

Lower Rim Substituted *tert*-Butyl calix[4]arene (part VII): Ionophoric Properties of Calix[4]arene-crown-6 Derivatives in Plasticized PVC-Membrane Electrodes and in Solution

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Abstract

The synthesis and characterization of *p-tert*-butylcalix[4]arene-crown-6 derivatives (compounds **2–9**) are presented. Their ability to complex alkali, alkaline earth and some “softer” cations was investigated by using these compounds as ionophores in ion-selective membrane electrodes and determining the potentiometric selectivity coefficients and the complex stability constants in the membrane. The selectivities of these compounds depend on the size and nature of the substituents on the distal phenolic oxygens. The complexing properties of the two *cone* and *partial cone* conformers of compound **2** in the PVC membrane were compared with those in acetonitrile solution studied by UV absorption spectrophotometry and with alkali metal picrate liquid–liquid extraction.

Introduction

Among the large number of known “calix” ionophores, 1,3-substituted tetrakis-(*tert*-butyl)calix[4]crowns play an important role because of their remarkable ability to complex selectively alkali metal ions. A correlation between the size of poly(ethylenoxy) loop of 1,3-calix[4]crown and the ligand selectivity in ion-selective membrane electrodes (ISEs) was established in our previous paper [1]. It is known that calix[4]crowns-4 with triethylenoxy bridge complex selectively sodium cations [2] calix[4]crowns-5 with tetraethylenoxy bridge complex selectively potassium cations [3] and calix[4]crowns-6 with pentaethylenoxy chain complex caesium ions [4]. The role of the conformation of 1,3-substituted *tert*-butylcalix[4]crowns on the complexation process was also investigated. However, most of the papers deal with 1,3-calix[4]crowns without *tert*-butyl substituents at the wide rim of the ligands [4–6].

The main task of our studies was to find new highly selective ionophores for ion selective membrane electrodes. Such application requires ligands of high lipophilicity. That is why we focused our attention on the narrow rim modifications only leaving *tert*-butyl groups on the wide rim of calix[4]crowns. Our goal was to

establish a correlation between the size and the nature of the substituents at the distal 2,4-positions of 1,3-calix[4]crowns-6 and their complexing ability.

Here, we present the procedure of the synthesis of *p-tert*-butylcalix[4]crowns-6 with different substituents (compounds **2–9**). The complexing properties of these ligands were studied by applying them as ionophores in ion-selective membrane electrodes and were expressed as potentiometric selectivity coefficients $\log K_{M,X}^{\text{pot}}$. We estimated the complex stability constants ($\log \beta_{LM}$) in the PVC- membrane electrodes by a potentiometric method, using the procedure described earlier by Pretsch and Bakker [7, 8]. In the case of compound **2**, which was isolated in the two *cone* and *p-cone* conformations (compounds **2c** and **2p-c**, respectively) the values of complex stability constants thus obtained were compared with the values derived from UV spectrophotometric studies in solution and with picrate extraction data.

Experimental

General

¹H NMR spectra were recorded in CDCl₃ on a Varian instrument (200 MHz or 500 MHz). Mass spectra (LSIMS technique, M⁺Na) were obtained on an

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AMD-604 Mass Spectrometer. Both structure and purity of the compounds were confirmed by ^1H NMR and mass spectra. UV spectra were recorded on a Cary 3 spectrophotometer (Varian).

Reagents

High molecular weight PVC, *o*-nitrophenyl octyl ether (*o*-NPOE) and lipophilic salt: potassium tetrakis(*p*-chlorophenyl)borate (KTPClPB) were from Fluka. Perchlorates used for the UV spectrophotometric titrations were of analytical grade from Fluka (NaClO_4) and from Alfa (RbClO_4 , CsClO_4); they were vacuum dried at room temperature before use. The alkali metal picrates were obtained by the procedure published before [9]. The solvents acetonitrile (Riedel de Haën) and dichloromethane (Prolabo) were used without further purification. All the other salts employed were of analytical grade.

Syntheses

Compounds **1–9** were synthesized according to Scheme 1. Synthesis of 5,11,17,23-tetrakis-*tert*-butyl-25,27-bis(hydroxy)calix[4]arene-crown-6 (**1**)

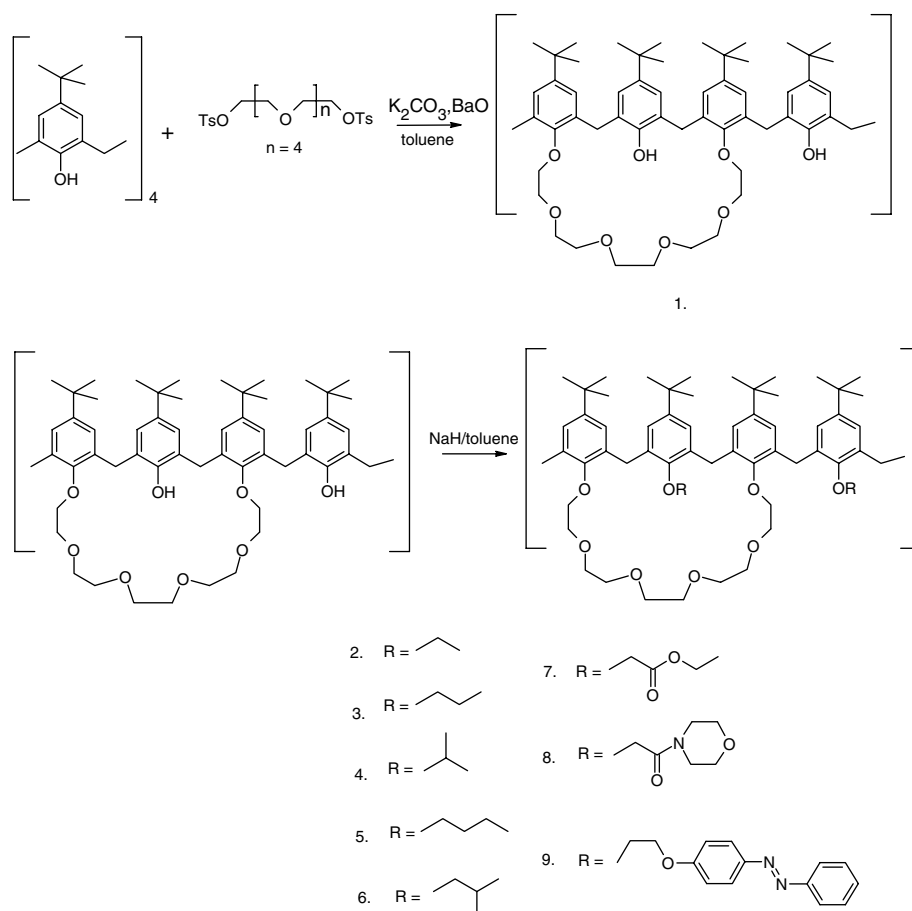
A suspension: 3 mmols of *p*-*tert*-butylcalix[4]arene, 3 mmols of K_2CO_3 and 1 mmol of BaO in 30 ml of toluene was stirred vigorously at 50 °C for 1.5 h. After

that time 3.5 mmols of the penta-ethylene glycol ditosylate in 20 ml of toluene was added dropwise within 1 h, and the stirring and heating were continued for 48 h at 85 °C. Then the mixture was filtrated and the solvent was evaporated under the reduced pressure. The crude product was dissolved in methylene chloride, washed with 0.1 M HCl and water, and dried with MgSO_4 . After solvent evaporation, the oily product was treated with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture in order to crystallize.

$\text{C}_{54}\text{H}_{74}\text{O}_8$, M.W. 850.6, in *cone* conformation, yield 68%, m.p. 228–232 °C; (m.p. 232–234 °C [3c]) ^1H NMR δ [ppm]: 0.92 (br s, 18H, *t-but*); 1.32 (m, 18H, *t-but*); 3.30 (d, $J = 12.5$ Hz, 4H, CH_2); 3.75 (s, 4H, OCH_2CH_2); 3.85–4.15 (m, 16H, OCH_2CH_2); 4.35 (d, $J = 12.5$ Hz, 4H, CH_2); 6.75 (s, 4H, H_{Ar}); 7.05 (s, 4H, H_{Ar}); 7.25 (s, 2H, OH).

Synthesis of compounds 2–9

A suspension: 0.5 mmol of *p*-*tert*-butyl-bis(hydroxy)calix[4]arene-crown-6 and 2.5 mmols of sodium hydride (50% in oil) in 50 ml of toluene was stirred vigorously at 50 °C for 1.5 h. After that time 2 mmols of the appropriate alcohol tosylates (for **7**, **8** α -chloro and for **9** α -bromo derivatives were used) in 20 ml of toluene was added dropwise within 1 h, and the stirring and heating were continued for 48 h at 100 °C. Then the mixture was filtrated and solvent was evaporated under the reduced pressure. The crude product was dissolved



Scheme 1.

in methylene chloride, washed with 0.1 M HCl and water, and dried with MgSO₄. After solvent evaporation, the oily product was crystallized from the mixture CH₂Cl₂/MeOH.

5,11,17,23-tetrakis-p-tert-butyl-bis(ethoxy)calix[4]arene-crown-6 (2)

C₅₈H₈₂O₈, M.W. 906.6, MS(LSIMS) M⁺/z (Na⁺): 929, total yield 66%. *Cone conformer (2e)* m.p. 202–204 °C, (203 °C [3]), yield 33%, ¹HNMR δ[ppm]: 0.88 (s, 18H, *t-but*); 1.29 (s, 18H, *t-but*); 1.53 (q, 6H, CH₃); 3.13 (d, J = 12.6 Hz, 4H, CH₂); 3.75–3.90 (m, 16H, OCH₂CH₂); 4.21 (s, 8H, OCH₂); 4.36 (d, J = 12.6 Hz, 4H, CH₂); 6.53 (s, 4H, H_{Ar}); 7.05 (s, 4H, H_{Ar}).

Conformer partial cone (2p-c), m.p. 182–186 °C, yield 33%, ¹HNMR δ[ppm]: 0.88 (m, 3H, CH₃); 1.07 (s, 18H, *t-but*); 1.29 (m, 3H, CH₃); 1.35 (s, 9H, *t-but*); 1.42 (s, 9H, *t-but*); 3.00 (d, J = 12.6 Hz, 2H, CH₂); 3.40–4.10 (m, 28H, OCH₂CH₂, and CH₂); 4.24 (d, J = 12.6 Hz, 2H, CH₂); 6.66 (d, J = 2.2, 2H, H_{Ar}); 6.89 (d, J = 2.2, 2H, H_{Ar}); 7.08 (s, 2H, H_{Ar}); 7.15 (s, 2H, H_{Ar}).

5,11,17,23-tetrakis-p-tert-butyl-bis(n-propoxy)calix[4]arene-crown-6 (3)

C₆₀H₈₆O₈, M.W. 934.7, MS(LSIMS) M⁺/z (Na⁺): 957, yield 52%, m.p. 269–271 °C, ¹HNMR δ[ppm]: 0.83 (s, 18H, *t-but*); 1.10 (m, 6H, CH₂CH₃); 1.37 (s, 18H, *t-but*); 2.00 (m, 4H, CH₂CH₂); 3.15 (brd, J = 12.8 Hz, 4H, CH₂); 3.68–3.82 (m, 16H, OCH₂CH₂); 4.24 (br.s, 8H, OCH₂CH₂); 4.30 (d, J = 12.6 Hz, 4H, CH₂); 6.46 (s, 4H, H_{Ar}); 7.14 (s, 4H, H_{Ar}).

5,11,17,23-tetrakis-p-tert-butyl-bis(i-propoxy)calix[4]arene-crown-6 (4)

C₆₀H₈₆O₈, M.W. 934.7, MS(LSIMS) M⁺/z (Na⁺): 957, yield 60%, m.p. 266–270 °C, ¹HNMR δ[ppm]: 0.82 (s, 18H, *t-but*); 1.36–1.38 (m, 18H, *t-but* and 12H, CH₃); 3.12 (d, J = 12.5 Hz, 4H, CH₂); 3.75–3.83 (m, 14H, OCH₂CH₂); 4.24 (s, 8H, CH and OCH₂CH₂); 4.35 (d, J = 12.5 Hz, 4H, CH₂); 6.43 (s, 4H, H_{Ar}); 7.13 (s, 4H, H_{Ar}).

5,11,17,23-tetrakis-p-tert-butyl-bis(n-butoxy)calix[4]arene-crown-6 (5)

C₆₂H₉₀O₈, M.W. 962.8, MS(LSIMS) M⁺/z (Na⁺): 985, yield 69%, m.p. 188–190 °C, ¹HNMR δ[ppm]: 0.81 (s, 18H, *t-but*); 1.00 (m, 6H, CH₃); 1.35 (s, 18H, *t-but*); 1.58 (m, 4H, CH₂CH₂); 1.95 (m, 4H, CH₂CH₂); 3.15 (d, J = 12.6 Hz, 4H, CH₂); 3.70–3.80 (m, 16H, OCH₂CH₂); 4.22 (s, 8H, OCH₂CH₂); 4.35 (d, J = 12.6 Hz, 4H, CH₂); 6.44 (s, 4H, H_{Ar}); 7.12 (s, 4H, H_{Ar}).

5,11,17,23-tetrakis-p-tert-butyl-bis(i-butoxy)calix[4]arene-crown-6 (6)

C₆₂H₉₀O₈, M.W. 962.8, MS(LSIMS) M⁺/z (Na⁺): 985, yield 63%, m.p. 198–200 °C, ¹HNMR δ[ppm]: *conformer cone*; 0.81 (s, 18H, *t-but*); 1.12 (d, J = 6.6, 12H, CH₃); 1.35 (s, 18H, *t-but*); 2.20 (m, 2H, CH(CH₃)₂); 3.15

(d, J = 12.6 Hz, 4H, CH₂); 3.50 (d, J = 6.6, 4H, OCH₂CH); 3.70 (brd, 12H, OCH₂CH₂); 4.20 (brd, 8H, OCH₂CH₂); 4.30 (d, J = 12.6 Hz, 4H, CH₂); 6.40 (s, 4H, H_{Ar}); 7.10 (s, 4H, H_{Ar}).

5,11,17,23-tetrakis-p-tert-butyl-bis(ethoxycarbamoyl-methoxy)calix[4]crown-6 (7)

Purified by column chromatography (SiO₂, hexane-methylene chloride 1:1), C₆₂H₈₆O₁₂, M.W. 1022.7, MS(LSIMS) M⁺/z (Na⁺): 1045, yield 40%, m.p. 124–126 °C, ¹HNMR δ[ppm]: 0.89 (s, 18H, *t-but*); 1.26 (s, 18H, *t-but*); 1.29–1.33 (m, 6H, CH₃); 3.15 (d, J = 12.8 Hz, 4H, CH₂); 3.76 (m, 16H, OCH₂CH₂); 4.22 (m, 8H, OCH₂CH₂ and CH₂CH₃); 4.52 (d, J = 12.4 Hz, 4H, CH₂); 4.60 (s, 4H, OCH₂); 6.56 (s, 4H, H_{Ar}); 7.02 (s, 4H, H_{Ar}).

5,11,17,23-tetrakis-p-tert-butyl-bis(morpholinocarbamoyl-methoxy)-calix[4]crown-6 (8)

Recrystallized from methanol, C₆₆H₉₂O₁₂N₂, M.W. 1104.7, MS(LSIMS) M⁺/z (Na⁺): 1127, yield 30%, m.p. 168–170 °C, ¹HNMR δ[ppm]: 0.90 (s, 18H, *t-but*); 1.30 (s, 18H, *t-but*); 3.18 (d, J = 12.8 Hz, 4H, CH₂); 3.40–3.85 (m, 12H, OCH₂CH₂ and 16H, H_{morph}); 4.20 (m, 8H, OCH₂CH₂); 4.45 (d, J = 12.8 Hz, 4H, CH₂); 4.80 (s, 4H, OCH₂); 6.56 (s, 4H, H_{Ar}); 6.79 (s, 4H, H_{Ar}).

5,11,17,23-tetrakis-p-tert-butyl-bis(azobenzoethoxy)-calix[4]crown-6 (9)

Purified by column chromatography (SiO₂, hexane-methylene chloride 1:1), C₈₂H₉₈O₁₀N₄, M.W. 1298.9, MS(EI) M⁺/z: 1298, yield 23%, m.p. 228–230 °C, ¹HNMR δ[ppm]: 1.05 (s, 18H, *t-but*); 1.13 (s, 18H, *t-but*); 3.15 (d, J = 12.0 Hz, 4H, CH₂); 3.60–3.71 (m, 12H, OCH₂CH₂); 4.10 (m, 8H, OCH₂CH₂); 4.46–4.58 (m, 8H, OCH₂CH₂ and 4H, CH₂); 6.74 (s, 4H, H_{Ar}); 6.86 (s, 4H, H_{Ar}); 7.10 (d, J = 9.5 Hz, 4H, H_{azobenzene}); 7.50 (s, 6H, H_{azobenzene}); 7.90 (s, 8H, H_{azobenzene}). UV/VIS [λ (nm), ε (dm³ mol⁻¹ cm⁻¹): acetonitrile λ = 280 nm (ε = 8.48 × 10³); λ = 352 nm (ε = 3.08 × 10⁴); λ = 440 nm (ε = 2.03 × 10³).

Ion-selective electrode studies

Membrane preparation

The membrane components: high molecular poly(vinyl chloride) (PVC) 60 mg, potassium tetrakis (4-chlorophenyl-borate) (KTPCIPB) 0.5 mg, *o*-nitrophenyl-octylether (NPOE) 120 mg and 4 mg of ionophore were dissolved in 1.5 ml of freshly dried and distilled THF. The solution was poured into a glass ring as described previously [1, 10]. After solvent evaporation the membranes were used for making the electrodes.

The membranes were incorporated into Ag/AgCl electrode bodies of IS 561 type (W. Moeller AG). A double-junction reference electrode Radelkis OP0820P was used with 1 M CH₃COOLi solution in the bridge cell. The potentials were measured at 20 °C, using a

METROHM 654 pH Meter. All the measurements were performed in unbuffered water salts solutions.

The characteristics of the electrodes 1–10 are presented in Table 1. The selectivity coefficients $\log K_{M,X}^{\text{pot}}$ were determined by the separate solution method (SSM) [11] and were calculated using the equation (1). The values are presented in Table 2.

$$\log K_{M,X}^{\text{pot}} = \frac{(E_X - E_M)z_M F}{2.303RT} + \left(1 - \frac{z_M}{z_X}\right) \log a_M \quad (1)$$

Determination of complex stability constants in the membrane

We estimated the values of the complex formation constants $\log \beta_{LM}$ for compounds **2**, **7** and **8** in PCV/NPOE membranes using the potentiometric method of Pretsch and Bakker [8]. The procedure compares the selectivity coefficient values of two electrodes. One of them is the ion-selective electrode with the studied ionophore (L) and the second one, ion exchanger electrode of exactly the same composition but without ionophore (IE). Tetramethylammonium cation (TMA^+) was used as reference ion [8a]. On the basis of the selectivity coefficients we determined the values of

Table 1. The characteristics of the electrodes 1–10

Electrode No	Compound No	Ion of preference	Plasticizer	S_M [mV]	Linear range
1	2c	Na^+	NPOE	65	5.0–1.0
2	2p-c	Cs^+	NPOE	62	5.0–1.0
3	3	Na^+	NPOE	61	5.0–1.0
4	4	TMA^+	NPOE	60	4.0–1.0
5	5	Na^+	NPOE	59	5.0–1.0
6	6	TMA^+	NPOE	60	5.0–1.0
7	7	K^+	NPOE	57	5.0–1.0
8	8	K^+	NPOE	60	5.0–1.0
9	9	Na^+	NPOE	59	5.0–1.0
10	–	TMA^+	NPOE	59	5.0–1.0

Table 2. Selectivity coefficients as $\log K_{\text{Na},M}^{\text{pot}}$ for the electrodes 1–9 and for electrode 10 as $\log K_{\text{Na},M}^{\text{pot}}$

Electrode No	Compound No	Selectivity coefficients $\log K_{\text{Na},M}^{\text{pot}}$												
		Li^+	Na^+	K^+	Rb^+	Cs^+	TMA^+	G^+	H^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	Ag^+	Hg^{2+}
1	2c	–1.8	0	–1.0	–1.1	–1.5	–1.6	–2.5	–3.5	–3.8	–3.8	–2.8	+0.8	–1.3
2	2p-c	–1.5	0	+0.5	+0.6	+1.0	–1.0	–2.4	–1.9	–3.5	–3.6	–2.5	+2.7	+0.4
3	3	–1.8	0	–0.9	–0.9	–1.4	–1.3	–2.2	–2.9	–4.2	–4.2	–2.8	+0.8	+0.4
4	4	–1.7	0	–0.3	+0.4	–0.2	+0.9	–0.4	–2.8	–3.5	–3.6	–2.6	+1.9	+2.2
5	5	–2.0	0	–1.0	–1.0	–1.5	–1.2	–2.3	–3.3	–4.1	–3.5	–2.9	+0.7	–0.5
6	6	–2.1	0	–0.3	–0.3	–0.7	+0.4	–1.1	–3.0	–3.8	–3.8	–2.9	+1.1	+1.6
7	7	–1.6	0	+0.9	+0.8	+0.4	–1.4	–1.2	–3.0	–3.3	–3.5	–2.6	+0.5	+0.4
8	8	–1.4	0	+0.8	+0.4	–1.1	–2.4	–2.4	–2.8	–3.4	–3.4	–2.8	+0.9	–0.6
9	9	–0.2	0	+0.5	+0.5	+0.4	+1.3	+1.9	–	–3.9	–4.0	–2.8	+1.1	+2.0
10	–	–4.6	–3.5	–3.2	–2.8	–2.4	0	–	–	–	–	–	–0.6	–0.9

G^+ guanidinium cation.

TMA^+ tetramethylammonium cation.

stability constants for complexes of monovalent cations with ligands **2**, **7**, **8**, using the equation (2), in which L_T is the total concentration of ionophore in the membrane and R_T the total concentration of the lipophilic salt (KTpClPB) in the membrane.

$$\beta_{LM}^{\text{pot}} = \frac{K_{M,TMA}^{\text{pot}}(IE)}{K_{M,TMA}^{\text{pot}}(L)[L_T - R_T]} \quad (2)$$

One of the assumption of the method is that the studied ionophore do not interact with TMA ion, which is used as a reference cation. We assume that at least hundred times higher selectivity for metal ion than for the reference TMA^+ cation means very weak interaction of ligand with TMA ion and allow for the calculations. Another assumption is that the studied calix[4]arene crowns form complexes of 1:1 stoichiometry with metal cations.

Determination of the complex stability constants in solution

Stability constants β equal to the concentration ratios $[\text{LM}^+]/[\text{L}][\text{M}^+]$ for alkali metal ion complexes with both conformers of ligand **2** ($L = \mathbf{2c}$ and $\mathbf{2p-c}$) were determined in acetonitrile by spectrophotometric titrations [12]. The addition of metal perchlorates (C_M) was done directly in the spectrophotometric cell (1 cm pathlength) containing 2 ml of a solution of ligand ($C_L = 10^{-4}$ M) in the presence of tetraethylammonium perchlorate as supporting electrolyte. The ratio $R = C_M/C_L$ reached at the end of the titration (2–10) depended on the stability of the complexes. Figure 1 presents, as an example, the experimental document corresponding to the complexation of caesium ions by the cone conformer **2c**. The absorbances, selected at several wavelengths where maximum spectral changes were observed, were interpreted using Sirko and Specfit softwares [13, 14].

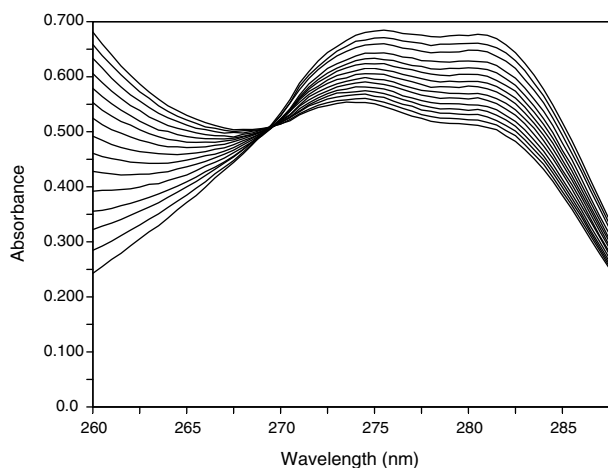


Figure 1. Changes in UV absorption spectra of compound **2c** upon addition of CsClO₄ in acetonitrile: C_L = 10⁻⁴ M, R = 5.

Extraction studies

Extraction experiments were carried out according to Pedersen's procedure [15]: 5 ml of metal picrate solution in water and 5 ml of ligand solution in CH₂Cl₂, each of concentration 2.5 × 10⁻⁴ M, were introduced into stoppered tubes. After 2 min of vigorous shaking, followed by 30 min of magnetic stirring in a thermostated water bath at 20 °C, the tubes were allowed to settle for another 30 min for phase separation. Absorbance (A) of aqueous phase was measured at λ_{max} = 355 nm. An experiment without the ligand was run under the same condition and the absorbance (A₀) was measured. The percentage of extracted cations was calculated from the equation:

$$\%E = 100(A_0 - A)/A_0$$

Results and discussion

The task of our studies was to find a correlation between the size of the substituents at the distal 2,4-positions of 1,3-substituted calix[4]crowns-6 and the complexing ability of the compounds. All the ligands studied were obtained with rather good yield (30–60%) in one-pot procedure, according to Scheme 1. The starting com-

pound 1,3-bis-hydroxy *p*-*tert*-butylcalix[4]crown-6 (**1**) in *cone* conformation was obtained with good yield (68%) in the reaction of *p*-*tert*-butylcalix[4]arene with pentaethyleneoxy glycol ditosylate in toluene in the presence of BaO and K₂CO₃, by modification of the procedure already described [3c]. The isolated compounds are in conformation *cone* with the exception of the bis(ethoxy)calix[4]crown-6 (**2**), which was obtained as two different conformers, *cone* and *partial cone*, as is clearly shown by their ¹H NMR spectra. The size of the residue R larger than ethyl prevent from the conformation changes.

Complexing properties of calix[4]crowns-6 were studied in ion-selective PVC-membrane electrodes plasticized with o-NPOE (o-nitrophenyloctylether). The electrodes were stable and long lasting due to the high lipophilicity of *p*-*tert*-butylcalix[4]crowns ionophores. The selectivity coefficients as log K_{M,X}^{pot} for all the electrodes are presented in Table 2. The results show that calix[4]crowns-6 **2c**, **3** and **5**, all in *cone* conformation are most selective for sodium cations unlike the corresponding bis-methoxy compound synthesized and studied earlier which is highly Cs⁺-selective (log K_{Cs,Rb}^{pot} = -1.7; log K_{Cs,Na}^{pot} = -2.8) [1].

We also found that the length of alkyl substituents does not significantly influence the complexing properties. The *partial cone* conformer **2p-c** is selective for cesium cations, but not as highly selective as the bis(methoxy) derivative [1] and is most selective for softer, Ag⁺ cation. Calix[4]crowns-6, modified with bulky substituents, such as *iso*-propyl (**4**) or *iso*-butyl groups (**6**) are selective neither for alkali nor alkaline earth metal ions, but they show selectivity for softer mercury and silver cations or TMA ions. This suggest that the pseudo-cavity formed by four bulky substituents R cannot be enter easily by any cations and the membrane electrodes with ligands **4** and **6** are similar to the electrode 10, with no ionophore. The presence of two carbonyl oxygen atoms in the substituents of compound **7** and **8** enables the formation of complexes with potassium or rubidium cations, which are usually octa-coordinated. The highest values of complex stability constants for potassium and rubidium (see Table 3) confirm this reasoning. Chromogenic derivative **9** of calix[4]crown-6 shows a selectivity for "soft" cations, of low electron density, such as mercury, silver or the large organic guanidinium (G⁺) and tetramethylammonium

Table 3. Calculated values of complex stability constants (log β_{LM}^{pot} ± σ)^{a)} for ligands **2**, **7** and **8** in the PVC/NPOE membrane

Electrode N°	Compound N°	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
1	2c	6.8 ± 0.03	*	*	*
2	2p-c	*	*	6.1 ± 0.05	5.9 ± 0.2
7	7	*	7.2 ± 0.1	6.7 ± 0.1	*
8	8	7.5 ± 0.2	8.0 ± 0.15	7.3 ± 0.1	*

^{a)}Standard deviation σ_{n-1} on the mean calculated out of several electrodes measurements (n ≥ 2).

* Not possible to calculate.

Table 4. Stability constants ($\log \beta \pm \sigma_{n-1}$)^{a)} of alkali metal ion complexes in acetonitrile ($T = 25\text{ }^\circ\text{C}$, $I = 10^{-2}$ (Et_4NClO_4)) and, in brackets, extraction percentage (%E)^{b)} of alkali metal picrates, from water into dichloromethane, at $20\text{ }^\circ\text{C}$, for the two conformers **2c** and **2p-c**

Compounds	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
2c	5.9 ± 0.1 (3.6)	4.6 ± 0.1 (1.3)	4.2 ± 0.1 (1.0)	4.4 ± 0.1 (2.3)
2p-c	3.1 ± 0.1 (1.7)	3.1 ± 0.2 (2.8)	5.1 ± 0.1 (3.3)	4.5 ± 0.4 (3.3)

^{a)}Arithmetic mean of n experiments ($n \geq 2$); the precision corresponds to $\pm \sigma_{n-1}$, σ_{n-1} being the standard deviations on the means.

^{b)}Standard deviation σ_{n-1} on the mean of several experiments : 0.5–1.

cations (TMA^+). The fact that this ligand does not display any selectivity within the alkali metal series suggests that the benzazo groups present in the substituents might also be involved in the complexation of “soft” ions. Two types of complex stability constants were compared: stability constants of the complexes in the membrane ($\log \beta_{\text{LM}}^{\text{pot}}$) (Table 3) and stability constants of the 1:1 complexes formed in acetonitrile solution ($\log \beta$) (Table 4). These results were also compared to extraction data (%E) (Table 4).

For the *cone* conformer (**2c**), values of $\log \beta_{\text{LM}}^{\text{pot}}$ show a marked affinity towards Na^+ , which is confirmed by the data obtained in acetonitrile.

For the *partial cone* conformer (**2p-c**), the results obtained in the membrane show a similar affinity, within the experimental error, for all larger than sodium alkali cations tested ($\log \beta_{\text{LM}}^{\text{pot}} = 5.9\text{--}6.2$), whereas those in acetonitrile show a better affinity for Cs^+ and especially Rb^+ ($\log \beta = 4.5$ and 5.1 , respectively) than for Na^+ ($\log \beta = 3.1$).

Although very low, the extraction efficiency (%E) follows the same trends as the stability constants in acetonitrile.

In conclusion, the *p-tert-butylcalix[4]crowns-6* reported here display selectivities depending on the nature of the 1,3-substituents and on the conformation. Their behavior is different from that of the related 1,3-bis-

methoxy derivative which is highly selective for cesium ions [1].

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