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Synthesis, structure, and redox properties of a quinone-bridged calix[6]arene

Shigehisa Akine, Kei Goto * and Takayuki Kawashima *

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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Abstract

The bridged calix[6]arene **1**, where a 1,4-benzoquinone moiety is covalently anchored in the cavity of the calix[6]arene macrocycle with a rigid cone conformation, was synthesized and its structure was determined by X-ray analysis. The cyclic voltammogram showed that the reduction potential of **1** is negatively shifted in comparison with the reference compounds without the calixarene macrocycle, whose shift can be explained in terms of the interaction between the quinone moiety and the oxygen atoms at the lower rim of the calixarene framework. © 2000 Elsevier Science Ltd. All rights reserved.

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The inner space of macrocyclic molecules provides a unique microenvironment to the included guest species.[1,2] Recently, the electrochemical behavior of redox-active species such as quinones included in the cavity of calixarenes and carcerands has been reported.[3,4] In these complexes based on the non-covalent interaction, however, only the averaged properties of the complexed and dissociated guest species are observable. Furthermore, the geometry of the guest molecule in the cavity of the macrocycle is often ambiguous. If a redox-active species is covalently anchored in the cavity with well-defined geometry, it is expected that the effect of the surrounding macrocycle on the properties of the species can be elucidated much more definitely. Although a large number of macrocyclic quinones such as calixquinones have been reported so far,[5] there has been no example of a compound bearing a quinone moiety covalently fixed in the cavity. We have been studying applications of calix[6]arenes bridged by a functionalized *m*-xylenyl unit,[6] whose cavity is expected to serve also as a reaction field for a redox-active moiety covalently anchored in it. In this communication, we report the synthesis, structure, and redox properties of the quinone-bridged calix[6]arene **1** with a rigid cone conformation.

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* Corresponding authors.

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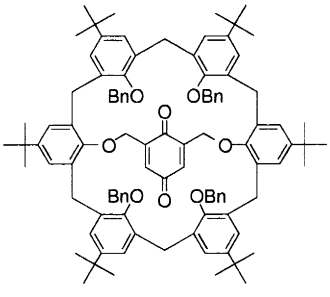

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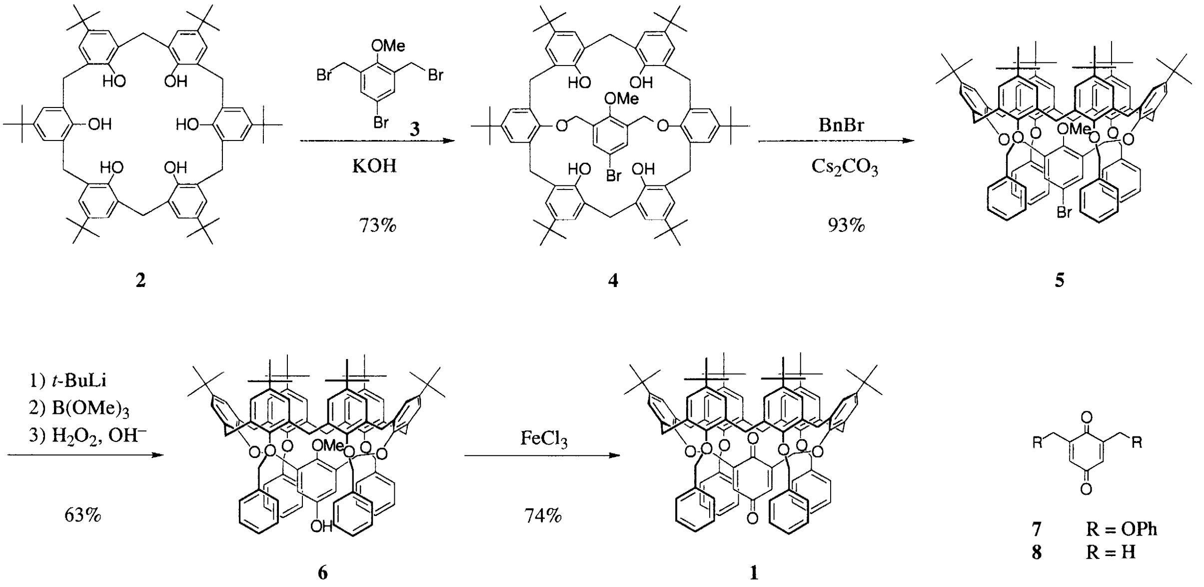
Synthesis of **1** was effected by the route shown in Scheme 1, where a *p*-bromoanisole derivative was used as a precursor of the 1,4-benzoquinone moiety. The bridged compound **4** was prepared by the reaction of *p*-*tert*-butylcalix[6]arene (**2**) and tribromide **3** in 73% yield. Benzylation of the four hydroxyl groups of **4** afforded the tetrasubstituted product **5** in 93% yield, whose spectral features are essentially the same as those of other bridged calix[6]arenes fixed in a cone conformation which we have reported so far.[6b–e] The bromide functionality of **5** was converted to a hydroxyl group via lithiation followed by the reaction with trimethyl borate and treatment with an alkaline solution of hydrogen peroxide. Oxidation of the *p*-methoxyphenol derivative **6** by iron(III) chloride afforded the target compound **1** as pale yellow crystals. Compound **1** was also found to adopt a cone conformation,[7] indicating that no conformational change occurred during the chemical modification of the bridging unit.



Scheme 1.

In the infrared spectrum of **1**, the C=O absorption was observed at 1653 cm^{-1}, which is almost the same as those of the reference compounds **7** (1657 cm^{-1}) and **8** (1653 cm^{-1}) without the calixarene framework. On the other hand, in the ^{1}H NMR spectrum, a strong upfield shift of H1 and H2 was observed for **1** in comparison with the phenoxymethyl derivative **7** (Table 1), indicating that the quinone moiety of **1** is magnetically shielded by the surrounding aromatic rings of the calixarene framework. This effect was also found in the ^{13}C NMR spectrum of **1**, which shows the upfield shift of C1 and C3. In the electronic absorption spectra, it was difficult to determine the maximum absorption wavelength and the absorption coefficient of the quinone moiety of **1** due to the strong absorption of ten benzene rings of the bridged calix[6]arene framework.

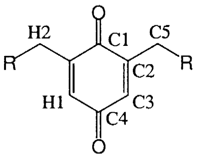


Table 1
^{1}H and ^{13}C NMR chemical shifts (δ)[a] of quinones **1**, **7** and **8**

Compd.	H1	H2	C1	C2	C3	C4	C5
1	6.36	2.47	182.99	143.58	127.44	187.28	67.38
7	6.96	4.96	186.29	144.03	132.09	186.86	63.11
8	6.56	2.06	187.59	145.76	133.26	188.16	15.93

[a] Measured in $CDCl_3$.

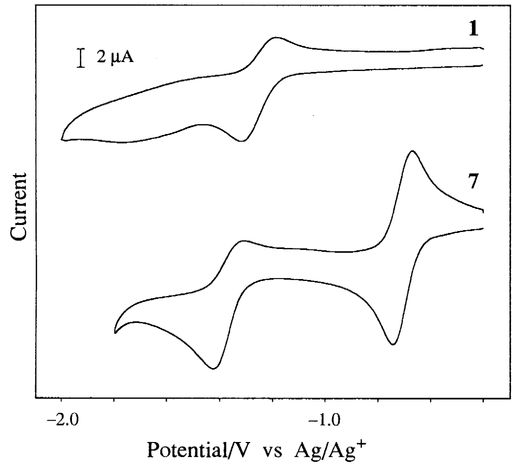


Fig. 1. Cyclic voltammograms of 5×10^{-4} M **1** and **7** in dichloromethane containing 0.1 M tetrabutylammonium perchlorate on a glassy carbon electrode. Reference electrode, Ag/Ag$^+$, scan rate, 100 mV·s^{-1}

The cyclic voltammograms of quinones **1** and **7** are shown in Fig. 1. For the quinone-bridged calix[6]arene **1**, two quasi-reversible waves were observed, the second one being considerably broadened. These two waves are considered to correspond to the formation of a monoanion radical and a dianion of the quinone moiety, respectively, similarly to other benzoquinone derivatives including **7** and **8**. The reduction/oxidation potentials of these quinones are summarized in Table 2. The reduction potential of **1** is shifted to a more negative region than that of the methyl derivative **8**, indicating that the quinone-bridged calix[6]arene **1** is more difficult to be reduced. Electrons are known to be one of the particles for which the tunneling is very important and, therefore, the steric factors of the macrocyclic framework consisting of six benzene rings are unlikely to interfere with the access of electrons to the central quinone moiety. In fact, sterically hindered 2,5- and 2,6-di-*tert*-butyl-1,4-benzoquinone are known to have reduction potentials not so different from those of the corresponding methyl derivatives.[8] Therefore, it can be reasonably concluded that the calixarene framework electronically affects the redox properties of the quinone moiety.

Table 2
Oxidation/reduction potentials ($E_{1/2}$/V)[a] of **1**, **7** and **8**

	1	**7**	**8**
0/–1	–1.25	–0.71	–0.91
–1/–2	–1.6 (br)	–1.37	–1.44

[a] Measured in 5×10^{-4} M dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate on a glassy carbon electrode. Reference electrode, Ag/Ag$^+$, scan rate, 100 mV/s.

On considering the fact that the potential of the phenoxymethyl substituted quinone **7** is more positive than that of the methyl derivative **8**, the two CH_2OAr substituents at the 2,6-positions of the quinone moiety of **1** would seem not to be responsible for the observed negative shift. Instead, the through-space interaction between the quinone moiety and the calixarene framework is considered to be more important. For clarification of the three-dimensional arrangements of the quinone moiety and the calixarene, the crystal structure of **1** was determined by X-ray analysis (Fig. 2).[9] It was revealed that the quinone moiety is located inside the cone-shaped calixarene framework and surrounded by the benzyloxy groups at the lower rim. The two carbonyl groups of the quinone moiety are not so close to the six aromatic rings of the calixarene macrocycle and the benzyl groups at the lower rim. On the other hand, there are significant non-bonded contacts observed between the olefinic carbon atoms of the quinone moiety and the oxygen atoms of the calixarene lower-rim (C2–O4: 3.172(3) Å, C6–O7: 3.218(3) Å). This interaction is considered to raise the LUMO level of the quinone, which results in the more negative reduction potential of **1**.

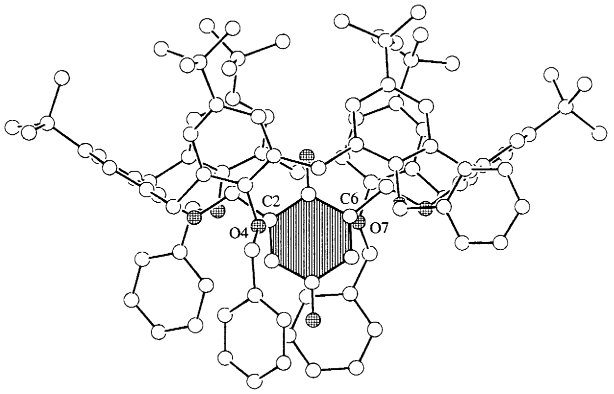


Fig. 2. X-Ray structure of **1**. Solvent molecules and hydrogen atoms are omitted for clarity

Acknowledgements

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References

1. For reviews, see: (a) Pochini, A.; Ungaro, R. *Comprehensive Supramolecular Chemistry, Vol. 2*; Vögtle, F., Ed.; Pergamon: Oxford, 1996; p. 103. (b) Gutsche, C. D. *Calixarenes* in *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1989. (c) *Calixarenes: a Versatile Class of Macrocyclic Compounds*; Vicens, J.; Böhmer, V., Eds.; Kluwer Academic Publishers: Dordrecht, 1991. (d) Gutsche, C. D. *Calixarenes Revisited* in *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1998.
2. Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests* in *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1994.
3. (a) Robbins, T. A.; Cram, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 12199. (b) Robbins, T. A.; Knobler, C. B.; Bellew, D. R.; Cram, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 111.
4. (a) Alvarez, J.; Wang, Y.; Gómez-Kaifer, M.; Kaifer, A. E. *Chem. Commun.* **1998**, 1455. (b) Wang, Y.; Alvarez, J.; Kaifer, A. E. *Chem. Commun.* **1998**, 1457.
5. For examples, see: (a) Morita, Y.; Agawa, T.; Kai, Y.; Kanehisa, N.; Kasai, N.; Nomura, E.; Taniguchi, H. *Chem. Lett.* **1989**, 1349. (b) Suga, K.; Fujihara, M.; Morita, Y.; Agawa, T. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1575. (c) Morita, Y.; Agawa, T.; Nomura, E.; Taniguchi, H. *J. Org. Chem.* **1992**, *57*, 3658. (d) Casnati, A.; Comelli, E.; Fabbi, M.; Bocchi, V.; Mori, G.; Ugozzoli, F.; Lanfredi, A. M. M.; Pochini, A.; Ungaro, R. *Recl. Trav. Chim. Pays-Bas* **1993**, *112*, 384.
6. (a) Saiki, T.; Goto, K.; Tokitoh, N.; Okazaki, R. *J. Org. Chem.* **1996**, *61*, 2924. (b) Saiki, T.; Goto, K.; Okazaki, R. *Chem. Lett.* **1996**, 993. (c) Saiki, T.; Goto, K.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2223. (d) Akine, S.; Goto, K.; Kawashima, T.; Okazaki, R. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2781. (e) Akine, S.; Goto, K.; Kawashima, T. *J. Incl. Phenom. Macrocycl. Chem.* in press.
7. Compound **1**: Pale yellow crystals; mp 187–198°C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (s, 36H), 1.46 (s, 18H), 2.47 (s, 4H), 3.23 (d, J=16.5 Hz, 2H), 3.31 (d, J=14.7 Hz, 4H), 4.48 (d, J=14.7 Hz, 4H), 4.50 (d, J=16.5 Hz, 2H), 4.63 (d, J=11.4 Hz, 4H), 4.68 (d, J=11.4 Hz, 4H), 6.36 (s, 2H), 6.86 (s, 4H), 7.02 (s, 4H), 7.17–7.25 (m, 20H), 7.38 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.78 (t), 29.80 (t), 31.41 (q), 31.75 (q), 34.19 (s), 34.39 (s), 67.38 (t), 75.35 (t), 125.19 (d), 125.43 (d), 127.44 (d), 127.72 (d), 127.76 (d), 127.79 (d), 128.38 (d), 130.99 (s), 133.90 (s), 134.45 (s), 137.31 (s), 143.58 (s), 145.41 (s), 146.16 (s), 152.71 (s), 153.54 (s), 182.99 (s), 187.28 (s); IR (KBr) 1653 cm^{-1} (C=O); HRMS (FAB) *m/z* found: 1465.8427; calcd. for $C_{102}H_{113}O_8$: 1465.8435 $[M+H]^+$. Anal. calcd for $C_{102}H_{112}O_8 \cdot 0.5H_2O$: C, 83.06; H, 7.71. Found: C, 82.92; H, 7.71.
8. Chambers, J. Q. *The Chemistry of the Quinonoid Compound*; Patai, S. Ed.; John Wiley & Sons: London, 1974; Chapter 14.
9. Crystallographic data for **1**: $0.5C_6H_6$: $C_{105}H_{115}O_8$, M=1505.06, monoclinic, $C2/c$, a=47.782(2) Å, b=11.969(1) Å, c=30.850(1) Å, β=99.895(1)°, V=17381(1) Å^3, Z=8, D_{calcd}=1.150 g cm^{-3}. The intensity data were collected at 120 K on a MAC Science DIP-2030 imaging plate area detector with MoK_α radiation (λ=0.71069 Å). Of the 47445 reflections which were collected, 16813 were independent. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement on F was based on 11856 observed reflections [$I>3.00\sigma(I)$]. R=0.068, R_w=0.073 for 1018 parameters.