**Supramolecular Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

# Synthesis and Electrochemical Properties of Calix[4]arene-triester-monoquinones

Weon Seok Oh[a]; Taek Dong Chung[b]; Jongwon Kim[b]; Hee-Soo Kim[b]; Hasuck Kim[b]; Dongmok Hwang[c]; Kimoon Kim[c]; Seung Gul Rha[a]; Jong-In Choe[a]; Suk-Kyu Chang[a]
[a] Department of Chemistry, Chung-Ang University, Seoul, Korea [b] Department of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul, Korea [c] Department of Chemistry, Center for Biofunctional Molecules, Pohang University of Science and Technology, Pohang, Korea

**To cite this Article** Oh, Weon Seok , Chung, Taek Dong , Kim, Jongwon , Kim, Hee-Soo , Kim, Hasuck , Hwang, Dongmok , Kim, Kimoon , Rha, Seung Gul , Choe, Jong-In and Chang, Suk-Kyu(1998) 'Synthesis and Electrochemical Properties of Calix[4]arene-triester-monoquinones', Supramolecular Chemistry, 9: 3, 221 — 229

**To link to this Article: DOI:** 10.1080/10610279808034990

**URL:** http://dx.doi.org/10.1080/10610279808034990

*SUPRAMOLECULAR CHEMISTRY*, Vol. 9, pp. 221–229
Reprints available directly from the publisher
Photocopying permitted by license only

# Synthesis and Electrochemical Properties of Calix[4]arene-triester-monoquinones

WEON SEOK OH [a], TAEK DONG CHUNG [b], JONGWON KIM [b], HEE-SOO KIM [b], HASUCK KIM [b,*], DONGMOK HWANG [c], KIMOON KIM [c], SEUNG GUL RHA [a], JONG-IN CHOE [a] and SUK-KYU CHANG [a,*]

[a] *Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea;*
[b] *Department of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Korea;*
[c] *Department of Chemistry, Center for Biofunctional Molecules, Pohang University of Science and Technology, Pohang 790-784, Korea*

*(Received 10 September 1997; In final form 19 February 1998)*

**Calix[4]arene-based monoquinones having three efficient ligating groups of alkoxycarbomethyl ethers were prepared and their ionophoric properties were investigated by electrochemical technique. Calix[4]-triester-monoquinones 3a and 3b were prepared from calix[4]arene and *p-tert*-butylcalix[4]arene by the selective trialkylation followed by oxidation with $Tl(NO_3)_3$ and $Tl(CF_3CO_2)_3$, respectively. X-ray crystal structural analysis revealed that the ligand 3a adopted a partial cone conformation with an *anti* quinone moiety. MM+ calculations suggested that the energy difference between the two conformations is relatively small (< 3.5 kcal mole$^{-1}$). Electrochemical studies also showed that the monoquinones 3a and 3b form strong complexes with $Na^+$ ion, and the positive shifts in the reduction potential exceeded those of the closely related diquiones 5a and 5b.**

*Keywords:* Carlix[4]arene, monoquinone, $Na^+$ ion, ionophore, electrochemistry

## INTRODUCTION

The molecular design of various electrochemically active ionophores for the recognition of biologically important species has been the subject of much recent interest and research activity [1]. Calix-quinones are one of the most attractive compounds for this purpose because of the versatile platform of calixarene frameworks suitable for the design of molecular recognition systems [2] as well as the well-known electrochemical behaviors of the quinone moiety. A series of quinones based upon the calix[4]arene, calix[5]arene, and calix[6]arene frameworks have been prepared by the direct oxidation of phenol units [3], and the redox and cation binding properties of calix[4]arene-quinones have been systematically investigated [4, 5]. In parallel to these, varying structures of calix[4]arene-diquinones derived from diesters, [6, 7], diamides [7, 8], calix-crown [7, 8], bipyridine [9], and conformational isomers of alkyl ether derivatives [10] have been successfully prepared and the electrochemical and/or molecular recognition properties have been characterized. Generally, the calix[4]arene-based quinones exhibited unique selectivity toward

---

*Corresponding authors.

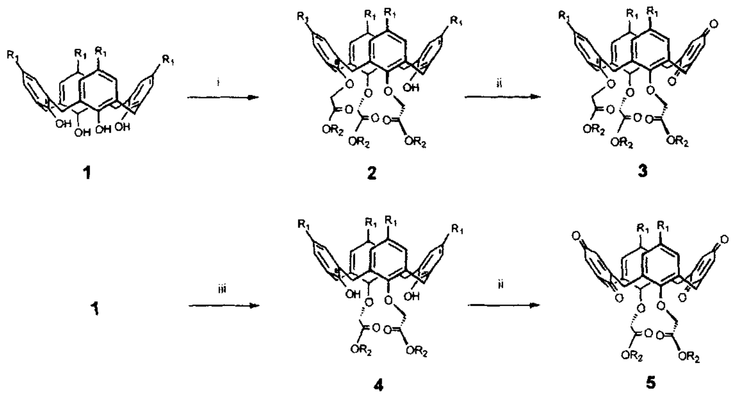
various metal ions, notably for $Na^+$ ion, to varying degrees when they were reduced to the monoanion state and showed a binding enhancement on the order of up to $10^6$ [4]. In addition to metal ions, $NH_4^+$ and various alkylammonium ions can form complexes with calix[4]arene-diquinones by making hydrogen bonds and give rise to a remarkable enhancement in the electrochemical reduction of the quinone moiety [6–9, 11].

Quite contrary to this, relatively little attention has been paid to calix-monoquinone compounds. With one quinone moiety as an integrating part of the calixarene framework, only simple alkyl ether derivative has been studied for its electrochemical [4] and conformational properties [5]. Although monoquinone derivatives of calix[4]arenes have been utilized as intermediates in the preparation of chromogenic ionophores [12] and as ion selective electrode materials [13], no redox properties for these intermediates have been reported. Another interesting study is concerned with the calix[4]arene-monoquinone bearing an anthraquinone bridge between diametrical phenolic oxygen atoms [14]. In calix[4]arene-monoquinones, with respect to the widely studied calix[4]arene-diquinones, one can either utilize one more ligating group for making the binding site of ionophore that may enhance the ion binding property or introduce diverse functionalities to the molecular framework of calix[4]arene. Furthermore, the simpler electrochemical behavior of the resulting quinone moiety would be another evident advantage in dealing with data. In this paper, we report the preparation of two typical calix[4]arene-triester-monoquinones having three efficient ligating groups of *tert*-butoxycarbomethyl or ethoxycarbomethyl ethers and their electrochemical behavior in the presence of alkali metal cations and representative alkylamines.

## RESULTS AND DISCUSSION

### Synthesis of Monoquinones

Monoquinones **3a** and **3b** were prepared as outlined in Scheme I [15]. Triester-monophenols **2a** and **2b** were prepared by the selective trialkylation of *p*-H-calix[4]arene ($CaH_2$, DMF) and *p*-*tert*-butylcalix[4]arene (BaO, DMF) with *tert*-butyl bromoacetate or ethyl bromoacetate,



a $R_1$ = H, $R_2$ = *t*-Bu
b $R_1$ = *t*-Bu, $R_2$ = Et

i, $BrCH_2CO_2t$-Bu, $CaH_2$, DMF for a and $BrCH_2CO_2Et$, BaO, DMF for b;
ii, $Tl(NO_3)_3$, MeOH/$CHCl_3$ for a and $Tl(CF_3CO_2)_3$, TFA/$CHCl_3$ for b;
iii, $BrCH_2CO_2t$-Bu, $K_2CO_3$, acetone for a and $BrCH_2CO_2Et$, $K_2CO_3$, acetone for b.

SCHEME 1

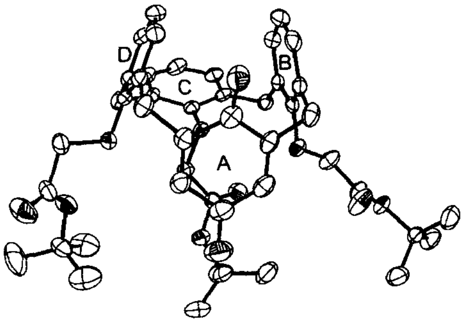
respectively [16,17]. Calix[4]arene-triester-monoquinone **3a** was prepared by the oxidation of triester **2a** with $Tl(NO_3)_3$ in $MeOH/CHCl_3$ [18]. Monoquinone **3b** was also prepared by the oxidation of **2b** with $Tl(CF_3CO_2)_3$ in TFA [6]. The structures of triester-monoquinone **3a** and **3b** were characterized by $^1H$ NMR, mass spectral, and elemental analysis data. In its $^1H$ NMR spectrum, monoquinone **3a** showed two pairs of doublets ($\delta$ 3.23 and 4.50, $J = 13.9$ Hz; $\delta$ 4.10 and 4.54, $J = 13.5$ Hz) corresponding to the bridging methylene groups, consistent with a *syn* orientation of three ester groups. The methylene groups of the $OCH_2CO_2$ moiety showed somewhat broadened singlet and a pair of doublets, which are attributable to the central and diastereotopic lateral $OCH_2$ protons, respectively.

## Crystal Structure and Molecular Modeling

The X-ray crystal structure of monoquinone **3a** was obtained for a crystal grown from a $CH_2Cl_2/MeOH$ mixture (Fig. 1) [19]. The structure reveals that in solid state **3a** adopts a partial cone structure with the quinone moiety positioning the *anti* orientation. The two distal benzene rings are in relatively parallel position, while the central benzene ring and quinone ring take a somewhat perpendicular arrangement to each other.

The angles that the rings A–D make with the best plane fitted to the carbon atoms of the bridging methylene groups are 81.97(10), 78.72(10), 28.28(13) and 71.67(9)°, respectively. The conformational parameters $\phi$ and $\chi$, which were defined as the two torsion angles between two adjacent phenolic units by Ugozzoli and Andreetti [20], of **3a** are shown in Figure 1. The sequence of signs of the parameter (+ –, + –, + +, – –) *also clearly shows that* **3a** *has a partial cone* conformation. A noticeable fact is that the benzene ring (C) opposite the quinone ring tilts inward markedly. The periphery comprising the lower rim phenol ether oxygens is in fact a relatively widened structure compared with their *p-tert*-butylcalix[4]arene tetraester analogs, as expected from the absence of bulky *p-tert*-butyl groups on benzene rings.

To gain an insight into the relative stability of the conformers of monoquinone, MM+ calculations (HyperChem) [21] were performed for the structures of the cone and partial cone conformation with *anti* quinone moiety of **3a**. The MD calculations were performed for the respective geometry optimized structures having the AM1 calculated charges, and the potential energies of the two representative conformers were averaged for the time period of 100 ps at 300 K. The partial cone conformation is found to be slightly more stable than the cone conformation; however, the difference in energy between the two conformers is not so large and the quinone unit might swing relatively freely between the two conformations: cone, 11.60 ± 5.59 kcal $mole^{-1}$;



Conformational parameters

| | $\phi$ | $\chi$ |
|---|---|---|
| A-B | -107.8 | -104.3 |
| B-C | 56.1 | -117.1 |
| C-D | 115.0 | -48.6 |
| D-A | 100.3 | 104.8 |

FIGURE 1 Crystal structure and conformational parameters of triester-monoquinone **3a**.

partial cone with *anti* quinone moiety, 8.16 ± 5.97 kcal mole$^{-1}$ (an average of 100 ps at 300 K) [22].

## Electrochemical Properties

Electrochemical properties of quinone-derivatized calix[4]arenes were investigated by cyclic voltammetry in $CH_3CN$ at 25°C. Cyclic voltammogram illustrated in Figure 2a indicates that **3a** exhibits typical redox behavior of simply modified quinone derivatives such as 2,6-dimethyl benzoquinone. Coulometric results indicate that two peaks in the cyclic voltammogram correspond to two one electron processes, respectively. With respect to the peak due to the first electron transfer, the difference between cathodic and anodic peak potential ($E_{p,a} - E_{p,c}$) is measured as 74 mV, which implies that the kinetics of the first electron transfer process falls on quasi-reversible regime. This redox property agrees with the results on calix[4]arene-monoquinone with three ethoxy groups in the lower rim [4].

According to the report on a variety of quinone-derivatized calix[4]arenes with simple ethoxy groups, only monoquinone can bind to $Na^+$ in neutral state, and the $\Delta E_p$ is very large compared to that of di-, tri-, or tetra-quinone [4]. $^1H$ NMR titrations indicate that monoquinones, **3a** and **3b**, form 1:1 complexes with $Na^+$ and the binding constants ($K$) are too large to be evaluated in $CD_3CN$ at 25°C. The height of peak current due to the complexes of monoquinone-$Na^+$ is proportional to the quantity of $Na^+$ up to 1 equiv with little change in the reduction potential. The cease of current increase upon more than 1 equiv of $Na^+$ is another evidence of

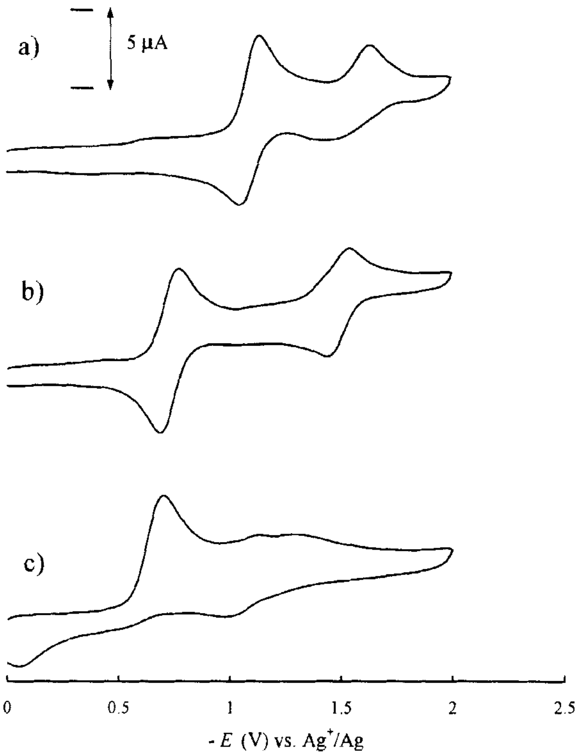


FIGURE 2 Cyclic voltammograms of **3a**: (a) in the absence of any guest, (b) in the presence of 1 equiv of $Na^+$, and (c) in the presence of 1 equiv of $NH_4^+$ guest.

1:1 complexation with a considerably large binding constant. In addition, the constant reduction potential of the new wave irrespective of the $Na^+$ concentration indicates that the peak potential shift results not from ion-pairing but from complexation.

The presence of alkali metal ions produces a significantly large shift in the peak potential of elctrochemical reduction ($\Delta E_p$) [23] of quinone moiety [4, 8, 11]. The complexes of $Na^+$ and most of quinone-derivatized calix[4]arenes are very stable and the reversibility of the second electron transfer of $Q^-/Q^{2-}$ improves. Figure 2b shows that the redox wave corresponding to $Q^-/Q^{2-}$ becomes markedly symmetric in the presence of $Na^+$ compared to that of **3a** only. On the other hand, protonated amines can also cause a large potential shift in the reduction of **3a**, but the redox behavior is quite different, as displayed in Figure 2c. This difference is because amines can act as a proton source and electron transfer is followed by fast proton transfer [11].

To examine the correlation between $\Delta E_p$ and the structure of quinone-derivatized calix[4]arenes, $\Delta E_p$ in the presence of various guests are summarized in Table I. With regard to the effect of alkali metal ions such as $Na^+$ and $K^+$, $Na^+$ makes larger $\Delta E_p$ than $K^+$ owing to the difference in the ratio of charge to size or ionic field strength [11b]. Considering the arrangement of ligating sites in the lower rim, monoquinones are belived to provide more favorable environment for the formation of stable complex with $Na^+$ and $K^+$ than diquinones with the similar structure. To compare the relative binding affinity of **3a**, **3b** and for comparison purpose **5b**, $^1H$ NMR titration with metal perchlorate in mixed solvent of THF-$d_8$/$CD_3CN$ (4:1, v/v) was performed. The binding constant was found to be 3.2 (**3a**), >5 (**3b**), and 4.8 (**5b**), respectively. In the viewpoint of the substitutent effect, *tert*-butyl groups in the upper rim and relatively small alkyl esters in the lower rim are considered to make **3b** more favorable for encapsulation of metal ions than **3a**. Fairly facilitated electrochemical reduction of **3b** compared to **3a** in the presence of $Na^+$ and $K^+$ can be interpreted based on these considerations. The same relationship holds for diquinones, **5a** and **5b**.

Quinone derivatives without ionophoric annular framework such as 1,4-benzoquinone or dimethyl benzoquinone can also give rise to remarkable $\Delta E_p$ in the presence of alkali metal ions. Since the peak potential shift is owing to ion-pairing between reduced quinone and metal ion, $\Delta E_p$ varies with the concentration of metal ions and is small compared to that due to complexation in the presence of 1 equiv of alkali metal ions. The difference between $\Delta E_p$ of quinone-derivatized calix[4]arenes and 1,4-benzoquinone in the presence of the same concentration of $Na^+$ and $K^+$ clearly shows the effect of complexation in Table I.

Contrary to the case of alkali metal ions, no remarkable difference between $\Delta E_p$ of quinone derivatives with and without ionophoric moiety is observed upon the addition of $NH_4^+$ or protonated alkylamines. Since the strength of the hydrogen bond between quinone and the proton source is a crucial factor in the reduction of quinone, $\Delta E_p$ is influenced by not only the acidity of the proton source but also the formation of an extra hydrogen bond. The larger $\Delta E_p$ due to benzylammonium ion than that due

TABLE I Reduction potential shift of quinone-derivatized calix[4]arenes due to cationic guests[a]

| Guest | $\Delta E_p$(mV) | | | | |
|---|---|---|---|---|---|
| | **3a** | **3b** | **5a** | **5b** | 1,4-benzoquinone |
| $Na^+$ | 360 | 372 | 320 | 348 | 12 |
| $K^+$ | 214 | 288 | 212 | 240 | 12 |
| $NH_4^+$ | 464 | 370 | 440 | 432 | 416 |
| $BuNH_3^+$ | 416 | 268 | 368 | 456 | 336 |
| $ArCH_2NH_3^+$ | 476 | 344 | 426 | 530 | 420 |

[a] All data were obtained by cyclic voltammetry of 0.5 mM of calix[4]arenes in $CH_3CN$ in the absence and presence of 1 equiv of cations as shown in Figure 2. $\Delta E_p$ is defined as the difference in peak potential due to first electron transfer between in the presence and the absence of cation. Scan rate; 50 mV $sec^{-1}$. Maximal error is less than <5 mV.

to butylammonium ion is supposed to stem from the difference in acidity of the guest. On the other hand, Table I indicates that **5a**, **5b**, and **3a** show an extra $\Delta E_p$ with comparison to 1,4-benzoquinone. However, **3b** exhibits a significantly reduced $\Delta E_p$ upon the addition of $NH_4^+$ and primary alkylamines, whereas relatively large $\Delta E_p$ is observed in the presence of $Na^+$ or $K^+$. Supposedly, since flexibility of the structure of **3b** is limited and also the lower rim is compact, hydrogen bond between quinone and $NH_4^+$ becomes weaker than **5a**, **5b**, and **3a**. This is evidenced by $^1H$ NMR titration result, which reveals very low $\log K$ value ($<1$) of **3b**-$NH_4^+$ complex compared with that of **5b**-$NH_4^+$ complex ($\log K = 3.7$) in $CD_3CN$.

As a consequence, $\Delta E_p$ depends on both the number of quinone and substituents in the upper as well as in the lower rim of calix[4]arenes. Both metal ions and proton sources lead to characteristic $\Delta E_p$ varying with different factors independently. Detailed relationships between the structure of calix[4]arene and $\Delta E_p$ requires further studies.

## EXPERIMENTAL SECTION

Most of the reagents including calix[4]arene (Janssen), *tert*-butyl bromoacetate, trifluoroacetic acid, Tl $(CF_3CO_2)_3$, and Tl $(NO_3)_3$ (Aldrich) were purchased and used without further purification. THF, $CH_2Cl_2$, and DMF were used after standard purification procedure. Chromatography was performed with a silica gel 60 (230 - 400 mesh, ASTM, Merck) or Chromatotron apparatus and TLC was carried out with silica gel precoated plate (silica gel 60 F254). Melting points were measured by Gallen - Kamp melting point apparatus. Extraction experiments were performed with a Haake F3 digital water bath and Vortex - Genie mixer. $^1H$ NMR spectra were obtained on a Varian VXR-200S (200 MHz) with TMS as an internal reference.

### Synthesis

Triesters **2a** and **2b** and diesters **4a** and **4b** were prepared by the trialkylation and dialkylation with alkyl bromoacetate in the presence of $CaH_2$ or BaO from the calix[4]arene and *p-tert*-butylcalix[4]arene according to the published procedure [16, 17]. Triester-monoquinones **3a** and **3b** and diester-monoquinones **5a** and **5b** were prepared by the oxidation with $Tl(NO_3)_3$ and $Tl(CF_3CO_2)_3$ respectively [6, 12].

### *p-H-Calix[4]arene-tris(tert-butyl ester) 2a*

(Yield: 71%); mp 155 - 157°C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.08 (d, $J = 7.5$ Hz, 2H), 7.03 (d, $J = 7.5$ Hz, 2H), 6.89 (t, $J = 7.2$ Hz, 1H), 6.69 (t, $J = 7.5$ Hz, 1H), 6.3 - 6.5 (m, 6H), 6.23 (s, 1H), 4.99 (s, 2H), 4.89 (d, $J = 13.2$ Hz, 2H), 4.59 (d, $J = 15.6$ Hz, 2H), 4.44 (d, $J = 13.5$ Hz, 2H), 4.37 (d, $J = 15.3$ Hz, 2H), 3.31 (d, $J = 13.4$ Hz, 2H), 3.29 (d, $J = 13.5$ H, 2H), 1.52 (s, 18H), 1.41 (s, 9H). Anal. Calcd. for $C_{46}H_{54}O_{10}$:C, 72.04; H, 7.10. Found: C, 71.57; H, 7.13.

### *p-H-Calix[4]arene-tris(tert-butyl ester)-monoquinone 3a*

To a mixture of Tl $(NO_3)_3$ (2.0 mmol) in MeOH (3.0 mL), the solution of **2a** (1.0 mmol) in $CHCl_3$/MeOH was added dropwise. The reaction mixture was stirred for 10 min at rt. The precipitate was filtered off and the solution was treated with water. Extraction with $CHCl_3$ followed by the recrystallization from $CH_2Cl_2$/MeOH afforded orange-yellow crystal. (Yield: 80%); mp 231 - 233°C; $^1H$ NMR ($CDCl_3$) $\delta$7.13 (d, $J = 7.4$ Hz, 2H), 6.94 (t, $J = 7.8$ Hz, 1H), 6.87 (s, 2H), 6.79 (d, $J = 7.8$ Hz, 2H), 6.47 (t, $J = 7.6$ Hz, 2H), 6.19 (d, $J = 7.6$ Hz, 2H), 4.47 (d, $J = 12.5$ Hz, 2H), 4.45 (d, $J = 15.4$ Hz, 2H), 4.36 (s, 2H), 4.10 (d, $J = 15.4$ Hz, 2H), 3.80 (d, $J = 12.4$ Hz, 2H), 3.55 (d, $J = 12.5$ Hz, 2H), 3.23 (d, $J = 13.9$ Hz, 2H), 1.48 (s, 18H), 1.36 (s, 36H). FABMS: *m/z* 803 $(M+Na)^+$. Anal. Calcd. for $C_{46}H_{52}O_{11}$: C, 70.75; H, 6.71. Found: C, 70.38; H, 6.79.

### *p-tert-Butylcalix[4]arene-(triethyl ester)-monoquinone 3b*

To a solution of $Tl(CF_3CO_2)_3$ (3.0 mmol) in $CF_3CO_2H$ (3.4 mL), triester-monophenol **2b** was added and stirred for 2 h under the dark condition. After the reaction, cold water was added and the reaction mixture was extracted with $CHCl_3$. The combined extracts were washed with water and dried. After evaporation of the solvent under reduced pressure, the crude product was purified with column chromatography ($CH_2Cl_2$/MeOH). (Yield: 32%); mp 165–168°C; $^1H$ NMR ($CDCl_3$) $\delta$7.22(s, 2H), 7.19 (d, $J = 2.7$ Hz, 2H), 6.81 (d, $J = 2.5$ Hz, 2H), 6.73 (s, 2H), 4.78 (d, $J = 16.2$ Hz, 2H), 4.55 (s, 2H), 4.47 (q, $J = 7.2$ Hz, 4H), 4.37 (q, $J = 7.2$ Hz, 2H), 4.27 (d, $J = 12.6$ Hz, 2H), 4.26 (d, $J = 16.2$ Hz, 2H), 4.00 (d, $J = 12.6$ Hz, 2H), 3.50 (d, $J = 12.6$ Hz, 2H), 3.12 (d, $J = 12.6$ Hz, 2H), 1.42 (t, $J = 7.2$ Hz, 6H), 1.39 (t, $J = 7.5$ Hz, 3H), 1.24 (s, 9H), 1.13 (s, 18H); FABMS: $m/z$ 887 $(M+Na)^+$. Anal. Calcd. for $C_{52}H_{64}O_{11}$: C, 72.20; H, 7.46. Found: C, 71.88; H, 7.24.

### *p-H-Calix[4]arene-bis(tert-butyl ester)-diphenol 4a*

(Yield: 59%); mp > 350°C (dec); $^1H$ NMR ($CDCl_3$) $\delta$ 7.67 (s, 2H), 7.05 (d, $J = 7.5$ Hz, 4H), 6.89 (d, $J = 7.5$ Hz, 4H), 6.75 (t, $J = 7.5$ Hz, 2H), 6.65 (t, $J = 7.5$ Hz, 2H), 4.58 (s, 4H), 4.47 (d, $J = 13$ Hz, 2H), 3.38 (d, $J = 13$ Hz, 2H), 1.56 (s, 18H). Anal. Calcd. for $C_{40}H_{44}O_8$: C, 73.60; H, 6.79. Found: C, 73.58; H, 6.82.

### *p-H-Calix[4]arene-bis(tert-butyl ester)-diquinone 5a*

(Yield: 38%); mp 151–153°C; $^1H$ NMR ($CDCl_3$) $\delta$ 6.82 (d, $J = 7.2$ Hz, 4H), 6.74 (s, 4H), 6.66 (t, $J = 7.5$ Hz, 2H), 4.34 (s, 4H), 3.96 (d, $J = 13$ Hz, 2H), 3.36 (d, $J = 13$ Hz, 2H), 1.49 (s, 18 H); FABMS: $m/z$ 703 $(M+Na)^+$. Anal. Calcd. for $C_{40}H_{40}O_{10}$: C, 70.58; H, 5.92. Found: C, 70.39; H, 5.96.

## Molecular Modeling

Molecular modeling study was performed by HyperChem [21] version 4.0 package. The structure was constructed and geometry optimized with MM+ force field. The charges were calculated with AM1 method and the structure was geometry optimized again. The process was repeated until a reasonable structure was obtained. The molecular dynamics study was performed using the AM1 charge optimized structure at 500 K to yield partial cone conformation. Finally the molecular dynamics simulation for the representative conformational isomeric structures was performed at 300 K for a time period of 100 ps and the energies were averaged.

## Electrochemical Measurements

Electrochemical experiments were performed with a Windows-driven electrochemical analyzer (BAS100B/W) (Bioanalytical Systems) in $CH_3CN$ using positive feedback routines to compensate for resistance. The working electrode, counter electrode, and reference electrode were a glassy carbon mini-electrode with an area of 0.071 $cm^2$, a Pt wire and a home-made $Ag/Ag^+$ electrode in which 0.01 M $AgNO_3$ was employed as an internal solution, respectively. The salt bridge, which connects the reference electrode and the sample solution, was composed of 0.1 M tetrabutylammonium perchlorate (TBAP) in $CH_3CN$. To remove the effect of dissolved oxygen and water, nitrogen gas was passed through zinc amalgam oxygen trap [24], sulfuric acid, calcium chloride, and silica gel before being bubbled into the sample solution. Acetonitrile (Fisher, HPLC grade) was refluxed with $CaH_2$ for more than 24 h before use. The supporting electrolyte was 0.1 M TBAP (Fluka, electrochemical grade) and used without further purification. The surface of the working electrode was polished with 0.05 µm alumina (Buehler) and then rinsed with deionized water and washed carefully with purified $CH_3CN$. The potential of the reference electrode was checked with ferrocene throughout experiments. All the guest salts were perchlorates. They were recrystallized three times from water for quaternary and primary alkylammonium salts, $CH_2Cl_2$/$Et_2O$ mixed solvent for secondary alkyl-, trimethyl-, and triethyl-ammonium salts and hexane/$CH_2Cl_2$ mixed solvent for tributylammonium salt. Nitrogen atmosphere in the cell was maintained throughout experiments at room temperature.

## X-ray Crystal Structure Determination of 3a

$C_{46}H_{52}O_{11}$, $M = 780.88$, Space group $= P{-}1$, $a = 10.820(1)$, $b = 12.277(2)$, $c = 17.056(2)$ Å, $\alpha = 81.13(1)$, $\beta = 77.31(1)$, $\gamma = 79.43(1)°$, $U = 2157.4(5)$ Å$^3$, $Z = 2$, $F(000) = 832$, Temp $= 23\,°C$, $D_C = 1.202\ g\ cm^{-3}$, $\lambda(MoK\alpha_1) = 0.71073$ Å, $\mu = 0.85\ cm^{-1}$. Crystals of **3a** suitable for X-ray work were grown from $CH_2Cl_2$/MeOH. A crystal was mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo$K\alpha$ radiation. Unit cell parameters were determined by least-squares refinement of 25 reflections. The intensities of three standard reflections, measured every 3 h of X-ray exposure, showed no systematic changes. The intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS-86) and refined by full-matrix least-squares methods (SHELXTL-93) [19]. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated (C—H = 0.95 Å) and were included as fixed contributions to the structure factor. Each hydrogen atom was assigned an isotropic thermal parameter 1.2 times that of the atom to which it is attached. The final cycles of refinement of $F^2$ with 4045 independent reflections and 514 variables converged to the agreement indices $R1(I > 2\sigma(I)) = 0.0535$ and $wR2$ (all data) $= 0.125$. Atomic coordinates and bond distances and angles have been deposited with the Cambridge Crystallographic Data Center.

## *Acknowledgments*

The financial supports from the KOSEF (96-0501-0401-3 and 95-0501-05-01-3), the Center for Molecular Catalysis (Seoul National University), Chung-Ang University (Special Grant, 1996), and the Center for Biofunctional Molecules are greatly appreciated.

## *References*

[1] Kaifer, A. and Echegoyen, L. (1990). In: Cation Binding by Macrocycles, Inoue, Y. Gokel, G. W., (Eds.), Marcel Dekker: New York, Chapter 9.

[2] (a)Böhmer, V. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 713. (b) Calixarenes: A Versatile Class of Macrocylic Compounds; Vicens, J., Böhmer, V., (Eds.), Kluwer: Dordrecht, 1991. (c) Gutsche, C. D. Calixarenes; Royal Society of Chemistry: Cambridge, 1989.

[3] (a)Reddy, P. A. and Gutsche, C. D. (1993). *J. Org. Chem.*, **58**, 3245. (b)Reddy, P. A., Kashyap, R. P., Watson, W. H. and Gutsche, C. D. (1992). *Isr. J. Chem.*, **32**, 89.

[4] Gómez-Kaifer, M., Reddy, P. A., Gutsche, C. D. and Echegoyen, L. (1994). *J. Am. Chem. Soc.*, **116**, 3580.

[5] Gómez-Kaifer, M., Reddy, P. A., Gutsche, C. D. and Echegoyen, L. (1997). *J. Am. Chem. Soc.*, **119**, 5222.

[6] Beer, P. D., Chen, Z. and Gale, P. A. (1994). *Tetrahedron*, **50**, 931.

[7] Beer, P. D., Gale, P. A., Chen, Z., Drew, M. G. B., Heath, J. A., Ogden, M. I. and Powell, H. R. (1997). *Inorg. Chem.*, **36**, 5880.

[8] Beer, P. D., Chen, Z., Drew, M. G. B. and Gale, P. A. (1994). *J. Chem. Soc., Chem. Commun.*, 2207.

[9] Bettega, H. C.-Y., Moutet, J.-C., Ulrich, G. and Ziessel, R. (1996). *J. Electroanal. Chem.*, **406**, 247.

[10] Casnati, A., Comelli, E., Fabbi, M., Bocchi, V., Mori, G., Ugozzoli, F., Lanfredi, A. M. M., Pochini, A. and Ungaro, R. (1993). *Recl. Trav. Chim. Pays-Bas*, **112**, 384.

[11] (a)Choi, D., Chung, T. D., Lee, S. K., Kang, S. K., Kim, T., Chang, S.-K. and Kim, H. (1995). *J. Electroanal. Chem.*, **387**, 133, (b) Chung, T. D., Choi, D., Lee, S. K., Kang, S. K., Kim, T., Chang, S.-K. and Kim, H. (1995). *J. Electroanal Chem.*, **396**, 431. (c) Chung, T. D. (1997). *Ph.D. Thesis* Seoul National University.

[12] (a)Yamamoto, H., Ueda, K., Sandanayake, K. R. A. S., and Shinkai, S. (1995). *Chem. Lett.*, 497. (b)Tóth, K., Lan, B. T. T., Jeney, J., Horváth, M., Bitter, I., Grün, A, Ágai, B. and Töke, L. (1994). *Talanta*, **41**, 1041. (c) King, A. M., Moore, C. P., Sandanayake, K. R. A. S. and Sutherland, I. O. (1992). *J. Chem. Soc., Chem. Commun.*, 582.

[13] Yamamoto, H., Ueda, K., Suenaga, H., Sakaki, T. and Shinkai, S. (1996). *Chem. Lett.*, **39**.

[14] Bethell, D., Dougherty, G. and Cupertino, D. C. (1995). *J. Chem. Soc., Chem. Commun.*, 675.

[15] While this paper was being reviewed, the preparation of **3b** and its *p*-H-calix[4]arene analog was reported; but no electrochemical studies were performed. Nam, K. C. Kang, S. O., Chun, J. C. (1997). *Bull. Korean Chem. Soc.*, **18**, 1050.

[16] Iwamoto, K. and Shinkai, S. (1992). *J. Org. Chem.*, **57**, 7066.

[17] (a)Ohseto, F., Sakaki, T., Araki, K. and Shinkai, S. (1993). *Tetrahedron Lett*, **34**, 2149 (b) Shimizu, H., Iwamoto, K., Fujimoto, K. and Shinkai, S. (1991). *Chem. Lett.*, 2147.

[18] McKillop, A., Perry, D. H., Edwards, M., Antus, S., Farkas, L., Nogradi, M. and Taylor, E. C. (1976). *J. Org. Chem.*, **41**, 282.

[19] (a)Sheldrick, G. M. (1985). SHELXS-86 User Guide, Crystallography Department, University of Göttingen, Germany. (b) Sheldrick, G. M. (1993). SHELXS-93 User Guide, Crystallography Department, University of Göttingen, Germany.

[20] Ugozzoli, F. and Andreetti, G. D. (1992). *J. Inclusion Phenom.*, **13**, 337.

[21] HyperChem, Release 4, Hypercube, Inc., 419 Phillip Street, Waterloo, Ontario N2L 3X2, Canada, 1994.

[22] This type of computational calculation results should be interpreted and applied with great caution, because many researchers reported the discrepancy between the calculations and the experimental observations. For a detailed discussion about the reliability and validity of the computational methods in predicting calixarene conformer stability, see: Lipkowitz, K. B. and Pearl, G. (1993). *J. Org. Chem.*, **58**, 6729.

[23] With respect to the use of $E_p$ instead of $E_{1/2}$ the half-wave potential ($E_{1/2}$) as an intrinsic and characteristic parameter has important meaning in a reversible system. But when the redox behavior is not reversible or subsequent chemical reaction is coupled, $E_{1/2}$ is hard to be determined and not so meaningful. In the case of $Na^+$ or $K^+$, both the peak potential difference ($\Delta E_p$) and $\Delta E_{1/2}$ can be used to determine the electrochemical binding enhancement because both values are the same when the redox process is reversible. When proton source such as $NH_4^+$ is employed as a guest, however, the quantitative evaluation of electrochemical binding enhancement becomes very complicated. Accordingly, $\Delta E_p$ instead of $\Delta E_{1/2}$ was used as a parameter indicating the extent of positive potential shift in the electrochemical reduction potential of quinone.

[24] Meites, L. (1965). Polarographic Techniques, John Wiley & Sons: New York, pp. 89.