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Lower Rim Substituted p-*tert*-Butyl Calix[4]arenes (V). Synthesis of New 5,11,17,22-tetrakis-p-*tert*-Butyl-25,27-bis(methoxy)-26,28-bis(dialkoxyphosphorylmethoxy)calix[4]arenes and Cation Complexation Studies in Ion-Selective Membrane Electrodes

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Abstract

The synthesis and characterization of the lower rim bis-phosphorylated tetrakis-p-*tert*-butyl-25,27-bis(methoxy)calix[4]-arenes (compounds **2–4**) is presented. The studied compounds were examined as ionophores in ion-selective membrane electrodes, showing selectivity for rubidium, potassium, and for the large and flat guanidinium cations (G^+). The correlation was studied between the stereochemical structure of the ligands and potentiometrically determined ion-selectivity. Complex formation constants in the PVC/BEHS (bis(ethyl)hexyl sebacate) membranes were determined. The crystal and molecular structures of compound **4** have been determined by single crystal X-ray diffraction study.

Introduction

Functionalized calixarenes are an important class of compounds that can complex cations, anions or neutral molecules [1]. *t*-Butyl-calix[4]arene can be treated as a building block for a versatile range of selective and useful complexing agents. They attracted our attention as preorganized for complexation of three-dimensional molecules of high lipophilicity, which is a requirement for good ionophores for ion-selective membrane electrodes (ISEs). The selectivity of the complexation depends on the presence of the certain size cavity, and also on the nature of the binding sites. It is possible to modulate the binding properties by introducing appropriate functional groups to the phenolic OH groups of calix[4]arenes (modification of the lower, narrow rim). It is already known that tetra-substituted-at-lower rim *t*-butylcalix[4]arenes possessing amide or ester groups show high selectivity for sodium cations [2]. However, bis-substituted-with-amide function calixarenes studied by us are not highly selective and show the following selectivity order: $G \geq Na \geq Li > K \geq NH_4$ [2]. Calix-crowns can complex selectively sodium, potassium or cesium cations depending on the size of the attached polyether macroring [3]. Only little attention has been paid so far to phosphoryl ester groups in the designing of synthetic calixarene ligands [4–9]. The P=O group plays an important role in nature, complexing not only metal ions but also organic molecules such as amino acids, for example arginine with guanidinium moiety [6]. While side arms containing $–CH_2PO(C_6H_5)_2$ introduced at the narrow rim of calix[4]arene have already been studied [9–12] there are only very few reports on the synthesis and properties of calixarenes containing $–CH_2PO(OR)_2$ functionality [4, 5].

The aim of our recent studies was to introduce the phosphonate site to the lower rim of *tert*-butyl calix[4]arene (synthesis of new compounds **2–4**) and to examine their complexing properties in ion-selective membrane electrodes (ISEs). Complexing properties of the compounds **2**, **3** and **4** as ionophores were investigated in the plasticized PVC-membrane electrodes. The complexation of alkali metal cations Li^+, Na^+ K^+, Rb^+ and Cs^+, alkali earth cations Mg^{2+}, Ca^{2+}, Sr^{2+}, some transition metal cations Ni^{2+}, Cu^{2+}, Zn^{2+}, and tetramethylammonium cation (TMA^+) was investigated. The possibility of hydrogen bond formation between $P{=}O\cdots HN$ was the reason for investigation of guanidinium chloride [13, 14] and ammonium chloride NH_4Cl as guest cations.

Experimental

General

The proton NMR spectra were recorded on Varian 200 MHz and 500 MHz spectrometers. The chemical shifts are reported in δ [ppm]. Mass spectra were obtained on a AMD-604

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Mass Spectrometer (EI technique or SIMS) and/or on a Bruker BIFLEX 3 Mass Spectrometer (MALDI TOF techniques). The NMR and mass spectra of the compounds confirmed their structure and purity. The organic reagents and solvents used were reagent grade.

Synthesis

Compounds **2–4** were synthesized as shown in Figure 1.

*Synthesis of 5,11,17,23-tetra-tert-butyl-25,27-bis (methoxy)-26,28-bis(ethoxyhydroxy-phosphoryl-methoxy) calix[4]arene (**2**) and 5,11,17,23-tetra-tert-butyl-25,27-bis (methoxy)-26,28-bis(diethoxyphosphoryl-methoxy)calix[4] arene (**3**)*

Solutions of 5, 11, 17, 23-tetrakis-*tert*-butyl-25, 27-bis(methoxy)calix[4]arene **1** (0.118 g, 0.174 mmol) and NaH (0.009 g, 0.38 mmol) in toluene (4 cm^3) were stirred at 80 °C for 3 h. Then $TsOCH_2P(O)(OEt)_2$ [15] (0.14 g, 0.43 mmol) in 3 cm^3 of toluene was added and the mixture was further maintained at 80 °C for 6 days. Excess of NaH was decomposed with MeOH (1 cm^3) and the solvent was evaporated *in vacuo*. The residue was taken up to CH_2Cl_2 (15 cm^3) and washed with 1M HCl (7 cm^3), then with water (2 × 7 cm^3) . The organic layer was dried with $MgSO_4$ and filtered. After evaporation of the solvent acetone was added and compound **2** was obtained as white solid. Yield 0.04 g, 25%. (R_f = 0.25, $CHCl_3$/MeOH, 20 : 1 v/v), m.p. 265–270°.

(**2**) $\mathbf{C_{52}H_{74}O_{10}P_2}$ 921.O6; MS (MALDI TOF) M/z 921 conformation *cone*, NMR: ^{1}H ($CDCl_3$). δ [ppm]: 7.05 and 6.55 (4H + 4H, 2br s, m-C_6H_2), 5.15(2 H, s, 2 POH), 4.40 and 3.20 [8H, AB system J(AB) 12Hz, $C_6H_2CH_2C_6H_2$], 4.35–4.10 (8 H, m, 2 CH_2P + 2 $POCH_2$), 4.00 (6 H, br s, 2 OCH_3), 1.45–1.20 (24 H, m, 2 $POCH_2CH_3$ + 2 $(CH_3)_3C$), 0.85 (18H, s, 2 $(CH_3)_3C$). ^{31}P ($CDCl)_3$). δ [ppm] 24.9.

The filtrate after separation of compound **2** was purified by flash chromatography using $CHCl_3$/MeOH 20 : 1 v/v as eluent. Compound **3** was obtained as white solid. Yield 0.034 g (20%), (R_f = 0.3, $CHCl_3$/MeOH 20 : 1 v/v), m.p. 145–150 °C.

(**3**) $\mathbf{C_{56}H_{82}O_{10}}$ $\mathbf{P_2}$ 977.15 conformation *cone*, MS (EI), M^+/z : 977; NMR: ^{1}H ($CDCl_3$) δ [ppm]: 7.15 and 6.42 (4H + 4H, 2br s, m-C_6H_2), 4.40 and 3.20 [8 H AB system, J(AB)12 Hz, $C_6H_2CH_2C_6H_2$], 4.30–4.05 (12 H, m, 2 CH_2P + 4 $POCH_2$), 4.00 (6 H, br s, 2 OCH_3), 1.50–1.20 (30H, m, 2 $C(CH_3)_3$ + 4 $POCH_2CH_3$), 0.75 (18 H, s, 2 $C(CH_3)_3$). ^{31}P ($CDCl)_3$). δ [ppm] 22.5.

*Synthesis of 5, 11, 17, 23-tetra-tert-butyl-25, 27-dimethoxy-26, 28-bis(diisopropoxyphosphoryl-methoxy)calix[4]arene (**4**)*

A solution of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(methoxy)calix[4]arene **1** (0.203 g, 0.3 mmol, and NaH (0.016 g, 0.66 mmol) in toluene (4 cm^3) were stirred at 80 °C for 3 h. Then $TsOCH_2P(O)(OiPr)_2$ [16] (0.234 g, 0.66 mmol) in 3 cm^3 of toluene was added and the mixture was further maintained at 80 °C for 7 days. Excess of NaH was decomposed with MeOH (2 cm^3) and the solvent was evaporated *in vacuo*. The residue was taken up in CH_2Cl_2 (30 cm^2) and washed with 1M HCl (10 cm^3), then with water (2 × 10 cm^3). The organic layer was dried with $MgSO_4$ and filtered. After evaporation of the solvent the solid residue was recrystallised from methanol. Yield of product (**4**): 0.174 g, 56%. (R_f = 0.25, $CHCl_3$/MeOH, 20 : 1 v/v), m.p. 225–228 °C.

(**4**): $\mathbf{C_{60}H_{90}O_{10}P_2}$ 1033.27, conformation *cone*, MS (SIMS technic) M/z 1056 (M^+ + Na). NMR: ^{1}H ($CDCl_3$). δ [ppm]: 7.15 and 6.42 (4H + 4H, 2br s, m-C_6H_2), 4.40 and 3.15 [8H, AB system J(AB) = 12Hz, $C_6h_2CH_2C_6h_2$], 4.00–4.15 (10H, m, 2 CH_2P + 2 OCH_3), 4.70-4.90 (4 H, m, 4 POC*H*), 1.25–1.50 (42 H, m, 2 $POCH(CH_3)_2$ + 2 $(CH_3)_3C$), 0.85 (18H, s, 2 $(CH_3)_3C$). ^{31}P ($CDCl_3$). δ [ppm] 20.5.

Collection of X-ray diffraction data, solution and refinement of the structure of **4**

Crystals suitable for diffraction study were obtained by recrystallization of compound **4** from methanol. The crystallographic data and details of data collection and refinement have been listed in Table 1. Structure of **4** was solved by direct methods with SHELXS97 [17], and refined using SHELXL97 [18] programs. Hydrogen atoms were calculated on stereochemical grounds and refined using the SHELX97 riding model. A significant static disorder of one isopropyl and one tert-butyl groups has been observed but refinement with anisotropic temperature factors converged successfully by using geometrical restraints.

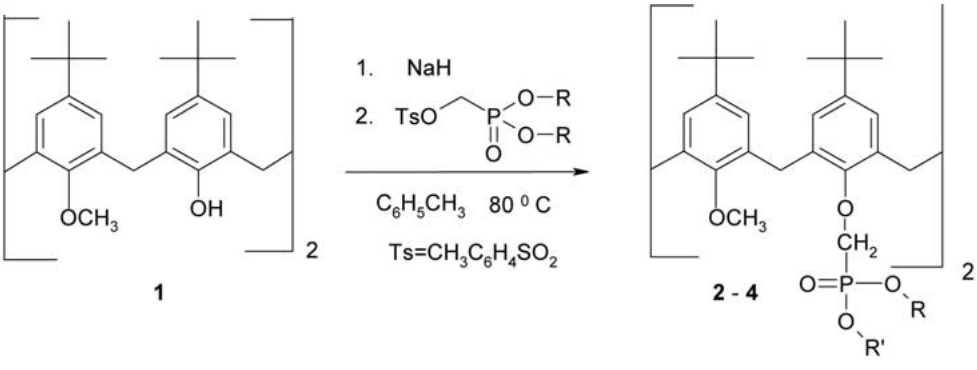
Membrane preparation and EMF measurements

General: Poly(vinyl chloride) (PVC, high molecular), and bis(2-ethylhexyl)sebacate (DOS or BEHS [19]) and potassium tetrakis(4-chlorophenyl)borate (KTClPB) were from Fluka. Tetrahydrofuran (THF) from POCh, was dried and freshly distilled before use. All aqueous solutions were prepared with redistilled water (conductivity < 1.8 μS/cm). The salts LiCl, NaCl, KCl, NH_4Cl, $MgCl_2$, $SrCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ (POCh) and $CaCl_2$, tetramethylammonium chloride (TMA^+ Cl^-), guanidinium chloride (G^+ Cl^-) (Fluka), RbCl and CsCl (Ubichem Ltd), were of p.a. grade.

The preparation of membrane for ion-selective electrodes was described earlier in [2]. The membrane composition: 4 mg of ionophore, 60 mg of poly(vinyl chloride) PVC, 120 mg of plasticizer (BEHS) and 0.5 mg of potassium tetrakis(p-chlorophenyl)borate (KTpClPB), about 190 mg in total, were dissolved in 1.5 mL of freshly distilled THF and the solution was poured into a glass ring. The membranes were incorporated into Ag/AgCl electrode bodies of IS 561 type (Fluka). A double-junction reference Radelkis 0P0820P electrode was used with 1M $CH_3COO^-Li^+$ solution in a bridge cell. The potentials were measured at 20 °C using multimeter METROHM 654 and the cells of the type:

$$\text{Ag} \mid \text{AgCl} \mid 1\text{M KCl} \mid 1\text{M } CH_3COOLi \mid \text{sample} \mid$$

$$\text{membrane} \parallel 0.01\text{M KCl} \mid \text{AgCl} \mid \text{Ag}$$



2, R = C_2H_5 R' = H
3, R = R' = C_2H_5
4, R = R' = i-C_3H_7

Figure 1. Synthesis of ionophores **2–4**.

Table 1. Crystal data and structure refinement for **4**

Identification code	**4**
Empirical formula	$C_{60}H_{90}O_{10}P_2$
Formula weight	1033.26
Temperature	293(2) K
Wavelength Cu K_α	1.54178 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	$a = 40.206(8)$ Å $b = 12.657(3)$ Å, $\beta = 129.03°$, $c = 31.810(6)$ Å
Volume	12575(5) Å^3
Z	8
Calculated density	1.092 Mg/m^3
Absorption coefficient	1.034 mm^{-1}
F(000)	4480
Crystal size	0.5 × 0.6 × 0.6 mm
θ range for data collection	2.83 to 72.08°
Limiting indices	$0 \leqq h \leqq 49, -15 \leqq k \leqq 0, -24 \leqq 1 \leqq 30$
Reflections collected/unique	6329/6329 [R(int) = 0.0000]
Completeness to $\theta = 72.08$	51.1%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6329/62/696
Goodness-of-fit on F^2	1.034
Final R indices $I > \sigma$ (I)]	$R_1 = 0.0567$, $WR_2 = 0.1583$
R indices (all data)	$R_1 = 0.0805$, $wR_2 = 0.1775$
Extinction coefficient	0.00098(6)
Largest diff. Peak and hole	0.271 and −0.212 e Å^{-3}

Table 2. The characteristics of the studied electrodes **1–4**

Electrode Ionophore/plasticizer	Ion A	S (mV)	Linear range ($-\log a_A$)
1	K^+	49(0.5)	−4.0–−1.3
2/BEHS	Rb^+	50(0.3)	−4.8–−1.3
	TMA^+	53(0.5)	−4.8–−1.3
2	K^+	53(0.3)	−5.0–−1.3
3/BEHS	RB^+	58(0.1)	−5.0–−1.3
	TMA^+	50(0.4)	−4.1–−1.3
3	K^+	52(0.5)	−4.8–−1.3
4/BEHS	Rb^+	56(0.3)	−4.8–−1.3
	TMA^+	38(1.0)	−4.1–−1.3
4	K^+	48(0.6)	−4.5–−1.3
-/BEHS	Rb^+	52(0.5)	−4.0–−1.3
	TMA^+	55(0.4)	−4.0–−1.3

Measured salt solutions were prepared by successive dilution of initial 5×10^{-2} mol/dm^3 stock solution. The sample was diluted until further dilution resulted in no potential change.

Selectivity coefficients and electrode characteristics

The selectivity coefficients ($\log K^{pot}_{Rb,M}$) were determined by the separate solution method (SSM) [19, 20] and were calculated using the equation:

$$\log K^{\text{pot}}_{\text{Rb,M}} = \frac{(E_{\text{M}} - E_{\text{Rb}}) \cdot z_{\text{Rb}} \cdot F}{2.303\text{RT}} + \left(1 - \frac{z_{\text{Rb}}}{z_{\text{M}}}\right) \log a_{\text{Rb}}$$

The calculated selectivity coefficients for the membrane electrodes **1–3** containing ionophores **2–4** and for the *blank* membrane electrode **4** (IE) are presented in Table 3. The characteristics of the studied electrodes are shown in Table 2.

Determination of complex formation constants

We estimated the values of the complex formation constants β_{LM} for bis-substituted compounds, phosphonates **3** and **4** using the procedure proposed by Ceresa, Pretsch and Bakker [23] in PVC/BEHS membranes. Tetramethylammonium cation (TMA^+) was used as a reference ion [2, 3, 23]. The values obtained for the complex formation constants are presented in Table 4.

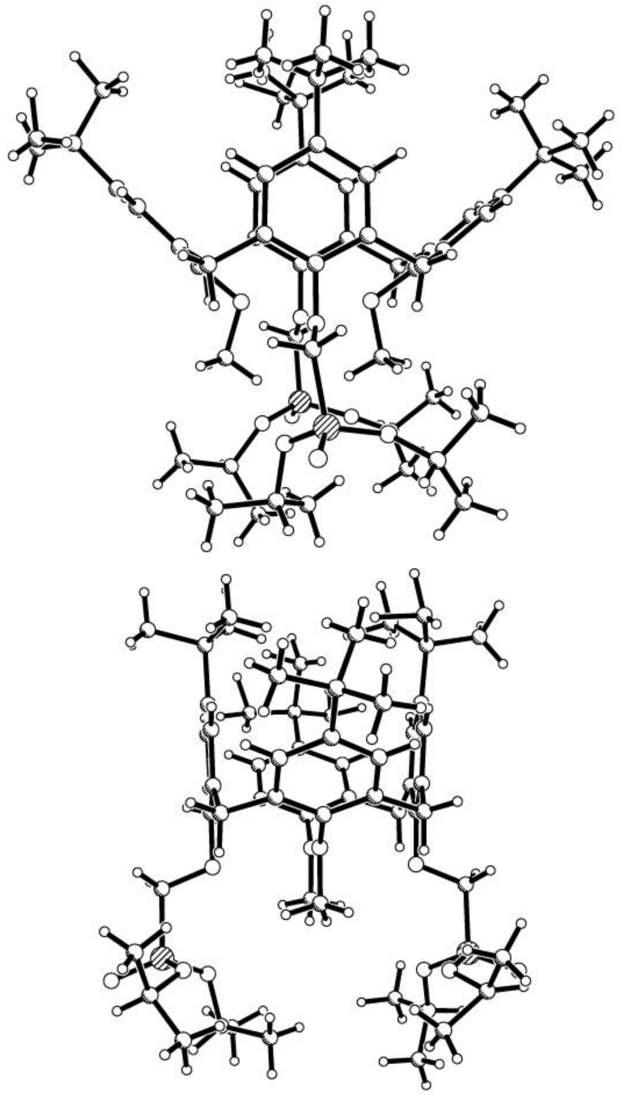


Figure 2. View of **4** in two perpendicular projections showing the pinched *cone* conformation and different orientation of phosphonato groups.

Table 3. The selectivity coefficients for the membrane electrodes **1–4**

Ion M	$\log K^{\mathrm{pot}}_{\mathrm{Rb/M}}$ 1 (**2**)	2 (**3**)	3 (**4**)	4 (blank)
G^+	+0.4	−0.58	−0.15	+2.45
TMA	+0.1	−1.74	−1.45	+1.85
H^+	−0.25	−1.17	−0.53	0.1
Li	−1.1	−2.1	−2.0	−0.9
Na	−0.56	−1.5	−1.06	−0.41
K	−0.31	−0.08	0.1	−0.06
Rb	0	0	0	0
Cs	−0.06	−0.52	−0.4	+0.39
NH_4	−0.34	−0.34	0.07	–
Mg	−3.0	−3.08	−2.8	−2.35
Ca	−3.05	−3.5	−3.4	−2.62
Sr	−2.62	−1.37	−2.2	−2.25
Cu	−2.25	−2.96	−2.62	−2.8
Ni	−2.56	−1.63	−2.44	−1.4
Zn	−2.9	−3.1	−2.6	−1.36
Cd	−2.75	−3.28	−3.15	−1.29
Pb	−1.0	−2.47	−2.03	−1.0
Ag	+0.87	+0.94	+1.0	+0.85
Hg	+0.25	+0.05	−0.02	−0.38

Table 4. The values of complex formation constants for ionophores **3-4**

Ligand	$\log \beta_{\mathrm{LK}}$	$\log \beta_{\mathrm{LRb}}$
3	4.90	5.15
4	4.94	4.80

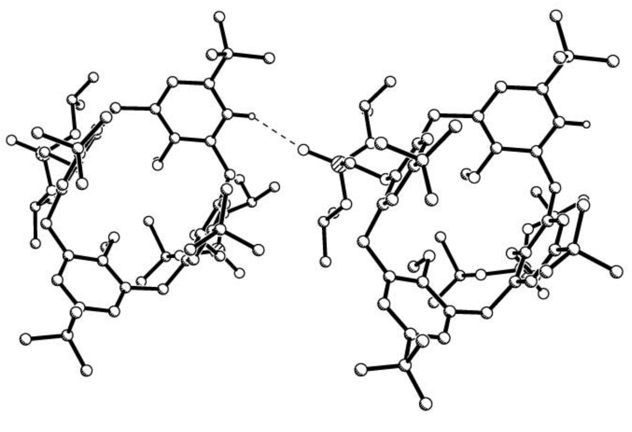


Figure 3. View of **4** showing the (P=O···H—C) hydrogen bond.

Results and discussion

Synthesis

The general method for the synthesis of the lower rim substituted calix[4]arenes is based on alkylation of phenolic groups with appropriate alkylating regents. Compounds **2**, **3** and **4** were prepared by alkylation of bis(methoxy)-p-*tert*-butylcalix[4]arene with diethyl or diisopropyl p-toluensulphonyloxymethylphosphonate in the presence of sodium hydride in toluene at 80 °C. In the synthesis of compound **3**, compound **2** was also isolated. Despite the fact that anhydrous conditions were maintained during the synthesis partial hydrolysis of phosphonate diethyl ester took place. In order to avoid or to limit the hydrolysis of phosphonate diesters, more resistant towards hydrolysis diisopropyl-p-toluenesulphonyloxymethylphosphonate was used as alkylating agent and only compound **4** was isolated. The compound in solid state exists in distorted *cone* conformation, which was found in the X-ray crystal structure of **4** and this conformation is also stable in solution, which was proved by NMR spectra.

Table 5. Selected bond lengths and angles for **4**

a. Bond lengths (Å)		b. Bond angles (°)	
P(1)—O(5)	1.456(2)	O(5)—P(1)—O(6)	114.88(18)
P(1)—O(6)	1.563(5)	O(5)—P(1)—O(7)	117.05(18)
P(1)—O(7)	1.567(3)	O(6)—P(1)—O(7)	103.9(2)
P(1)—C(29)	1.800(3)	O(5)—P(1)—C(29)	110.98(18)
P(2)—O(8)	1.451(3)	O(6)—P(1)—C(29)	107.58(19)
P(2)—O(9)	1.547(4)	O(7)—P(1)—C(29)	101.17(15)
P(2)—O(10)	1.552(5)	O(8)—P(2)—O(9)	115.94(19)
P(2)—C(45)	1.786(3)	O(8)—P(2)—O(10)	115.2(3)
O(1)—C(1)	1.409(3)	O(9)—P(2)—O(10)	102.8(2)
O(1)—C(29)	1.424(3)	O(8)—P(2)—C(45)	110.71(15)
O(2)—C(7)	1.376(4)	O(9)—P(2)—C(45)	104.9(2)
O(2)—C(40)	1.426(4)	O(10)—P(2)—C(45)	106.3(2)
O(3)—C(13)	1.401(3)	C(1)—O(1)—C(29)	111.4(2)
O(3)—C(45)	1.417(3)	C(7)—O(2)—C(40)	114.8(4)
O(4)—C(19)	1.376(7)	C(13)—O(3)—C(45)	111.63(18)
O(4)—C(56)	1.433(4)	C(19)—O(4)—C(56)	114.1(4)
O(6)—C(30)	1.428(6)	C(30)—O(6)—P(1)	121.9(3)
O(7)—C(33)	1.444(5)	C(33)—O(7)—P(1)	123.2(3)
O(9)—C(46)	1.440(4)	C(46)—O(9)—P(2)	123.3(3)
O(10)—C(49)	1.440(3)	C(49)—O(10)—P(2)	121.0(4)

Complexing properties of the compounds

The properties of the compounds **2**, **3** and **4** were studied by using them in ion-selective membrane electrodes (ISE). The electrodes were stable and long lasting due to the high lipophilicity of the *tert*-butylcalix[4]arene ligands. They show near Nernstian characteristics for rubidium and potassium cations (Table 2). The selectivity coefficients for the electrodes with studied ionophores **2–4** for the membrane with bis(2-ethylhexyl)sebacate (BEHS) as plasticiser are presented in Table 3. The electrodes are most selective for rubidium ions. Complexing ability order of ligands **3–4** towards alkali metal cations was: $Rb^+ \geq K^+ \geq Cs^+ > Na^+ > Li^+$, and towards alkali earth cations: $Rb^+ \gg Sr^{2+} > Mg^{2+} > Ca^{2+}$; some transition metal cations: Ni^{++}, Cu^{++}, and tetramethylammonium cation (TMA^+) were also tested but complexation was rather negligible. The possibility of hydrogen bond formation between P=O$\cdots$HN was the reason for investigation of the large and flat guanidinium cation (G^+) [13, 14] and ammonium cation (NH_4^+). Compound **2** possessing two —CH$_2$PO(OH)(OEt) groups more strongly bind TMA^+ and guanidynium cations than phosphonates **3** and **4** with —CH$_2$PO(OR)$_2$groups. Presented values of selectivity coefficients give the idea about the complexing ability of the studied bis-phophorylated calixarenes. Very similar extraction orders of alkali picrates were observed for tetra(phosphineoxide) calixarenes: $K^+ \geq Rb^+ > Li^+ > Cs^+ > Na^+$ [10]. This suggest that P=O fragment plays most important role in the ligating properties of phosphonates. We did not found very strong interaction with guanidinium ion nor with NH_4^+, the complexation of these cations was similare: $G^+ \geq Rb \geq K^+ \geq NH_4^+$. The synthesized compounds are not highly and particularly selective, but they show preference for alkali cations such as potassium and rubidium. The kind and number of coordination centers and geometry of the ligating groups in molecule determines the binding properties and selectivity of complexation.

The value of ion-ligand complex stability constant, β_{LM}, in the membrane is useful parameter for judging the ligand interaction with different ions and for making optimalization of the membrane composition.

$$nL_{(m)} + M^{z+}_{(\mathrm{aq})} \leftrightarrows L_n M^{z+}_{(m)}$$

$$\beta = \frac{[L_n M^{z+}]}{[L]^n [M^{z+}]}.$$

The values of complex formation constants could only be determined for ionophores **3** and **4**, because only these compounds do not complex the TMA^+ cation which was used as a referee in the procedure [2, 3, 23]. The calculated values of complex formation constants for ligands **3** and **4** with K and Rb ions ($\beta_{\mathrm{LK}}, \beta_{\mathrm{LRb}}$), are presented in Table 4. When comparing these values with the values obtained for other good ionophores, for example calixarenes with amide moiety complexing preferably sodium ions they are about two orders of magnitute lower [2]. The conclusion can be made that the —CH$_2$PO(OR)$_2$ group is a softer base than CH$_2$CONR$_2$ studied by us earlier [2], but also that the P=O coordination centers are not forming a cavity of certain size. We will compare these results with the properties of our new tetrasubstituted calix[4]arene compound, possessing similar ligating functions [24]. It is hoped that in the tetra-substituted calixarene four P=O groups will form a cavity suitable for complexing cation.

X-ray structure of compound **4**

Compound **4** in crystal structure adopts a pinched *cone* conformation. Its geometry can be related to the mean plane through the CH_2 bridges which link the aromatic rings, where the carbon atoms show out-of-plane distances less than 0.01 Å. The calix conformation is defined by the dihedral angles that the aromatic rings make with this mean reference plane, which are: 91.09(8)° (A), 139.79(13)° (B), 93.25(9)° (C), 136.75(13)° (D). Two opposite aromatic rings bearing phosphonate groups are nearly parallel (with angle between mean planes of these rings of 4.6(2)°), the other two aromatic rings bearing methoxy groups are nearly perpendicular (angle 83.4(2)° (Figure 2). The angles between neighbouring aromatic rings vary between 86.5° to 89.2° indicating slightly distorted C_{2v} symmetry of the *cone* conformation. Molecules along two-fold axis form chains joined by C—H···O type hydrogen bonds (with C(ar)H···O(=P) distance of 3.399(5) Å and angle at H atom of 148°) (Figure 3). Diisopropoxyphosphoryl groups show slightly different orientation with regard to its carriers (Figure 2, Table 5).

Supplementary material available

Crystallographic data (excluding structure factors) for the structure **4** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-200328. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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