500 mL) at room temperature. After stirring for 14 h at room temperature, Me_2SiCl_2 (19.1 g, 148 mmol) in Et_2O (20 mL) was added to the mixture. After stirring for 5.5 h at room temperature, the mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined, washed with water and brine, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure. Recrystallization from $CHCl_3$/EtOH gave **8** (36.7 g, 110 mmol, 76%). **8**: colorless crystals; mp 77−80 °C; ^1H NMR ($CDCl_3$, δ) 0.52 (s, 6H), 3.67 (s, 6H), 3.71 (s, 6H), 6.7−6.9 (m, 6H); ^{13}C NMR ($CDCl_3$, δ) −1.96, 55.68, 55.76, 110.69, 114.82, 122.02, 127.74, 153.37, 158.62; ^{29}Si NMR ($CDCl_3$, δ) −8.48; MS (70 eV) *m/z* 332 (M^+); UV (CH_2Cl_2) λ_{max}/nm (ϵ) 301 (7730). Anal. Calcd for $C_{18}H_{24}O_4Si$: C, 65.03; H, 7.28. Found: C, 64.80; H, 7.22.

Preparation of Silicon-Bridged Quinone Dimer 9. A mixture of **8** (1.40 g, 4.20 mmol), CAN (11.1 g, 20.3 mmol), CH_3CN (65 mL), and H_2O (50 mL) was stirred at room temperature for 6 h. A workup similar to that of **5** gave **9** (702 mg, 2.58 mmol, 61%). **9**: orange crystals; mp 106−107.5 °C; ^1H NMR ($CDCl_3$, δ) 0.45 (s, 6H), 6.7−6.75 (m, 4H), 6.9−6.95 (m, 2H); ^{13}C NMR ($CDCl_3$, δ) −3.61, 136.61, 137.59, 144.44, 148.89, 186.11, 190.25; ^{29}Si NMR ($CDCl_3$, δ) −9.52; MS (70 eV) *m/z* 272 (M^+); IR $\nu_{C=O}$ 1648, 1656 cm^{-1}; UV (CH_2Cl_2) λ_{max}/nm (ϵ) 249 (27100), 368 (sh, 120). Anal. Calcd for $C_{14}H_{12}O_4Si$: C, 61.75; H, 4.44. Found: C, 61.58; H, 4.54.

Preparation of Bis(4-bromo-2,5-dimethoxyphenyl)-dimethylsilane (10). A hexane (108 mL) solution of *n*-BuLi

(1.55 N, 167 mmol) was added to an Et_2O (700 mL) solution of 1,4-dibromo-2,5-dimethoxybenzene (48.0 g, 162 mmol) at −78 °C and stirred at −78 °C for 1.5 h. Then an Et_2O (20 mL) solution of Me_2SiCl_2 (10.4 g, 80.4 mmol) was added to the solution at −78 °C. The mixture was stirred at room temperature overnight and then refluxed for 1.5 h, and subsequently hydrolyzed with water. A workup similar to that of **6** yielded **10** (18.3 g, 37.3 mmol, 46%). **10**: colorless crystals; mp 67.6−67.8 °C; ^{1}H NMR ($CDCl_3$, δ) 0.52 (s, 6H), 3.67 (s, 6H), 3.76 (s, 6H), 6.84 (s, 2H), 7.02 (s, 2H); ^{13}C NMR ($CDCl_3$, δ) −2.23, 55.88, 56.94, 113.67, 115.30, 119.62, 126.07, 149.99, 158.59; ^{29}Si NMR ($CDCl_3$, δ) −7.77; MS (70 eV) *m/z* 488 (M^+). Anal. Calcd for $C_{18}H_{22}Br_2O_4Si$: C, 44.10; H, 4.52. Found: C, 43.99; H, 4.66.

Preparation of Chloro(2,5-dimethoxyphenyl)dimethylsilane (11). A hexane (72.0 mL) solution of *n*-BuLi (1.55 N, 112 mmol) was added to a mixture of 1,4-dimethoxybenzene (15.2 g, 110 mmol), TMEDA (18.0 mL, 119 mmol), and Et_2O (450 mL) at room temperature. After stirring for 17 h at room temperature, the mixture was added to an Et_2O (500 mL) solution of Me_2SiCl_2 (18.0 mL, 131 mmol) at 0 °C. After stirring at 0 °C for 5 h and at room temperature for 3 h, bulb-to-bulb distillation [110−175 °C (bath temperature)/1 mmHg] yielded **11** (20.0 g, 86.5 mmol, 79%) as a pale yellow oil. **11**: ^{1}H NMR ($CDCl_3$, δ) 0.64 (s, 6H), 3.776 (s, 3H), 3.782 (s, 3H), 6.7−6.9 (m, 2H), 7.19 (d, $J = 3$ Hz, 1H); ^{13}C NMR ($CDCl_3$, δ) 3.08, 56.06, 56.09, 111.12, 117.15, 121.06, 125.20, 153.96, 158.17; ^{29}Si NMR ($CDCl_3$, δ) 20.56; MS (70 eV) *m/z* 230 (M^+). Anal. Calcd for $C_{11}H_{15}ClO_2Si$: C, 52.05; H, 6.55. Found: C, 52.35; H, 6.71.

Preparation of Silicon-Bridged Arene Tetramer 12. A hexane (10.0 mL) solution of *n*-BuLi (1.55 N, 15.5 mmol) was added to a mixture of **10** (3.49 g, 7.11 mmol) and Et_2O (300 mL) at −78 °C. After stirring for 2 h at −78 °C, an Et_2O (20 mL) solution of **11** (3.50 g, 15.2 mmol) was added to the mixture at −78 °C. After stirring for 1.5 h at −78 °C and then at room temperature for 16 h, a workup similar to that of **6** yielded **12** (3.16 g, 1.35 mmol, 62%). **12**: colorless crystals; mp 38−39 °C; ^{1}H NMR ($CDCl_3$, δ) 0.53 (s, 12H), 0.54 (s, 6H), 3.59 (s, 6H), 3.60 (s, 6H), 3.67 (s, 6H), 3.71 (s, 6H), 6.7−6.9 (m, 10H); ^{13}C NMR ($CDCl_3$, δ) −1.91 (4C), −1.85 (2C), 55.64 (2C), 55.69 (2C), 55.78 (2C), 55.80 (2C), 110.50 (2C), 114.63 (2C), 117.43 (2C), 117.73 (2C), 122.21 (2C), 127.94 (2C), 128.49 (2C), 128.74 (2C), 153.35 (2C), 158.39 (4C), 158.57 (2C); ^{29}Si NMR ($CDCl_3$, δ) −8.46; MS (70 eV) *m/z* 721 (M^+); UV (CH_2Cl_2) λ_{max}/nm (ϵ) 307 (28300). Anal. Calcd for $C_{38}H_{52}O_8Si_3$: C, 63.30; H, 7.27. Found: C, 63.06; H, 7.54.

Preparation of Silicon-Bridged Quinone Tetramer 13. A mixture of **12** (502 mg, 0.696 mmol), CAN (10.1 g, 18.4 mmol), CH_3CN (400 mL), and H_2O (250 mL) was stirred at room temperature for 16 h. A workup similar to that of **5** gave **13** (191 mg, 0.319 mmol, 46%). **13**: orange crystals; mp 214 °C (dec); ^{1}H NMR ($CDCl_3$, δ) 0.436 (s, 6H), 0.441 (s, 12H), 6.7−6.75 (m, 4H), 6.869 (s, 2H), 6.871 (s, 2H), 6.9−6.95 (m, 2H); ^{13}C NMR ($CDCl_3$, δ) −3.64 (2C), −3.62 (4C), 136.60 (2C), 137.62 (2C), 144.48 (2C), 145.64 (4C), 148.79 (4C), 148.87 (2C), 186.16 (2C), 189.00 (4C), 190.30 (2C); ^{29}Si NMR ($CDCl_3$, δ) −10.60; MS (70 eV) *m/z* 600 (M^+); HRMS *m/z* found 600.1068, calcd for $C_{30}H_{28}O_8Si_3$, 600.1090; IR $\nu_{C=O}$ 1639 cm^{-1}; UV (CH_2Cl_2) λ_{max}/nm (ϵ) 250 (52000), 434 (sh, 1810). Anal. Calcd for $C_{30}H_{28}O_8Si_3$: C, 59.97; H, 4.70. Found: C, 59.83; H, 4.95.

X-ray Crystal Structure Determination. Intensity data were collected on a Bruker SMART 1000 CCD system[23] using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The integration was accomplished using the SAINT[24] program. Absorption correction was achieved using the empirical method with the program SADABS.[25] Subsequent calculations were carried out using SHELXTL.[26] Crystallographic data for **5**, **6**, and **9** have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-213340, CCDC-213339, and CCDC-235305, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax, (+44)1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Theoretical Calculations. All density functional theory (DFT) calculations were performed using the Gaussian 03 program.[27] We first optimized the structures of four conformers of **5** and **6** at the B3LYP/3-21G(d) level of theory. Then the optimized structures were confirmed to be real minima by frequency analysis in order to choose initial structures for the final optimization at the B3LYP/6-31G(d) level. Zero-point energy corrections were made at the B3LYP/3-21G(d) level.

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Supporting Information Available: Tables are available listing the details of the X-ray structure determination, thermal ellipsoid plots, fractional atomic coordinates, anisotropic thermal parameters, bond lengths, and bond angles for **5**, **6**, and **9**. Experimental procedures for the preparation of the starting products are also available. These materials are available free of charge via the Internet at http://pubs.acs.org.

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