JOC Note

A Series of Tetrahomodioxacalix[4]biscrown-*n*. Syntheses, Crystal Structures, and Metal Binding Abilities

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Abstract: A series of novel tetrahomodioxacalix[4]biscrowns with crown-2, crown-3, crown-4, crown-5, and crown-6 units were synthesized. Conformations of each product are dependent on the base used and their conformation stabilities. All conformations were proven by NMR spectra and/or X-ray crystal structures. The 1,3-alternate homodioxacalix[4]biscrown-4 (**4b**) shows the best selectivity for K^+, whereas the 1,3-alternate homodioxacalix[4]crown-5 (**5**) does for Cs^+. Those selectivities are attributable to electrostatic interaction between the metal ion and the crown ring, as well as a π-metal complexation. However, the C-1,2-alternate conformation does not take the metal ions regardless of the crown species as a result of steric hindrance from the methylene bridge of an $ArCH_2Ar$ unit.

Calixarenes are synthetic macrocycles that are available in a variety of ring sizes. They have long been of interest both as complexation hosts for ions and molecules and as frameworks for elaborating more complex structures.[1−3] In contrast to the calix[4]arenes, homooxacalix[4]arenes, which contain extra oxygen atoms in the macrocyclic ring, have received little attention, mainly because they can only be synthesized in relatively low yields.[4−6] Tetrahomodioxa *p-tert*-butylcalix[4]arene was prepared by Gutsche in 44% yield by dehydration of a bishydroxymethylated dimer of *p-tert*-butylphenol, which was synthesized by a multistep reaction starting from the bromination of *p-tert*-butylphenol.[6] There have only been limited studies on the solution conformations, solid-state structures, and complexation behavior of homooxacalix[4]arenes.[7−10] No and Kim reported that there are five conformations in tetrahomodioxacalix[4]arene with appropriate nomenclature (cone, partial cone, C-1,2-alternate, COC-1,2 alternate, and 1,3-alternate) as represented in Figure S1 in Supporting Information.[11] Recently, we reported a solid-state structure of C-1,2-alternate *N*,*N*-diethyl tetrahomodioxacalix[4]arene tetraamide complexing Pb^{2+} with the metal ion bound to the carbonyl oxygen atoms of two adjacent amide substituents and an aryl−alkyl ether oxygen of one of them, proven by X-ray structure.[12] For a corresponding monoalkyl amide, the conformation changed to 1,3-alternate because of intramolecular hydrogen bonding, resulting in weak binding of metal ions.[12]

Calix[4]crown molecules with appropriate crown loops attached to the calix[4]arene framework have been intensively studied for their selectivity in separating radioactive Cs^+ ion from nuclear wastes.[13] We reported the syntheses and X-ray crystal structures of tetrahomodioxacalix[4]biscrown-5 and crown-6 and their complexation abilities toward metal cations.[14]

In a continuation of the synthetic research on the tetrahomodioxacalix[4]biscrowns, the preparation of a series of the compounds with crown loop variation from

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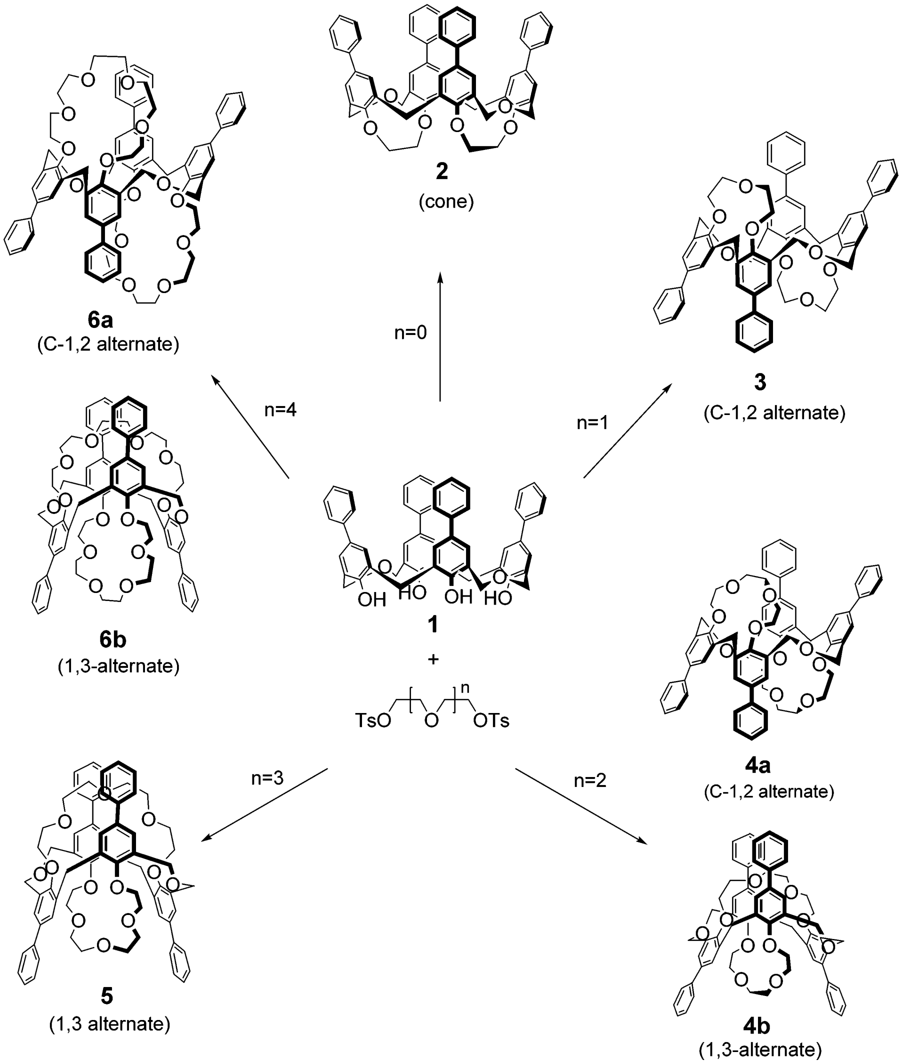
SCHEME 1. Synthetic Route for the Preparation of the Series of Tetrahomodioxacalix[4]biscrowns 2−6



crown-2 to crown-6 was undertaken. We report here the synthetic methods, solid-state conformations, and metal ion encapsulation capabilities of these molecules.

Tetrahomodioxa *p*-phenylcalix[4]arene (**1**) was reacted with 2 equiv of poly(ethylene glycol) ditosylate and 2 equiv of M_2CO_3 (M = Li, Na, K, or Cs) in refluxing CH_3CN for 48 h. After evaporation of solvent, the resulting crude residue was purified by flash chromatographic separation and/or recrystallization to produce homodioxacalix[4]biscrown derivatives **2**−**6** (Scheme 1; also see Table S1 in Supporting Information and Experimental Section). For homodioxacalix[4]biscrown-2 (**2**), **1** was refluxed with ethylene glycol ditosylate in acetonitrile in the presence of K_2CO_3 or Na_2CO_3 as the base to afford **2** in about 35% yield. However, with Li_2CO_3 and Cs_2CO_3, **2** was not produced even when the reaction time was extended up to 6 days. For **2**, AB doublets at δ 4.52 and 4.01 ($\Delta\nu$ = 204 Hz) were observed in the ^{1}H NMR spectrum with a geminal coupling constant of 10.5 Hz corresponding to the dimethyleneoxy protons of the ArCH_2OCH_2Ar bridge, as well as AB doublet peaks at δ 4.39 and 3.49 ($\Delta\nu$ = 360 Hz) with a geminal coupling constant of 15.4 Hz for the methylene protons of ArCH_2-Ar. In the ^{13}C NMR spectrum, two peaks were observed at 69.79 and 66.85 ppm for the ArCH$_2$O bridged methyleneoxy carbons and one peak at 31.46 ppm for the ArCH$_2$Ar bridge carbons. These NMR spectra for **2** indicate that two adjacent aryl moieties joined by a CH_2 group and CH_2OCH_2 group are in *syn* orientation, respectively. Judging from the NMR spectra, one can deduce that **2** is in the cone conformation in solution. The cone conformation in the solid state was evidenced by the X-ray crystal structure shown in Figure S2 in Supporting Information.

When **1** was refluxed with diethylene glycol ditosylate and K_2CO_3 in CH_3CN, homodioxacalix[4]biscrown-3 (**3**) was produced in 45% yield. Upon changing the base to Na_2CO_3, no significant difference in yield was noted. In the ^{1}H NMR spectrum of **3**, the dimethylenoxy protons of the ArCH_2OCH_2Ar bridge showed AB doublets at δ4.81 and 4.23 ($\Delta\nu$ = 232 Hz) with a geminal coupling constant of 11.2 Hz. In addition, a pair of doublet peaks for the methylene protons of ArCH_2Ar appeared at δ4.69 and 4.20 ($\Delta\nu$ = 196 Hz) with a geminal coupling constant of 13.7 Hz. The ^{13}C NMR spectrum showed one peak at 66.08 ppm for the methyleneoxy bridge carbons of ArCH$_2$O and one peak at 27.69 ppm for the ArCH$_2$Ar bridge carbons, implying that two adjacent benzene rings are in a *syn* orientation. The ^{1}H and ^{13}C NMR spectra indicate that **3** is in the C-1,2-alternate conformation.

This conformation was verified in the solid-state structures (Figure S3, Supporting Information). Other reactions with variation of reaction time and solvents gave no other conformations.

For reaction of **1** with triethylene glycol ditosylate and K_2CO_3, two isomers of homodioxacalix[4]biscrown-4 (**4a** and **4b**) were isolated in 49% and 11% yields, respectively. From their NMR spectra, **4a** and **4b** are assigned the C-1,2-alternate and 1,3-alternate conformations, respectively. In the ^{1}H NMR spectrum, the methylene protons of the ArCH_2Ar bridge for **4a** showed an AB doublet at δ 5.21 and 3.41 ($\Delta\nu = 720$ Hz) with a geminal coupling constant of 14.1 Hz. An AB pattern for the dimethyleneoxy protons of ArCH_2OCH_2Ar appeared at δ 4.60 and 4.48 ($\Delta\nu = 48$ Hz) with a geminal coupling constant of 10.5 Hz. The ^{13}C NMR spectrum showed a single peak at 66.97 ppm for the ArCH_2O bridge methyleneoxy carbons and one peak at 31.40 ppm for the ArCH_2Ar bridge carbons implying that two adjacent benzene rings are in a *syn* orientation. For **4b**, the ^{1}H NMR spectrum exhibited for the dimethyeneoxy protons of the ArCH_2OCH_2Ar bridge an AB doublet at δ 4.76 and 4.47 ($\Delta\nu = 116$ Hz) with a geminal coupling constant of 13.3 Hz. In addition, a singlet peak for the methylene protons of ArCH_2Ar appeared at δ 4.09. The ^{13}C NMR spectrum exhibited one peak at 65.03 ppm for the ArCH_2O of bridge methyleneoxy carbons and one peak at 38.27 ppm for the ArCH_2Ar bridge carbons, suggesting that two adjacent benzene rings are in an *anti* conformation. Therefore, it is certain that **4b** is in the 1,3-alternate conformation in solution. This conformation was verified in the solid-state structure (Figure S4, Supporting Information). When the same reaction was performed with Cs_2CO_3 as the base, the yields of **4a** and **4b** were 46% and 20%, respectively. It is known that among five different conformations the C-1,2-alternate conformation is the most stable from a thermodynamics point of view.[4b] So, in this cyclization, the thermodynamic control was driven to preferentially give the C-1,2-alternate conformation, although the 1,3-alternate provided a potassium ion selectivity.

Reaction of **1** with tetraethylene glycol ditosylate and K_2CO_3 or Cs_2CO_3 gave 1,3-alternate **5** as a sole product. The cyclization reaction with Cs_2CO_3 was complete in 24 h, whereas that using K_2CO_3 reached completion after 4 days. So, one might conclude that a template effect plays an important role in this cyclization reaction, which is in accordance with the binding ability for Cs^+ (Table 1, see below). The structure of 1,3-alternate **5** was verified by ^{1}H and ^{13}C NMR spectroscopy and single-crystal X-ray structure determination.[14]

When **1** was refluxed with pentaethylene glycol ditosylate and Cs_2CO_3, the two products **6a** (C-1,2-alternate) and **6b** (1,3-alternate) were obtained in 30% and 26% yields, respectively. The structure of **6a** in solution was determined by ^{1}H and ^{13}C NMR spectroscopy and in the solid structure by single-crystal X-ray structure determination.[14] In the ^{1}H NMR spectrum of **6b**, the dimethyeneoxy protons of the ArCH_2OCH_2Ar bridge showed an AB doublet at δ 4.91 and 4.48 ($\Delta\nu = 172$ Hz) with a geminal coupling constant of 12.0 Hz. A singlet for the methylene protons of ArCH_2Ar appeared at δ 4.24. The ^{13}C NMR spectrum showed one peak at 65.92 ppm for the ArCH_2O of bridge methyleneoxy carbons and one peak at 38.39 ppm for the ArCH_2Ar bridge carbons, indicating that two adjacent benzene rings are in an anti conformation. Thus, it is estblished that **6b** is in the 1,3-alternate conformation.

TABLE 1. Extractabilities of 2−6 for Alkali Metal Picrates[a]

	extractability for metal cations (%)							
compd	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ag^+	Sr^{2+}	Ba^{2+}
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
4a	0.0	0.1	0.1	0.2	0.0	0.0	0.1	0.1
4b	20.1	85.2	77.0	24.2	40.0	44.9	10.8	15.0
5	1.2	7.4	22.8	73.0	0	17.0	1.6	0.8
6a	1.2	1.4	1.7	3.0	0.4	11.0	0.2	0.0
6b	14.5	28.0	37.5	75.3	29.6	55.0	14.6	25.4

[a] Conditions: ligand, 0.10 mM/$ClCH_2CH_2Cl$; metal picrate, 0.20 mM in water. The intensities of the extracted picrates ($\lambda_{max} = 378$ nm) from the water into the organic layer were measured. The extractability is an average value from three independent experiments.

To gain insight into the metal ion affinities of homodioxacalix[4]biscrown-based ligands, extractabilities of **2**−**6** for metal ions were determined by two-phase picrate extraction. The results are listed in Table 1. For **2** (cone-biscrown-2) and **3** (C-1,2-alternate biscrown-3), extraction of metal picrate was undetectable. For **3**, the crown cavity would seem to be appropriate for Na^+. However, there are two methylene units in $ArCH_2Ar$ (C13 and C13′ in Figure S3), which hinder complexation of any metal ions. This is consistent with the fact previously reported that C-1,2-alternate homodioxacalix[4]biscrown-6 exhibited a low extractability toward tested metal ions because of a steric hindrance caused by the methylene hydrogen atoms of the ArCH_2Ar.[14]

In contrast, the 1,3-alternate **4b** selectively binds K^+ over the other cations, whereas the C-1,2-alternate **4a** is an ineffective extractant. A Job plot experiment was performed to obtain the complexation ratio between **4b** and K^+pic^- under conditions of invariant total concentration. A maximum at a molar fraction of [**1**]/([**1**] + [K^+]) of about 0.5 was consistent with a 1:1 complex. This can be ascribed either to electrostatic repulsion between two metal ions or to an allosteric effect.[3a] The K^+ selectivity of the 1,3-alternate **4b** is due to size compatibility between the crown-4 ring, as well π-metal complexation between inverted aromatic units and K^+.

The high extractabilities of 1,3-alternate homodioxacalix[4]biscrown-5 (**5**) and homodioxacalix[4]biscrown-6 (**6b**) for Cs^+ can be explained with the same reasons, depending on the loop size and a possibility for π-metal complexation. In particular, regarding the Cs^+ selectivity, **5** exhibits extractability higher than that of **6b** because the crown-6 size of **6b** is likely to be somewhat larger than the Cs^+.

In conclusion, a series of five tetrahomodioxacalix[4]biscrowns with crown rings varing from crown-2 to crown-6 were synthesized. From the ^{1}H and ^{13}C NMR spectra and crystal structures, their 3-D conformations were elucidated. Among the ligands, the 1,3-alternate homodioxacalix[4]biscrown-4 **4b** showed the best extraction for K^+, and the 1,3-alternate homodioxacalix[4]biscrown-5 **5** did for Cs^+. Those selectivities are attributable to electrostatic interaction between the metal ion and oxygen atoms of the crown loop, as well as a π-metal complexation between inverted phenoxy aromatic units and the target metal ion. By contrast, the C-1,2-alternate conformation does not accept metal ions regardless of the crown species, presumably because of steric hindrance from the methylene bridge of the $ArCH_2Ar$. Calculations for these compounds by molecular mechanics are now in progress and will be reported elsewhere.

Experimental Section

Synthesis. Syntheses for compounds **1**, **5**, and **6a** have been reported.[14]

General Procedures for Homodioxacalix[4]biscrowns 2−6. Tetrahomodioxacalix[4]arene **1** (590 mg, 0.75 mmol), metal carbonate (1.50 mmol), and acetonitrile (100 mL) were stirred magnetically for 20 min in a 250-mL flask. Poly(ethylene glycol) ditosylate (1.55 mmol) was then added, and the mixture was refluxed for 2 days. After cooling to room temperature, the solvent was evaporated to dryness. The residue was acidified with dilute HCl, and the resulting mixture was extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with water, dried over $MgSO_4$, and evaporated in vacuo. The residue was triturated with MeOH to give the product mixture, which was separated with flash chromatography or purified by recrystallization to afford the homooxacalix[4]biscrowns **2**−**6** as white solids. For new compounds, IR and NMR spectra are given in Supporting Information.

Homodioxacalix[4]biscrown-2 (2) was purified by recrystallization from chloroform/hexane and obtained in 35% yield: mp 304 °C (dec). Anal. Calcd for $C_{58}H_{48}O_6$: C, 82.83; H, 5.75. Found: C, 82.78; H, 5.65.

Homodioxacalix[4]biscrown-3 (3) was purified by recrystallization from chloroform, and a 45.5% yield was realized: mp 288 °C. Anal. Calcd for $C_{62}H_{56}O_8$: C, 80.15; H, 6.07. Found: C, 80.08; H, 6.15.

Homodioxacalix[4]biscrown-4 (4a) (C-1,2-alternate**)** was purified by flash chromatography with acetone/hexane (2:7) as eluent and recrystallization from methylene chloride/methanol to give a 49% yield of the title compound: mp 291 °C. Anal. Calcd for $C_{66}H_{64}O_{10}$: C, 77.93; H, 6.34. Found: C, 78.01; H, 6.25.

Homodioxacalix[4]biscrown-4 (4b) (1,3-alternate**)** was purified by flash chromatography with acetone/hexane(2:7) as eluent and recrystallization from methylene chloride/methanol to provide a 20% yield: mp 150 °C. Anal. Calcd for $C_{66}H_{64}O_{10}$: C, 77.93; H, 6.34. Found: C, 78.01; H, 6.25.

Homodioxacalix[4]biscrown-6 (**6b)** (1,3-alternate) was purified by flash chromatography with acetone/hexane (1:2) as eluent and recrystallization from methylene chloride/methanol to give 26% yield of the title compound: mp 216 °C. Anal. Calcd for $C_{74}H_{80}O_{14}$: C, 74.48; H, 6.76. Found: C, 74.41; H, 6.75.

Metal Picrate Extraction. Metal picrates were prepared by reaction of picric acid with the appropriate metal carbonate.[15] To determine the extractability of the ligand for a metal picrate, an aqueous solution (2.0 mL) containing 0.20 mM metal picrate and a 1,2-dichlorethane solution (2.0 mL) of the extractant (0.10 mM) were shaken for 30 min at 25 °C. The concentration of picrate anion extracted from the aqueous phase into the organic layer was determined by UV spectrophotometry ($\lambda_{max} = 373$ nm). Three independent experiments were carried out for each combination of ligand and metal picrate. The extractabilities listed in Table 1 are average values.

X-ray Crystallography. Colorless single crystals **2**, **3**, and **4a** were grown from ethyl acetate/methanol and were mounted and aligned on a CAD-4 diffractometer with graphite monochromated Mo Kα radiation. The programs employed were SMART (Bruker, 1999); cell refinement, SMART; data reduction, SAINT-plus (Bruker, 1999); program(s) used to solve structure, SHELXS97 (Sheldrick, 1997);[16] structure refinement, SHELXL97 (Shjeldrick, 1997);[16] and molecular graphics (Ortep-3 for windows (Farrugia, 1997).[17]

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Supporting Information Available: Preparative procedures and analytical data for compounds **2**−**6** and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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