Studies on the Synthesis and Property of A New Podand-armed Calix[4]arene Derivative

Yan Jun XING, Zhi Xian ZHOU*, Li MA, Zhen Wei LU

Chemistry Department, Zhengzhou University, Zhengzhou 450052

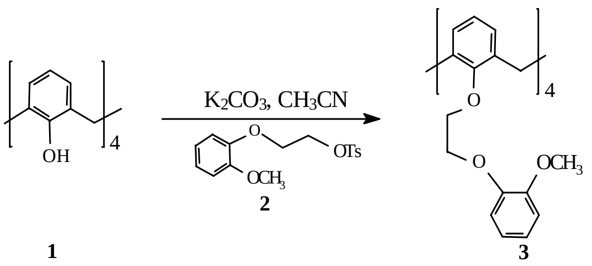
Abstract: A new ligand 25, 26, 27, 28-tetrakis[2-(o-methoxyphenoxy)ethoxy]calix[4]arene **3** was synthesized by direct base-strength-driven O-alkylation of calix[4]arene **1**. **3** has been used as ionophore for cesium selective PVC membrane electrode. The extraction for cesium and sodium with **3** have been also studied.

Keywords: Podand-armed calixarene, cesium.

Pendant groups such as esters, amides, carboxylic acids, *etc.* have been grafted at the lower rim of calix[4]arene to produce a variety of novel ionophores[1]. The calix[4]arenes with different functional groups have showed coordination diversity for alkali metal cations[2]. In this paper we described the synthesis of a new calixarene derivative with podand-armed functional group and the property as ionophore and extractant for cesium ion.

25, 26, 27, 28-Tetrakis[2-(*o*-methoxyphenoxy)ethoxy]calix[4]arene **3** was synthesized from 25, 26, 27, 28-tetrakishydroxycalix[4]arene **1** with 2-tosyloxyethyl *o*-methoxyphenyl ether **2** in the presence of K_2CO_3 in dry CH_3CN (**Scheme 1**). The residue was purified by silicagel column chromatography using 8:1 petroleum ether: EtOAc as eluent to give pure **3** as a white solid in 51% yield. The compound **3** was characterized by IR, ^1H, ^{13}C NMR and elemental analysis[3].

Scheme 1



The structure of **3** was analyzed by ^1H- and ^{13}C NMR spectroscopy. The characteristic singlet at δ 3.69 for the methylene bridge protons[1] was indicative of 1,3-

alternative conformation. The alternative conformation of **3** was also confirmed by ^{13}C NMR. The absorption of Ar-CH_2-Ar was present at δ36.05, which slightly deviated from that of about 37.0 mentioned by de Mendozu *et al*[4] for calix[4]arene in the 1,3-alternative conformation.

The cesium selective electrode with **3** incorporated in the PVC membrane was studied. The electrode gave a linear, near Nernstian response, the slope is 56.4mV/decade in the concentration range of 10^{-4}~10^{-1}mol/L. The selectivities of the electrode were estimated against a range of common interfering ions by the fixed interference method. The potentiometric coefficients $\log K^{pot}_{Cs/M}$ for H^+, Li^+, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+} were –3.22, -3.54, -3.39, -0.41, -0.64, -3.76 and –3.67, respectively. It can be seen that the ionophore **3** is selective for cesium. In the presence of 0.50mol/L CsCl and 0.10mol/L CsOH, 2.5×10^{-4}mol/L of **3** can extract 53.6% of 2.5×10^{-4}mol/L cesium picrate. However, no detectable sodium picrate can be found in the organic phase at the same condition. So ligand **3** may be used as a new extractant for cesium.

Acknowledgment

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References and Notes

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3. mp 167-169°C (from 1:1 $CHCl_3$: CH_3OH). ^1H NMR: 7.10 (8H, d, Ar**H**, J=7.6Hz), 6.90-6.95 (4H, m, Anisyl-**H**), 6.57 (4H, t, Ar**H**, J=7.6Hz), 4.13 (8H, t, ArOC**H**$_2$, J=5.2Hz), 4.03 (8H, t, Anisyl-OC**H**$_2$, J=5.2Hz), 3.86 (12H, s, OC**H**$_3$), 3.70 (8H, s, ArC**H**$_2$Ar). Found: C, 75.08; H, 6.32%. Calcd. for $C_{64}H_{64}O_{12}$: C, 74.98; H, 6.29%.
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