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A Novel Type of Double-Calixcrown: Spirobiscalix[4]crowns

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Abstract : The synthesis and complexation properties of a novel type of double-calixcrown in which two cone-conformational calix[4]crown subunits were linked via a spiro C-atom incorporated into poly(oxyethylene) chains were described . © 1998 Elsevier Science Ltd. All rights reserved.

Calixcrowns are a family of calixarenes in which the phenolic oxygens are linked by poly(oxyethylene) chains intramolecularly. The first member, *p-tert*-butylcalix[4]crown-6, was reported as early as 1983.[1] Since then, a variety of calixcrowns have been synthesized, such as double-crowned calixarenes and Schiff-base-type calixcrowns, which exhibit extraordinary complexation abilities toward alkali metal ions and other cations.[2] Double-calixarenes are a kind of intermolecularly-bridged calixarenes,[3] which also exhibit special molecular recognition abilities. They can be divided into three sorts according to their linking arrangements, i.e.lower-rim-connected ones,[3a,b] upper-rim-connected ones,[3c] and lower-rim-to-upper-rim-connected ones.[3d] Recently, as a successful combination of calixcrowns and double-calixarenes, double-calixcrowns have been reported and attracted much attention due to their sophisticated molecular structures. The first example, double-*p-tert*-butylcalix[4]crown-5, was obtained by reacting *p-tert*-butylcalix[4]arene with tetraethylene glycol ditosylate in covalent self-assembly process, in which two calix[4]arene subunits were linked by two tetraethylene glycolic chains and the calix[4]arene moieties are in a 1,3-alternate conformation.[4] Mesitol-based double-calix[4]crowns were also reported, in which two calix[4]arene subunits were linked by two diethylene glycolic chains or two dihydroxy benzene diethylene glycolic chains.[5]

In this paper, we wish to report a novel type of double-calixcrown, spirobiscalix[4]crowns **3**, in which two calix[4]arene subunits are connected via a spiro C-atom and the two calix[4]arene moieties are in a cone conformation. The synthesis of **3** are described as follows .

Tetra(tosyloxyethoxyethoxymethyl)methane **1**[7] was prepared from pentaerythritol via bromination with phosphorus tribromide, followed by treating with sodium diethyleneglycolate/diethyleneglycol, and

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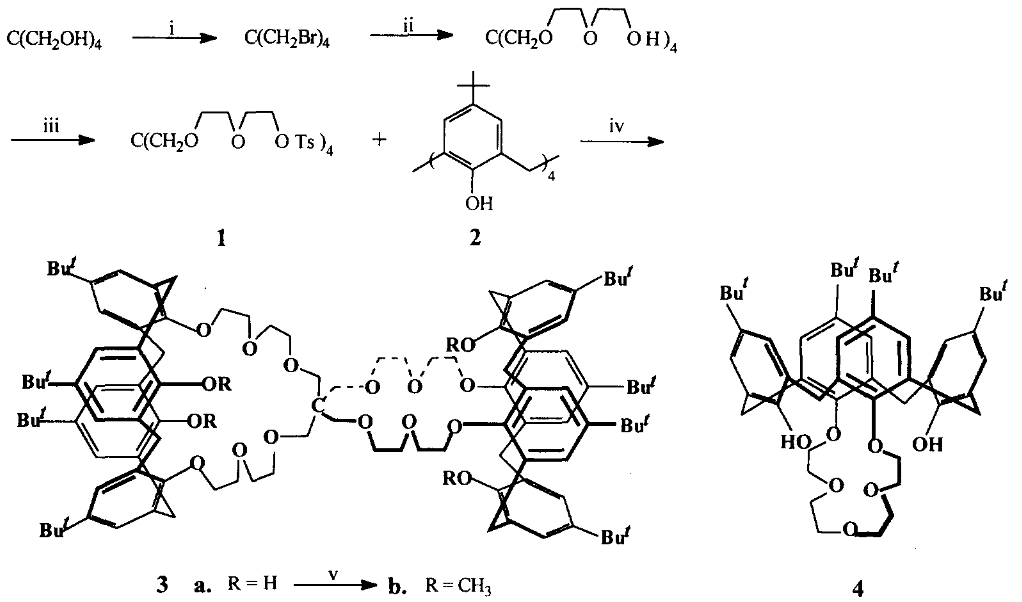
then tosylating with tosyl chloride. A mixture of compound **1** (1 mmol) and *p-tert*-butylcalix[4]arene **2** (2 mmol) in 170 ml of benzene was refluxed for 2 days in the presence of K_2CO_3 (2.5 mmol) under nitrogen atmosphere. After purification by column chromatography, the expected spirobiscalix[4]crown **3a** was isolated in 80% yield, m.p. 173~174℃.[7] Fully methylated **3b** was obtained in 86% yield by reacting **3a** with excess methyl iodide in dioxane (1 mmol of **3a** in 30 ml of dioxane) using excess NaH as a base , m.p.178~179 ℃.[7,8]



Scheme 1. *Reagents and Conditions.* i. PBr_3 ; ii. $NaOCH_2CH_2OCH_2CH_2OH$
iii. TsCl , pyridine ; iv. benzene , K_2CO_3 ; v. NaH/dioxane , MeI.

Tablel . Percentage extraction (% E) of picrate salts from water into $CHCl_3$ at 25℃.[a] Arithmetic mean of several experiments-standard deviation on the mean : $\sigma_{N-1} \leq 1$.

Host	**% E**						
	Li^+	**Na^+**	**K^+**	**NH_4^+**	**$n\text{-}PrNH_3^+$**	**$Me_2NH_2^+$**	**$Et_2NH_2^+$**
3a	12.3	13.2	22.5	24.5	20.6	15.1	14.7
3b	13.1	14.3	13.0	11.9	11.9	10.3	14.4
4b[b]	0.08	0.3	11.8	1.5			

[a] 1.00 ml of 0.0025 mol dm^{-3} receptor solution in $CHCl_3$ was shaken (10 min) with 1.00 ml of 0.005 mol dm^{-3} picrate salt solution in H_2O and the percentage extraction was measured from the resulting absorbance at 380 nm .

[b] These data were quoted from ref. 6 .

The spirobiscalix[4]crowns **3a** and **3b** give satisfactory elemental analysis results and the FAB-MS spectra show expected molecular ion peak as base peak for **3a** and **3b**, respectively.[7] The ^1H NMR spectrum of **3a** show two singlets for the *tert*-butyl groups, one AB system for the methylene bridges of the calix[4]arene skeleton, two singlets for the aromatic protons, one singlet for the hydroxy protons, one singlet and two pairs of distorted triplets for the protons in the spiro-crown moiety. The ^{13}C NMR spectrum of **3a** shows five oxymethylene carbons (69.29 , 69.99×2C , 71.03 and 71.39 ppm) and a spiro carbon (75.99ppm). These spectral features are in good accordance with its structure shown in Scheme 1, in which the two calix[4]arene moieties are in a cone conformation and are bridged at the opposite oxygen atoms (lower rim) .

Examination of the CPK molecular models revealed that **3** are highly preorganized for binding cations. The *p-tert*-butylcalix[4]crown-5 **4** was used as a reference compound . Percentage extraction (%E) of the hosts **3a** and **3b** toward seven picrate salts and the host **4** toward alkali metal picrate salts [6] is summarized in Table 1. The extraction level of **3b** is lower than that of **3a** except for Li^+ and Na^+. In comparison with **4**, the extraction level of **3a** and **3b** toward Li^+, Na^+ and NH_4^+ is higher, but the selectivity is lower.

ACKNOWLEDGEMENTS

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6. Zhong,Z.-L.; Tang,C.-P.; Wu,C.-Y.; and Chen,Y.-Y. *J.Chem.Soc.,Chem.Commun.* **1995**, 1737.
7. **1.^{1}H NMR** (90MHz, CDCl$_3$): 2.40(s, 12H, ArCH$_3$), 3.23(s, 8H, OCH$_2$), 3.40~3.80(m, 24H, OCH$_2$CH$_2$), 4.00~4.20(m, 8H, OCH$_2$CH$_2$), 7.32(d, J=7.7Hz, 8H, ArH), 7.68(d, J=7.7Hz, 8H, ArH). **3a.^{1}H NMR** (200MHz, CDCl$_3$): 0.97(s, 36H, ArC(CH$_3$)$_3$), 1.28(s, 36H, ArC(CH$_3$)$_3$), 3.32(d, J=8.7Hz, 8H, ArCH$_{eq}$-Ar), 3.43(s, 8H, OCH$_2$), 3.67(bs, 8H, OCH$_2$CH$_2$), 3.90(bs, 8H, OCH$_2$CH$_2$), 4.00(bs, 8H, OCH$_2$CH$_2$), 4.13(bs, 8H, OCH$_2$CH$_2$), 4.33(d, J=8.7Hz, 8H, ArCH$_{ax}$-Ar), 6.81(s, 8H, ArH), 7.04(s, 8H, ArH), 7.41(s, 4H, ArOH). **^{13}C NMR** (50MHz, CDCl$_3$): δ 30.94, 31.45, 31.64, 33.71, 33.83, 69.29, 69.99×2C, 71.03, 71.39, 75.99, 124.90, 125.43, 127.66, 132.65, 141.10, 146.72, 149.75, 150.62.
   MS (FAB): m/z=1713(MH$^+$, 100%), 1736(MH$^+$+Na, 40%), 1752(MH$^+$+K, 20%).**Anal. Calcd** for C$_{109}$H$_{148}$O$_{16}$: C, 76.37; H, 8.70. **Found**: C, 76.18; H, 8.81.
   3b. ^{1}H NMR (200MHz, CDCl$_3$): 0.86(s, 36H, ArC(CH$_3$)$_3$), 1.29(s, 36H, ArC(CH$_3$)$_3$), 3.28(d, J=8.5Hz, 8H, ArCH$_{eq}$-Ar), 3.32(s, 12H, ArOCH$_3$), 3.39(s, 8H, OCH$_2$), 3.61(bs, 8H, OCH$_2$CH$_2$), 3.84(bs, 8H, OCH$_2$CH$_2$), 4.08(bs, 8H, OCH$_2$CH$_2$), 4.20(bs, 8H, OCH$_2$CH$_2$), 4.45(d, J=8.5Hz, 8H, ArCH$_{ax}$-Ar),6.83(s, 8H, ArH), 7.13(s, 8H, ArH). **MS (FAB)**: m/z=1769(MH$^+$, 100%), 1791(M$^+$+Na, 20%). **Anal.. Calcd** for C$_{113}$H$_{156}$O$_{16}$: C, 76.67; H, 8.88. **Found**: C, 76.41; H, 8.96.
8. In 1995, Casnati *et al.* reported that similar dimethylated calixcrowns are usually mixtures of different conformers, Casnati, A.; Pochini, A.; Ungaro, R.; Ugozzoli, F.; Arnaud, F.; Fanni, S.; Schwing, M.-J.; Egberink, R.J.M.; de Jong, F.; and Reinhoudt, D.N. *J. Am. Chem. Soc.* **1995**, 117, 2767. But their reaction conditions were different from ours. The fully methylated **3b** is observed to be in a cone conformation at ambient temperature.