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Lower Rim Substituted *tert*-Butylcalix[4]arenes (I). The Structure and Complexing Properties in Ion-Selective PVC Membrane Electrodes *

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Abstract

Some di- and tetraamide *tert*-butylcalix[4]arenes were synthesized and described. Their ionophoric properties were studied in liquid membrane ion-selective electrodes. The correlation between the chemical structure (conformation in solution determined by ^{1}H NMR) and potentiometric ion-selectivity and complex formation constant have been studied. The PVC membrane electrodes based on tetraamides **8–11** show high sodium selectivity, are stable and long lasting. Disubstituted amides **1–7** are selective for larger and more lipophilic ions, as for example guanidinium ion. The crystal structure of the diamide **4** was determined by single crystal X-ray analysis. Crystals of **4** are triclinic, space group P-1, with: a = 16,669(8), b = 17.795(10), c = 20.984(8) Å, α = 91.08(4)°, β = 91.60(3)°, γ = 90.73(4)° and Z = 4. Ionophore **4** posseses a distorted *cone* conformation and is substituted at the *proximal* phenol rings.

Introduction

Tert-butyl calix[4]arenes attracted our attention as prospective ionophores for ion-selective electrodes. They possess rather rigid and lipophilic macrocyclic structures in which four hydroxyl groups are arranged around the central cavity and can be modified by introducing different electron donating substituents, for example ester or amide groups [1, 2]. Functionalized calixarenes represent an important class of compounds that can complex both cations and neutral molecules [3].

Unsubstituted *tert*-butylcalix[4]arenes adopt favorably a *cone* conformation as a result of stabilization by intramolecular hydrogen bond formation between OH groups [4]. In lower rim substituted calix[4]arenes, in the absence of hydrogen bonds, the *cone* conformation is not always stabilized and theoretically all four conformers can be formed: *cone, partial cone, 1,2- and 1,3-alternate*. The ratio of these conformers depends not only on the substituents but also on the reaction condition and on the polarity of the solvent used in the synthesis [4].

We synthesized several tetra- and disubstituted *tert*-butyl calix[4]arenes, all being the tertiary amides shown in Scheme 1. Using the same reaction condition, only with morpholide, piperidide, *N*, *N*-dibutyl and *N*, *N*-methylheptyl amide were tetra substituted products (**8–11**) obtained, however we managed to isolate the respective diamides **4**, **6** and **7** from the reaction mixture. Amides **1**, **2** and **3** were obtained as di-substituted calix[4]arenes. The tetrakis-substituted analogs of **1** and **2** are known and were obtained by different synthetic routes [1, 4]. Compounds **1–5** and **7** were obtained in the *cone* conformation in which both amide groups are in proximal positions. Their conformation was determined on the basis of ^{1}H NMR spectra. Compound **6** was substituted on the A and C phenol rings.

Experimental

The synthesis of the compounds

Compounds **1–11** were synthesized by the following reaction scheme:

The chloroamides were prepared as described earlier [5]. The proton NMR spectra were recorded on Varian 200 MHz and 500 MHz spectrometers. The chemical shifts are reported in δ [ppm] using TMS as internal standard. Infrared (IR) spectra were recorded on a Specord 480 (Carl-Zeiss-Jena). Mass spectra were obtained on a AMD-604 Mass Spectrometer (EI and LSIMS(+) techniques: 70 eV, 8 kV, 5 kHz). The NMR and mass spectra of the compounds confirmed their structure and purity. The organic reagents and solvents used were reagent grade.

*General procedure for preparation of the bis-(**1–7**) and tetrakissubstituted calix[4]arenes (**8–11**)*

1 mmole (0.649 g) of *p-tert*-butylcalix[4]arene was dissolved in 30 mL of the mixture (5 : 1) of dried tetrahy-

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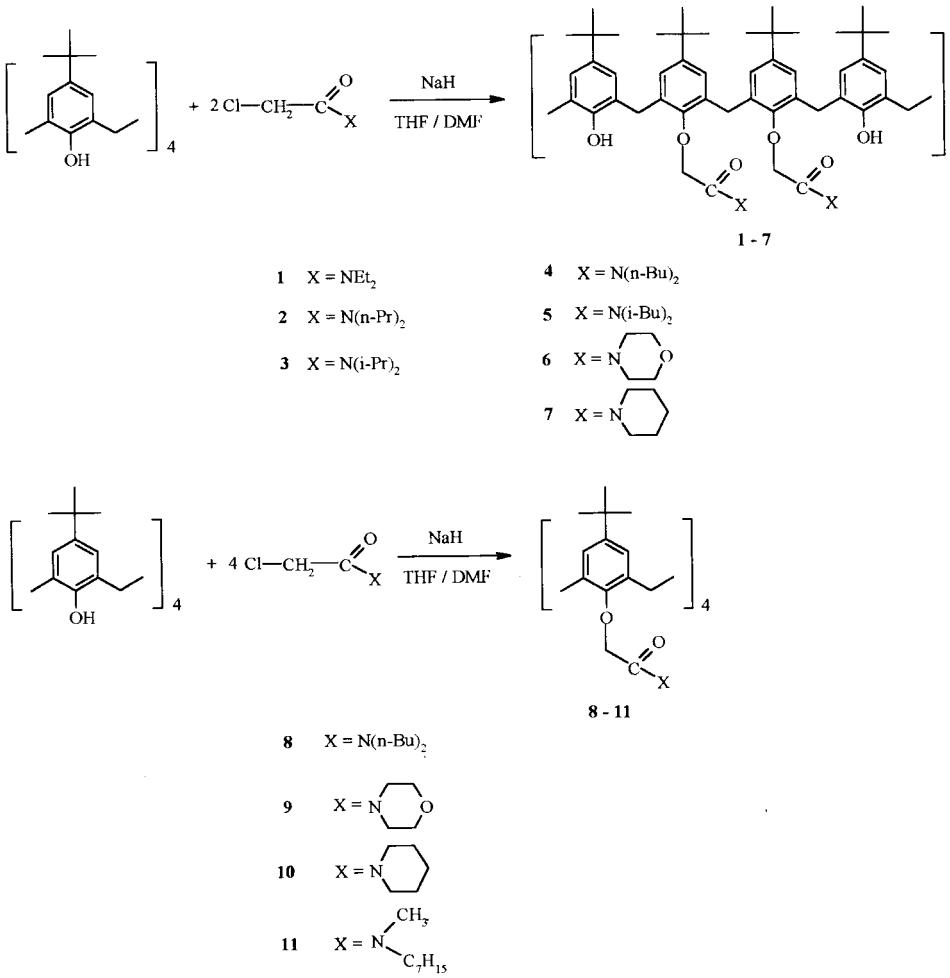

Scheme 1. The synthesis of calix[4]arenes **1–11**.

drofuran (THF) and dimethylformamide (DMF) during 30 minutes of stirring and heating to about 50 °C. After that time 10 mmoles of sodium hydride (55% in oil) were added and the mixture refluxed for about 1 h. This was followed by the addition of the appropriate α-chloroacetamides in two-fold excess (8 mmoles). The mixture was stirred for another 15 hours at 60 °C. Then the solution was evaporated to dryness and the mixture was treated with 10 mL of water, acidified with 1M HCl and the product was extracted with methylene chloride. The combined organic layers were washed with water and dried with $MgSO_4$. After solvent evaporation the oily product was treated with ethyl ether in order to crystallize. The obtained products **1–11** were white solids and were purified by further crystallization from a methanol/methylene chloride mixture. The sodium complexes of amides **10** and **11** were obtained by the procedure already described for the free ionophores but the crude organic solution of the ionophore was washed with water only.

The yields of the reaction, melting points and other properties of the compounds obtained are presented below:

5,11,17,23-tetra-*tert*-butyl-25,26-bis(di-ethylcarbamoylmethoxy)-27,28-dihydroxycalix[4] arene (compound **1**): $C_{56}H_{78}O_6N_2$, M.W. 875.24, M^+ 874, yield 79%, m.p. 252–256 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 1.01 (s, 18H, *t-but*); 1.17 (s, 18H, *t-but*), 1.22 (t, 12H, CH_2CH_3), 3.25 (d, J = 12.5Hz, 4H, ArCH_2, Ar), 3.31–3.55 (m, 8H,NCH_2), 4.32 (d, J = 12.5Hz, 1H, ArCH_2Ar), 4.67 (d, J = 12.5Hz, 2H, ArCH_2, Ar), 4.94 (d, J = 12.5Hz, 1H, ArCH_2, Ar), 4.68 (d, 2H, OCH_2), 5.28 (d, J = 14.6Hz, 2H, OCH_2), 6.8 (s, 4H Ar), 6.9 (m, 4H, $H_{arom.}$), 9.48 (s, 2H, OH).

5,11,17,23-tetra-*tert*-butyl-25,26-bis(di-*n*-propylcarbamoylmethoxy)-27,28-dihydroxycalix[4]arene (compound **2**): $C_{60}H_{86}O_6N_2$, M.W. 931.35, M^+ 931, yield 71%, m.p. 219-222 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 0.83–0.98 (m, 12H, CH_3), 1.01 (s, 18H, *t-but*); 1.17 (s, 18H, *t-but*), 1.52–1.72 (m, 8H, CH_2), 3.20–3.37 (m, 4H, ArCH_2, Ar & *12*H, NCH_2), 4.34 (d, 1H, ArCH_2, Ar), 4.68 (d, 2H, ArCH_2, Ar), 4.95 (d, 1H, ArCH_2, Ar), 4.70 (d, 2H, OCH_2), 5.28 (d, 2H, OCH_2), 6.72–6.95 (m, 8H, $H_{arom.}$), 9.5 (brs, 2H, OH).

5,11,17,23-tetra-*tert*-butyl-25,26-bis(di-*i*-propylcarbamoylmethoxy)-27,28-dihydroxycalix[4]arene (compound **3**): $C_{60}H_{86}O_6N_2$, M.W. 931.35, M^+ 930, yield 80%, m.p. 246-250 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 1.01 (s, 18H, *t-but*); 1.17 (s, 18H, *t-but*), 1.46 (m, 12H, CH_3), 3.23 (d, 4H, CH_2, H_{eq}) *3.45–3.62* (*m, 2*H, *NCH*), 3.90–4.07 *(m,2*H,*NCH)*, 4.44 (d,1H, ArCH_2, Ar), 4.60 (d,2H, ArCH_2, Ar), 4.84 (d, 1H, ArCH_2, Ar), 4.71 (d, 2H, OCH_2), 5.27 (d, 2H, OCH_2), 6.73–6.92 (m, 8H, $H_{arom.}$), 9.45 (brs, 2H, OH).

5,11,17,23-tetra-*tert*-butyl-25,26-bis(di-*n*-butylcarbamoylmethoxy)-27,28-dihydroxycalix[4]arene (compound **4**): $C_{64}H_{94}O_6N_2$, M.W. 987.46, M^+ 987, yield 59%, m.p. 178-180 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 0.83–0.98 (m, 12H, *CH*$_3$), 1.01 (s, 18H, *t-but*); 1.17 (s, 18H, *t-but*), 1.22–1.42 (m, 8H, *CH*$_2$CH$_3$), 1.48–1.64 (m, 8H, NCH$_2$*CH*$_2$), 3.20–3.42 (m, 12H, N*CH*$_2$, & Ar*CH*$_2$Ar), 4.34 (d, 1H, Ar*CH*$_2$, Ar), 4.66 (d, 2H, Ar*CH*$_2$, Ar), 4.95 (d, 1H, Ar*CH*$_2$, Ar), 4.69 (d, 2H, *OCH*$_2$), 5.28 (d, 2H, *OCH*$_2$), 6.74–6.93 (m, 8H, Ar), 9.35 (s, 2H, OH).

5,11,17,23-tetra-*tert*-butyl-25,26-bis(di(2-metylpropyl)-carbamoylmethoxy)-27,28-dihydroxycalix[4]arene (compound **5**): $C_{64}H_{94}O_6N_2$, M.W. 987.46, M^+ 987, yield 69%, m.p. 188–189 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 0.93 (m, 24H, *CH*$_3$), 1.01 (s, 18H, *t-but*); 1.17 (s, 18H, *t-but*), 1.85–2.15 (m, 4H, CH$_2$ ***CH***(CH$_3$)$_2$), 3.2 (d, J = 13.5Hz, 4H, Ar*CH*$_2$, Ar), 3.25 (m, 8H, N*CH*$_2$), 4.34 (d, J = 13.5Hz, 1H, Ar*CH*$_2$, Ar), 4.67 (d, J = 13.5, 2H, Ar*CH*$_2$, Ar), 4.96 (d, J = 13.5, 1H, Ar*CH*$_2$, Ar), 4.72 (d, 2H, *OCH*$_2$), 5.28 (d, 2H, *OCH*$_2$), 6.75 and 6.98 (m, 8H, Ar), 9.38 (s, 2H, OH).

5,11,17,23-tetra-*tert*-butyl-25,27-bis(morpholinecarbamoylmethoxy)26,28-dihydroxycalix[4]arene (compound **6**): $C_{56}H_{74}O_8N_2$, M.W. 902.3, M^+ = 902, yield 32%, m.p. 286-288 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 0.96 (s, 18H, *t-but*), 1.26 (s, 18H, *t-but*), 3.32 (d, J = 13.2Hz, 4H, Ar*CH*$_2$,*H*$_{eq}$), 3.76 (m, 16H,.N*CH*$_2$*CH*$_2$0), 4.34 (d, J = 13.2Hz, 4H Ar*CH*$_2$, H$_{ax}$), 4.75 (s, 4H, 0CH$_2$CO), 6.8 (s, 4H, H$_{arom.}$), 7.02 (s, 4H, H$_{arom}$), 7.18 (br, s, 2H, OH). It has been isolated from mother liquier after cristallization of compound **9**.

5,11,17,23-tetra-*tert*-butyl-25,26-bis(piperididecarbamoylmethoxy)27,28-dihydroxycalix[4]arene (compound **7**): $C_{58}H_{78}O_6N_2$, M.W. 898.6, M^+, yield 27%, m.p. 197–204 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 1.05 (s, 18H, *t-but*), 1.2 (s, 18H, *t-but*), 1.65 (m, 12H, (CH$_2$)$_3$), 3.25 (d, J = 12.5, 4H, Ar*CH*$_2$, Ar), 3.55 (m, 8H, N*CH*$_2$), 4.38(d, J = 12.5, 1H), 4.68(d, J = 12.5, 2H, Ar*CH*$_2$Ar), 4.82(d, J = 12.5, 1H), 5.3 (d, 2H, O*CH*$_2$CO), 6.82 (s, 4H, H$_{arom.}$), 6.9 (s, 4H$_{arom}$), 9.45 (s, 2H, OH).

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(di-*n*-butylcarbamoyl methoxy)calix[4]arene (compound **8a** – Na complex): $C_{84}H_{132}O_8N_4$,, M.W. 1324.46, M^+ 1324, yield 38%, m.p. 248–252°C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 0.96 (m, 24H, *CH*$_3$), 1.15 (s, 36H, *t-but*); 1.33 (m, 168H,*CH*$_2$CH$_3$), 1.5–1.72 (m, 16H, NCH$_2$*CH*$_2$), 3.25 (t, 8H, N*CH*$_2$), 3.45 (t, 8H, N*CH*$_2$), 3.56 (d, J = 12.5Hz, 4H, *CH*$_2$*H*$_{eq}$), 4.3 (d, J = 12.5Hz, *CH*$_2$, 4H$_{ax}$), 4.98 (s, 8H, *OCH*$_2$CO), 7.14 (s, 8H, H$_{arom.}$).

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(morpholinecarbamoylmethoxy)calix[4]arene (compound **9** *cone*): $C_{68}H_{92}O_{12}N_4$, M.W. 1157.50, M^+ 1156, yield 57%, m.p. 302-305 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 1.09(s, 36H,*t-but*); 3.21 (d, 4H, Ar*CH*$_2$, *H*$_{eq}$, J = 13Hz), 3.45–3.65 (m, 32H, H$_{morph}$), 4.98 (d, J = 13Hz, 4H, Ar*CH*$_2$, H$_{ax}$), 5.01 (s, 8H, O*CH*$_2$), 6.8 (s, 8H, H$_{arom.}$).

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(morpholinecarbamoylmethoxy)calix[4]arene (compound **9**: *1,3-alternate*): $C_{68}H_{92}O_{12}N_4$, M.W. 1157.50, M^+ 1156, yield 28%, m.p. 265–272 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 1.08 (s, 18H, *t-but*); 1.22 (s, 18H, *t-but*), 3.21 (d, 4H, *CH*$_2$, H$_{eq}$), 3.45–3.75 (m, 32H, H$_{morph}$), 4.98 (d, 4H, *CH*$_2$, H$_{ax}$, J = 12.74Hz), 5.06 (s, 8H, O*CH*$_2$), .7.06 (s, 4H, H$_{arom.}$), 7.25 (s, 4H, H$_{arom.}$).

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(piperididecarbamoylmethoxy)calix[4]arene (compound **10** *cone*): $C_{72}H_{100}O_8N_4$, M.W. 1149.61, M^+ 1149, yield 27%, m.p. 267–270 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 1.09 (s, 36H, *t-but*), 1.45 (m, 24H, (CH$_2$)$_3$), 3.2 (d, 4H, Ar*CH*$_2$,*H*$_{eq}$), 3.38–3.58 (m, 16H, N*CH*$_2$), 5.0 (s, 8H, O*CH*$_2$CO), 5.1 (d, 4H, Ar*CH*$_2$, H$_{ax,}$, J = 12.8Hz), 6.79 (s, 8H, H$_{arom.}$).

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(piperididecarbamoyl methoxy)calix[4]arene (compound **10a** – Na complex): $C_{72}H_{100}O_8N_4$—Na, yield 82%, m.p. 245–250 °C, $IR_{C=O}$ 1648 cm^{-1}, ^1H NMR δ[ppm]: 1.15 (s, 36H, *t-but*), 1.67 (br, s, 24H, (CH$_2$)$_3$), 3.22 (br, s, 8H.N*CH*$_2$) 3.32 (d, J = 12.5Hz, 4H, Ar*CH*$_2$, H$_{eq}$), 3.62 (br, s, 8H.N*CH*$_2$), 4.48 (d, 4H, Ar*CH*$_2$, H$_{ax}$, J = 12.5Hz), 4.6 (s, 8H, O*CH*$_2$CO), 7.12 (s, 8H, H$_{arom.}$).

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(methylheptylcarbamoylmethoxy)[4]arene (compound **11a** – Na complex): $C_{84}H_{132}O_8N_4$, M.W. 1324, M^+ 1325.2, yield 46%, m.p. 102-106 °C, $IR_{C=O}$ 1652 cm^{-1}, ^1H NMR δ[ppm]: 0.88 (m, 12H, CH$_3$) 1.09 (s, 36H, *t-but*), 1.3 (m, 32H, (CH$_2$)$_4$), 1.6 (m, 8H, CH$_2$), 2.88 (s, 3H, N-CH$_3$), 2.96 (s, 3H, N-*CH*$_3$), 3.07 (m, 4H, N-*CH*$_2$), 3.33 (d, J = 13.5, 4H, Ar*CH*$_2$,*H*$_{eq}$), 3.34 (m, 4H, N-CH$_2$), 4.42 (d, J = 13.5, 4H, Ar*CH*$_2$, *H*$_{ax}$), 4.5 (s, 8H, O*CH*$_2$CO), 7.1 (s, 8H, H$_{arom.}$).

Synthesis of Na$^+$-complex of calix[4]arene **9**

Complex **9-NaI** *cone*: $C_{68}H_{92}O_{12}N_4$-NaI.

Compound **9** (100 mg) and sodium iodide (30 mg) were dissolved in methanol (with a small amount of methylene chloride) under reflux. After evaporation of the CH_2Cl_2 and after several days of storage at room temperature, single crystals appeared; m.p. 273-277 °C. They were stable but not suitable for X-ray analysis.

^1H NMR δ[ppm]: 1.13 (s, 36H, *t--but*), 3.35 (m, 4H, Ar*CH*$_2$Ar & 8H,N-CH$_2$), 3.65 (m, 8H NCH$_2$), 3.75(m, 24H, O-*CH*$_2$), 4.5 (d, J = 12, 8Hz, 4H, Ar*CH*$_2$,Ar), 4.7 (s, 8H, O*CH*$_2$), 7.1 (s, 8H, H$_{arom.}$).

Membrane preparation and emf measurements

The membrane components (2.5 wt.-% of ionophore, 33 wt.-% PVC, 65 wt.-% plasticizer and 10 mol-% KTpClPB with respect to the ionophore), about 200 mg in total, were dissolved in 1.5 mL of freshly distilled THF. The solution was poured into a glass ring as described previously [6]. After solvent evaporation the membranes were used for making the electrodes. Three different plasticizers: NPOE (2-nitrophenyl octyl ether), BBPA [bis(1-butylpentyl)adipate] and DOS [bis(2-ethylhexyl)sebacate] were used.

The membranes were incorporated into Ag/AgCl electrode bodies of IS 561 type (Fluka). Unless otherwise stated 0.01 M NaCl was used as internal electrolyte. A double-junction reference Radelkis 0P0820P electrode was used

Table 1. The membrane composition and characteristic of the electrodes based on ionophores **1–11**.

	PVC-membrane composition		Electrode characteristic			
	Ionophore	Plasticizer	S_{Na} [mV]	Linear range $[-\log c_{Na}]$	Selectivity coefficients* Log $K^{pot}_{Na,Li}$	Log $K^{pot}_{Na,K}$
1	**1**	DOS	50	5.0-1.3	−0.45	−0.67
2	**1**	NPOE	56	4.5-1	−0.10	−0.50
3	**2**	DOS	54	5.0-1	−0.30	−0.55
4	**2**	NPOE	55	4.5-1	0.30	−0.25
5	**3**	DOS	51	4.5-3.1	−0.35	−0.60
6	**3**	NPOE	58	3.6-1	0.90	−0.10
7	**4**	DOS	53	4.0-1	0.95	−0.80
8	**4**	NPOE	58	3.8-1	0.65	−0.10
9	**5**	DOS	54	4.5-1	−0.10	−0.55
10	**5**	NPOE	58	3.6-1	0.40	0.15
11	**6**	DOS	51	4.8-1.3	−1.75	0.50
12	**7**	DOS	53	5.0-1	−0.30	−0.50
13	**7**	NPOE	48	4.2-1	−0.20	−0.35
14	**8**	DOS	50	5.5-1	−2.55	−2.18
15	**8**	BBPA	52	5.4-1	−2.50	−2.30
16	**9**	DOS	56	5.6-1	−2.23	−2.25
17	**9**	BPPA	55	5.8-1	−2.50	−2.30
18	**10**	DOS	55	5.5-1	−2.45	−2.34
19	**10**	BPPA	54	5.5-1	−2.45	−2.40
20	**11**	DOS	50	5.8-1	−2.56	−2.20
21	**11**	BBPA	52	5.2-1	−2.70	−2.50

* Determined by SSM II method [7a].

with 1M NH_4NO_3 solution in a bridge cell. The potentials were measured at 20 °C using a METROHM 654 pH Meter.

Selectivity coefficients and electrode characteristics

The selectivity coefficients ($\log K^{pot}_{Na,M}$) were determined by the separate solution method (SSM II) and were calculated by the matched potential method using the equation: $\log K^{pot}_{Na,M} = \log a_{Na} - (z_{Na}/z_M) \log a_M$ at $a_M = 0.1 \cdot f$ [7]. The values are presented in Table 2. The characteristics of the studied electrodes with ionophores **1–11** are shown in Table I.

Determination of complex formation contants

We estimated the values of the complex formation constants $\log \beta_{LA}$ for tetrasubstituted *tert*-butylcalix[4]arenes, compounds **9-11**, using the method proposed recently by Pretsch and Bakker [8, 9] in PVC/DOS membranes. Tetramethylammonium cation (TMA^+) was used as a reference ion [9a].

The values obtained for the complex formation constants are presented in Table 3.

Table 3. The complex formation constants as $\log \beta$ for ligands **9-11** with lithium, sodium and potassium cations determined by the potentiometric method.

Ionophore	Log $\beta_{L,Li}$	Log $\beta_{L,Na}$	Log $\beta_{L,K}$
9	4.64 (0.23)	6.74 (0.32)	4.04 (0.12)
10	5.04 (0.29)	6.84 (0.15)	4.44 (0.18)
11	4.92 (0.28)	7.40 (0.60)	4.64 (0.24)

Crystallization

Compound **4** was crystallized from a CH_2Cl_2-methanol mixture. After several days at room temperature single crystals suitable for X-ray analysis appeared; m.p. 178-180 °C.

*X-ray structure analysis of compound **4***

Crystals of **4** are clear, colourless, well defined and have a slightly distorted octahedron habitus. A crystal of size 0.5 × 0.5 × 0.5 mm was used for the investigation. The X-ray diffraction data were measured at room temperature on a KUMA diffractometer equipped with graphite-monochromated MoK_α radiation. Lattice constants were refined by least squares fits of 27 reflections in the θ-range 7.0–10.8°. Intensity data were collected up to θ = 20.5° using a $\omega - 2\theta$ scan mode and corrected for Lorentz and polarization effects. Three standard reflections were measured after every 200 reflections showing no decay of the crystal during the data collection. Crystal data and details of data collection together with structure refinement are summarized in Table 4.

An initial structure model was obtained by direct methods and all the non-hydrogen atoms were refined with anisotropic thermal parameters by a full-matrix least-squares procedure based on F^2. The crystals diffracted poorly and only 3268 (27%) reflections could be labeled 'observed' ($I > 2\sigma(I)$) among 11773 measured. To decrease the number of parameters the aromatic residues were refined as

Table 2. Selectivity coefficients $\log K^{pot}_{Na,M}$(M = H, Li, K, TMA, NH_4, G, Mg, Ca) for the electrodes with ionophores **1–11** and PVC/DOS and potassium tetrakis(4-chlorophenyl)borate additives.

Iono-phore number	Selectivity coefficients $\log K^{pot}_{Na,M}$								
	H^+	Li^+	Na^+	K^+	TMA^+	NH_4^+	G^+	Mg^{2+}	Ca^{2+}
1	−0.12	−0.45	0	−0.67	−1.15	−0.91	0.69	−2.60	−2.62
2	−0.50	−0.30	0	−0.55	–	−0.87	0.60	−2.60	−2.40
3	−0.25	−0.35	0	−0.60	–	−0.80	0.50	−2.70	−2.40
4	0.35	0.95	0	−0.80	–	−1.00	0.55	−2.45	−2.20
5	−0.30	−0.10	0	−0.55	–	−0.85	0.40	−2.30	−1.80
6	−1.52	−1.75	0	0.50	−1.92	−0.48	−0.38	−1.92	−2.97
7	−0.25	−0.30	0	−0.50	–	−0.60	0.87	−3.00	−1.85
8	−3.20	−255	0	−2.18	–	–	–	−4.30	−3.44
9	−3.20	−2.23	0	−2.25	−3.70	–	−3.90	−4.20	−2.75
10	−3.30	−2.45	0	−2.34	−3.80	–	−3.75	−4.10	−1.75
11	−3.35	−2.56	0	−2.20	−3.80	–	–	−4.40	−3.35

rigid regular hexagon moieties of ideal geometry (C— C = 1.39Å). Restraints were applied to make chemically but not crystallographically equivalent bonds approximately equal.

The OH group hydrogen atoms were found on a differential Fourier map; the hydrogen atoms of the CH_3 groups were refined assuming their trigonal pyramidal geometry by rotation around the C—CH_3 bond. The residual hydrogen atoms were placed in calculated positions and were refined as constrained to bonding atoms. All H atoms were included in the model of the structure with isotropic U values fixed at 1.5 times U_{eq} of the corresponding O or C atoms for OH and CH_3 groups and $1.2U_{eq}$ for others.

Neutral atom scattering factors with anomalous dispersion corrections were taken from [10]. All calculations were performed using the SHELXS-86 and SHELXL-93 program packages [11]. Atomic coordinates and equivalent isotropic thermal parameters have been deposited, the summary of bond lengths are listed in Table 6, selected torsion angles in Table 7.

Results and discussion

Synthesis

The amides **1–11** were obtained by the same procedure, shown in Scheme 1. Using the same reaction condition (NaH/THF+DMF, 60 °C, 24 h) only with *N*, *N*-di(*n*-butyl)amide, morpholide, piperidide and *N*, *N*-methylheptyl amide were the products (**8-11**) tetra substituted, however we managed to isolate the bis(morpholide) **6**, and the bis(piperidide)**7** in small yields from the reaction mixtures and bis(di-*n*-butylamide) **5** together with a small amount of tetrakis substituted product **8**.

We have found that the tetrakis substituted amides **8–11** are strong Na^+ cation receptors. In the synthesis route sodium ions probably play a role of template cation stabilising the *cone* conformation of the products. The amides **8–11** can be obtained in the form of stable sodium complexes. The presence of the alkyl groups on each nitrogen atoms leads to encapsulation of the cation within the complex. The proton NMR spectra are excellent tools for distinguishing between complexed and uncomplexed host calixarenes. In the ^{1}H NMR spectra of these compounds we observed a singlet typical for the 36H of *tert*-butyl groups (at 1.07 ppm), a singlet of 8 methylene protons of the O—CH_2-CON groups (at about 5 ppm), a singlet of 8 aromatic protons (at 6.8 ppm) and a pair of doublets of Ar**C**$\mathbf{H}_2$Ar bridge atoms (at 3.2 and 5.0 ppm respectively), which is typical for the *cone* conformer. Upon complexation the signal of the 8 methylene protons of the O—CH_2-CO groups moves about 0.3 ppm upfield and the signal of the 8 aromatic protons is shifted about 0.2–0.3 ppm downfield and the pair of doublets of ArCH_2Ar also moves (3.35 and 4.5 ppm). These suggest conformational changes in the molecule due to complexation.

Bis-substituted compounds **1–7** were also obtained in the *cone* conformation. This conformation, found in the X-ray structure of **4** is also stable in solution. The interesting point to note is the fact that all bis(amides) are substituted at the proximal positions, on the A and B phenolic rings (see Figure 1a). In the ^{1}H NMR spectra of these compounds, the signal (pair of doublets) of the calix[4]arene methylene bridge Ar**C**$\mathbf{H}_2$Ar protons is split into four doublets, (the intensity of which is: 4 : 1 : 2 : 1). The possibility of formation of hydrogen bond between two OH groups on proximal phenols and between OH and the carbonyl oxygen shown in the structure of **4** might be responsible for the difficulty in formation of tetrakis(substitutiuted)calixarene amides and for the preferred proximal substitution. Only in the case of calix **6** we obtained in a small yield the product substituted at alternate A,C positions.

Complexing properties of the compounds

Membranes were prepared containing ionophores **1–10** and different plasticizers. Complexing properties of the synthesized compounds were studied by using them in ion-selective membrane electrodes (ISE). All the electrodes were stable and long lasting due to the high lipophilicity

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

Empirical formula	$C_{64}H_{94}N_2O_6$
Formula weight	987.41
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, *P-1*
Unit cell dimensions	a = 16.669(8) Å
	b = 17.795(10) Å
	c = 20.984(8) Å
	α = 91.08(4)°
	β = 91.60(3)°
	γ = 90.73(4)°
Volume	6220(5) Å^3
Z,	4,
Calculated density	1.054 g/cm^3
Absorption coefficient	0.066 mm^{-1}
F(000)	2160
Crystal size	0.50 × 0.50 × 0.50 mm
θ-range for data collection	1.14 to 20.41°
Index ranges	$-16 \le h \le 16$, $0 \le k \le 17$, $-20 \le l \le 20$
Reflections collected/unique	11773/11465 $R_{\text{int}} = 0.0414$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11465/1553/1206
Goodness-of-fit on F^2	1.035
Final R indices for 3268F_o with $I > 2\sigma(I)$	R_1[a] = 0.1207, wR_2[b] = 0.3195
R indices (all data)	$R_1 = 0.3297$, $wR_2 = 0.3964$
Extinction coefficient	0.0032(7)
Largest diff. Peak and hole	0.449 and −0.322 e. Å^{-3}

[a] $R_1 = \sum[\| F_o| - |F_c\ \|]/\sum |F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_0^2)^2]^{0.5}$.
$w = 1/[\sigma^2(F_o^2) + (0.2000 \cdot P)^2]$, where $P = (\max(F_o^2, 0) + 2 \cdot F_c^2)/3$.

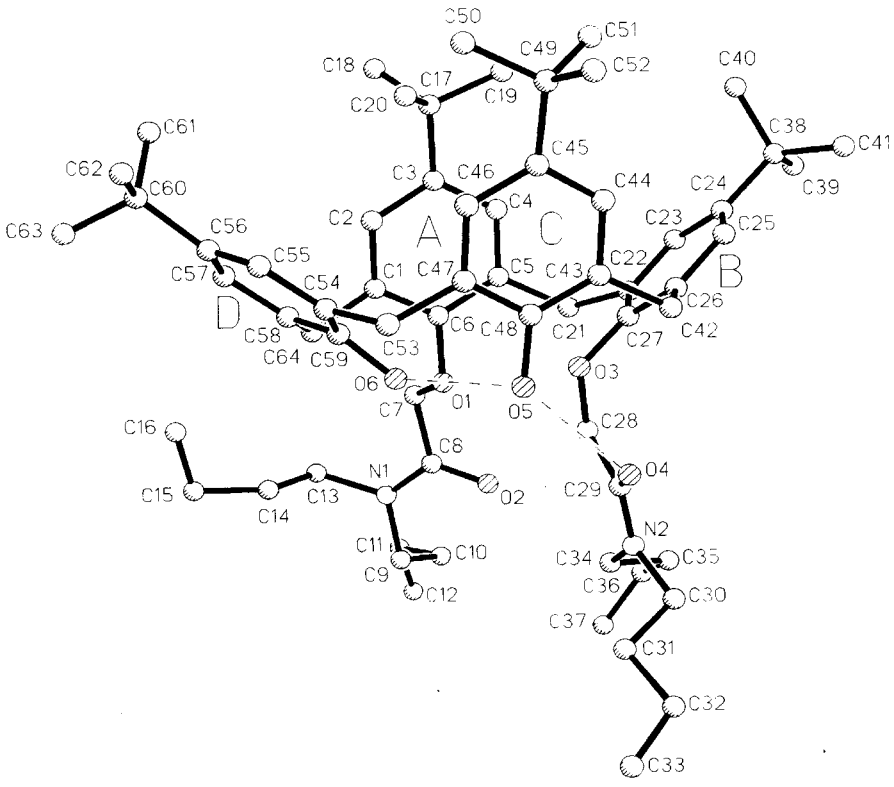

Figure 1a. A general view of molecule ***a*** with the common numbering scheme for both independent molecules. H-atoms are omitted for the sake of clarity.

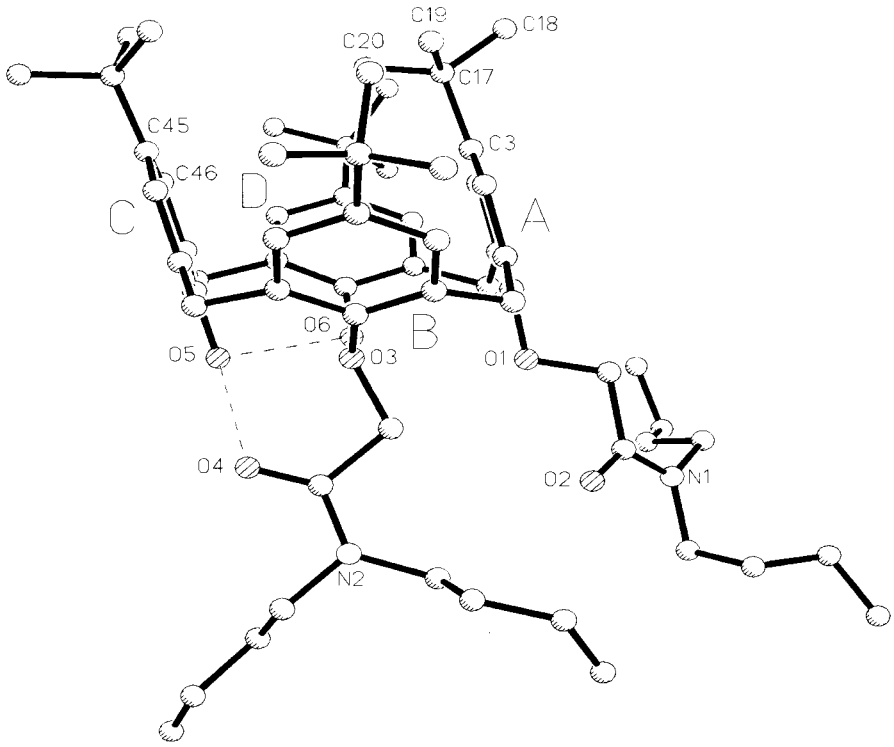

Figure 1b. A view of molecule ***a*** (in the direction approximately perpendicular with respect to Figure 1a) illustrating its distorted closed cone conformation.

of the *tert*-butylcalix[4]arene ionophores. Bis-substituted calix[4]arenes (compounds **1–7**) show Nernstian characteristics for the large guanidinium cation (G^+), slightly worse for sodium and lithium, but the selectivity towards other alkali metal ions was rather low. Tetrasubstituted amides (compounds **8–11**) have very good characteristics for sodium ion and the electrodes are very stable and highly selective ($\log K^{\text{pot}}_{\text{Na,K}} \cong -2.4$; $\log K^{\text{pot}}_{\text{Na,Li}} \cong -2.5$). The plasticizers used do not affect the selectivity very much, however the best results when concerning stability were obtained with DOS [bis(2-ethylhexyl)sebacate] and BBPA [Bis(1-butylpentyl)adipate]. The selectivity coefficients for the electrodes with ionophores **1–11** and plasticiser DOS for sodium cations against: H^+, Li^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+},G^+, TMA^+ are presented in Table 2. Full characteristics of the discussed electrodes are in Table 1.

In planning the structure of ionophores for ISEs one should consider several aspects of complexation. The specific geometry of the ligand molecule, the number and kind of coordination centers and the lipophilicity of the ionophore and of its complex are taken into account. These affect the complex stoichiometry and complex stability constants, which reflects the selectivity of complexation.

The aim of our studies in the field of ion-selective electrodes is to find a relationship between the optimal structure of an ionophore and the selectivity of ion selective electrodes based on this ionophore. As the selectivity coefficient is influenced by the binding properties of the incorporated lipophilic carrier, knowledge of the ion-ligand complex stability constants, β, in the membrane and the complex stoichiometry are useful parameters for making optimalization of the membrane composition.

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

The correlation between the values of the complex stability constants determined by classical methods in rather polar solvents and the selectivity coefficients of ISEs only in few cases were good and well understood [12]. One such positive example was the valinomycin K^+-electrode ($\log K^{\text{pot}}_{\text{K,Na}} = -3.5$) [13]. The stability constants for valinomycin complexes with potassium and sodium are: $\log \beta_{\text{LK}} = 4.9$ and $\log \beta_{\text{LNa}} = 0.67$. The stoichiometry of both complexes are the same, they were estimated as 1 : 1 [13b].

Potentiometric selectivity coefficients ($K^{\text{pot}}_{\text{A,B}}$) reflect the ion-ligand complex formation constant directly within the membrane. That is why it is possible to use the values of $K^{\text{pot}}_{\text{A,B}}$ for determination of the effective complex formation constants. Recently such a method of determination was proposed by Pretsch and Bakker [8, 9]. Applying one of these methods (with tetramethylammonium cation TMA^+ as a reference ion) [9] we estimated the values of the complex stability constants $\log \beta_{\text{LA}}$ in PVC/DOS membranes for substituted *tert*-butylcalix[4]arenes **9–11**. They are presented in Table 3. The calculation was based on the following assumptions:

1. The polymeric membrane phase is homogenous and is in equilibrium with the contacting aqueous solution.
2. The equilibria constants determined are related to the estimated concentration of the species in the organic membrane phase and to activities in the aqueous phase, so they cannot be treated as thermodynamic parameters.
3. The ionophores form stable complexes of 1 : 1 stoichiometry with Li^+, Na^+ and K^+ ions.

$$\beta = \frac{K^{\text{pot}}_{\text{M,TMA}}(IE)}{K^{\text{pot}}_{\text{M,TMA}}(L)[L_T - R_T]},$$

L_T is the total concentration of ionophore within the membrane, R_T, the total concentration of lipophilic anionic site (KTpClPB) in the membrane, $K^{\text{pot}}_{\text{M,TMA}}(IE)$, the selectivity coefficient for the membrane without ionophore, $K^{\text{pot}}_{\text{M,TMA}}(L)$, the selectivity coefficient for the membrane with ionophore L; M = Li, Na, K.

Complexation studies in solution

The complexation of the tetrakis-substituted *tert*-butylcalix[4]arenes **8–11** with sodium ions were studied by the proton NMR technique in solution. Deuterated chloroform was used as the solvent. Both spectra, of the free ligand and of its complex differ signifficantly, as seen in Table 5. Similar changes in NMR spectra of different ionophores on complexation were described by us previously [14].

The signal of the 8 aromatic hydrogen atoms is shifted on complexation to the lower field direction by 0.3 ppm, whereas the 8 bridge protons of the O-**CH**$_2$—CO groups are shifted 0.3ppm to the high field direction, the pair of doublets of Ar—**CH**$_2$—Ar are in the free ligand at 3.2 and 4.98 ppm, but in the complex at 3.7 and 4.5 ppm for equatorial and axial protons respectively. Also the signals of amide N-CH$_2$ protons are changed due to complexation. In the free ligands 16 N-CH$_2$ protons give a multiplet at 3.5 ppm and in the complex they split in to two signals: at 3.3 and 3. 6 ppm each for 8 protons. All these suggest conformational changes in the calix[4]arene structure, which is more rigid in the complex.

The spectra for amide **9** and its sodium complex **9a** are presented in Figure 2.

X-ray structure of compound **4**

X-ray analysis of the single crystal unambiguously proved that the product **4** is indeed the *syn-proximal*-5,11,17,23-tetra-*tert*-butyl-25,26-bis(*N*, *N*-dibutylcarbomoylmethoxy)-27,28-dihydroxy-calix[4]arene. The crystal structure data show that two similar crystallographically independent molecules (molecule ***a*** and molecule ***b***) are present in the asymmetric part of the unit cell. Due to these molecules similarity only the view of molecule ***a*** in two different orientation are depicted in Figure 1. The aromatic rings bearing substituents on the lower rim are labelled A and B, while the two free phenolic rings are labelled C and D.

Most of the molecular dimensions, summarised in Table 6, are anticipated for such calixarenes, except for the C—C bond lengths in the butyl side-chain of the two pendant *syn-proximal* *N*, *N*-dibutylcarbomoylmethoxy groups, which are appreciably shorter than the expected value for a C(sp^3)—C(sp^3) bond. The reason for the observed shortening is the high thermal motion of the corresponding carbon atoms and librational effects. The different conformations of the butyl chain moieties (see Table 7) in molecule ***a*** and ***b*** indicate their mobility and is the main difference of their conformation. One may speculate that it is due to the intermolecular packing effects.

Molecules clearly show a distorted, 'oblique' *cone* structure, Figure 1a,b. Their 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 0.047 and 0.029 Å for molecule ***a*** and ***b*** respectively. The calix conformation is defined by the dihedral angles that the aromatic rings make with this mean reference plane, which are 75.6(3)° (A), 135.9(3)° (B), 106.0(3)° (C), and 141.1(4)° (D) for molecule ***a*** and 78.2(3)° (A), 138.7(3)° (B), 106.7(3)° (C), and 139.6(4)° (D) for molecule ***b***. Three interplanar angles in each molecule are larger than 90° and indicate that the *t*-butyl group of the rings B, C and D are pointed outwards from the cavity whereas the angle smaller than 90° shows that the *t*-butyl group on ring A points inwards and covers the cavity. Methyl atom C(20) of this *t*-butyl group is directed inside the calixarene cavity but there is no evidence of its $CH_3 \cdots \pi$ interaction. The shortest CH$_3$-'rings' distance are from C(20) to the C(45) carbon atom of the opposite ring C and longer than 4.08 and 4.15 Å for molecule ***a*** and ***b*** respectively. The interplanar angles between each pair of distal rings additionally define the calix conformation. Rings A and C are almost parallel to each other (interplanar angle 1.7(4)° (***a***) and 5.4(4)° (***b***) while rings B and D are close to normal (interplanar angle 97.1(4)° (***a***) and 98.6(4)° (***b***). A similar mutual arrangement of opposite aromatic rings (2.2(3)° and 92.4(3)°) have been found in the relevant 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(*N*, *N*-diethylcarbamoylmethoxy)calix[4]arene [1]. The relative dihedral angles between two adjacent rings in **4** are in the range 74.1–79.4°. The torsion angles about the methylene bridges (see Table 7) vary essentially, but corresponding values in the molecule ***a*** and ***b*** are rather similar. There are significant differences in the distal O···O separation: 5.10(1), 5.08(1) Å between O(1) and O(5) and 3.43(1), 3.45(1) Å between O(3) and O(6) (for molecule ***a*** and ***b*** respectively). At the same time the transannular distances between bridging carbon atoms C(21)···C(53) and C(42)···C(64) are in the narrow region 7.09(2)–7.21(2) Å for both molecules.

The actual conformation adopted by any calixarene in the solid state is clearly the result of a subtle interplay of intramolecular interactions, intermolecular packing effects and the presence of the appropriate solvent molecules [15, 16]. For the calixarene derivative under discussion here, the major intramolecular interaction is the existence of two intramolecular O—H···O hydrogen bonds, one between adjacent phenolic oxygens and another between the phenolic oxygen and the proximal carbonyl oxygen of the pendant arm substituent on ring B. Their parameters for the molecule are O(6)···O(5) 2.756(13), 2.785(13) Å; H···O(5) 2.03. 2.13 Å, O(6)—H···O(5) 147, 136° and O(5)···O(4) 2.768(12), 2.775(14) Å, H···O(4) 2.03, 2.02 Å, O(5)—H···O(4) 149, 152° respectively. The O(5)···O(3) distances of 2.853(12) Å in molecule ***a*** and 2.909(12) Å in mo-

Table 5. ^{1}H NMR spectra (500 MHz) in $CDCl_3$ of ligands **9** and **10** and their complexes **9a** and **10a**.

Compound	$8H_{ar}$ 8H	OCH_2CO 8H	$ArCH_2Ar$ 4H	4H	$O(CH_2)_2$ 16H	$N(CH_2)_2$ 16H	$(CH_2)_3$ 24H	*t*-Butyl 36H
9	6.79(s)	4.99(s)	4.96(d) J = 12.7	3.2(d) J = 12.7	3.64(m)	3.52(m)		1.07(s)
9a	7.08(s)	4.72(s)	4.55(d) J = 12.7	3.36(d) J = 12.7	3.75 (m)	3.66(s) 3.38(s)		1.14(s)
10	6.8(s)	5.0(s)	5.05(d) J = 12.8	3.2(d) J = 12.8		3.48(m)	1.55(m)	1.07(s)
10a	7.1(s)	4.58(s)	4.48(d) J = 12.8	3.3(d) J = 12.8		3.5(m)	1.65(m)	1.14(s)

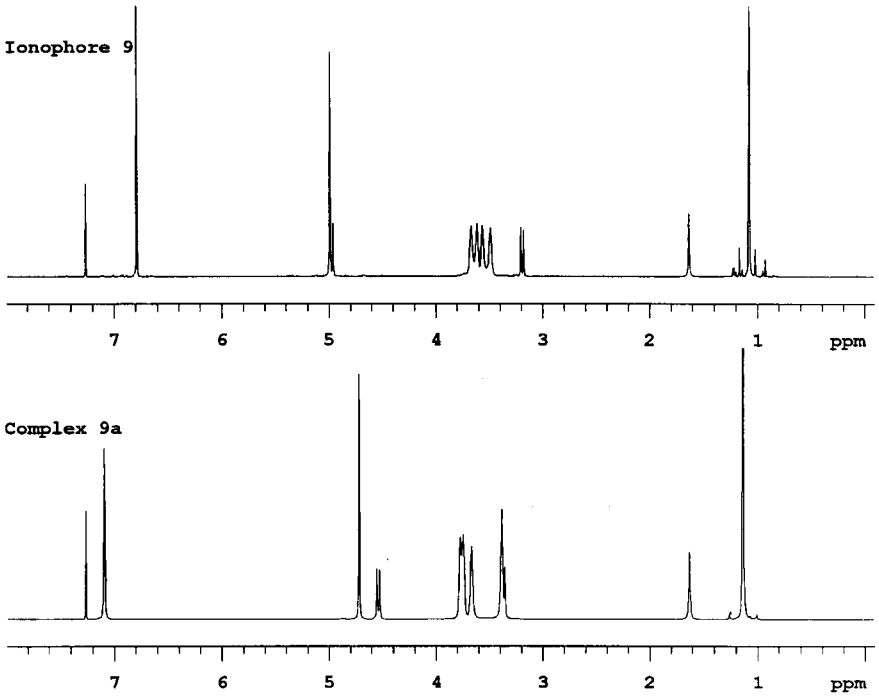

Figure 2. ^{1}H NMR spectra of free ionophore **9** (upper trace) and its NaI-complex **9a** (lower trace) in $CDCl_2$ (500 MHz).

Table 6. Summary of bond lengths (Å) for **4**.

Bond	Range	Mean
C(ar)—O(phen)	1.358(8)–1.382(8)	1.367(8)
C(ar)—O(ether)	1.379(9)–1.393(8)	1.386(8)
$C(sp^2)$—O(ether)	1.421(11)–1.452(11)	1.439(11)
$C(sp^2)$=O	1.203(12)–1.227(121)	1.217(12)
$C(sp^2)$—$N(sp^2)$	1.320(13)–1.347(12)	1.332(12)
$C(sp^3)$—$N(sp^2)$	1.469(12)–1.507(12)	1.481(12)
$C(sp^2)$—$C(sp^3)$	1.515(13)–1.540(13)	1.525(13)
C(ar)—$C(sp^3)$	1.477(14)–1.573(13)	1.523(14)
C(ar)—C(*t*-Bu)	1.532(16)–1.578(13)	1.553(15)
C(*t*-Bu)—C(*t*-Bu methyl)	1.468(13)–1.522(11)	1.498(12)
$C(sp^3)$—$C(sp^3)$	1.413(14)–1.503(14)	1.457(14)
$C(sp^3)$—$C(sp^3$terminal)	1.404(15)–1.455(15)	1.430(15)

lecule ***b*** are only a little longer than the corresponding distances O(5)···O(4) however the latter are more favourable for H-bond formation. The lower rim substituent (the carbonyl) on ring A is not involved in hydrogen bonding. The closest distances are O(1)···O(3) 3.382(11), 3.322(11) Å and O(1)···O(6) 3.365(12), 3.317(11) Å for molecule ***a*** and ***b*** respectively.

In the structure of the related *syn*-1,2-bis(ethoxyethyl) ether of calix[4]arene [17, 18] there are two independent molecules and two different modes of intramolecular O—H···O hydrogen bonding. In one molecule both hydrogen bonds are between the calix[4]arene phenolic oxygen atoms; in the second molecule one of the hydrogen bonds is to a side-chain oxygen (similar to that in calixarene derivative **4**). The first molecule has a relatively open *cone* conformation whereas the second is more closed. In neither case is the solvent included. This example shows the influence of intramolecular H-bond formation on the adopted conformation by an asymmetrically sub-

Table 7. Selected torsion angles (°) for **4**.

Atoms	Molecule ***a***	Molecule ***b***
C(4)—C(5)—C(21)—C(22)	49.6(10)	54.4(11)
C(5)—C(21)—C(22)—C(23)	−99.1(9)	−104.5(9)
C(25)—C(26)—C(42)—C(43)	98.0(10)	103.4(10)
C(26)—C(42)—C(43)—C(44)	−75.6(10)	−78.5(10)
C(46)—C(47)—C(53)—C(54)	79.8(10)	77.9(11)
C(47)—C(53)—C(54)—C(55)	−106.8(9)	−103.5(10)
C(57)—C(58)—C(64)—C(1)	101.7(10)	100.8(10)
C(58)—C(64)—C(1)—C(2)	−43.4(11)	−46.8(11)
C(1)—C(6)—O(1)—C(7)	83(1)	83(1)
C(6)—O(1)—C(7)—C(8)	171(1)	165(1)
O(1)—C(7)—C(8)—O(2)	−40(2)	30(2)
O(2)—C(8)—N(1)—C(9)	4(3)	−1(3)
C(8)—N(1)—C(9)—C(10)	−83(3)	−94(2)
N(1)—C(9)—C(10)—C(11)	−84(3)	−170(3)
C(9)—C(10)—C(11)—C(12)	−127(3)	158(3)
O(2)—C(8)—N(1)—C(13)	175(2)	172(2)
C(8)—N(1)—C(13)—C(14)	−84(3)	−88(2)
N(1)—C(13)—C(14)—C(15)	−163(2)	174(2)
C(13)—C(14)—C(15)—C(16)	−100(4)	−81(3)
C(22)—C(27)—O(3)—C(28)	62(1)	60(1)
C(27)—O(3)—C(28)—C(29)	109(1)	108(1)
O(3)—C(28)—C(29)—O(4)	6(2)	5(2)
O(4)—C(29)—N(2)—C(30)	10(3)	8(3)
C(29)—N(2)—C(30)—C(31)	93(2)	84(2)
N(2)—C(30)—C(31)—C(32)	177(2)	177(2)
C(30)—C(31)—C(32)—C(33)	−175(3)	143(4)
O(4)—C(29)—N(2)—C(34)	167(2)	170(2)
C(29)—N(2)—C(34)—C(35)	106(2)	107(2)
N(2)—C(34)—C(35)—C(36)	−177(2)	−166(2)
C(34)—C(35)—C(36)—C(37)	−55(3)	−47(4)

stituted calix[4]arene. However the hydrogen bond itself is not sufficient to ensure the adopted conformation of the compound in the solid state. In the crystal structure of the *syn-proximal*-5,11,17,23-tetrakis-*tert*-butyl-25,26-bis[(2-pyridylmethyl)oxy]-27,28-dihydroxy-calix[4]arene ethanol 1 : 1 inclusion complex the intramolecular hydrogen bonding is very similar to that found here for the structure of **4** but the interplanar angles of 65.1(3) and 50.7(3)° between opposite aromatic rings indicate the open cone conformation and facilitate the inclusion of an ethanol molecule within the calixarene cup. One may speculate that the factors which control the closed calix distorted cone conformation of **4**, are hydrogen bonds and the repulsion of bulky substituents (steric factors) on the lower calixarene rim.

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References

1. A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, G. D. Andreetti, G. Calestani, and F. Ugozzoli: *J. Incl. Phenomen.* **6**, 119 (1988); F. Arnaud-Neu, G. Barrett, S. Cremin, M. Deasy, G. Ferguson, S. Harris, A. J. Lough, L. Guerra, M. A. McKervey, M. Schwing-Weill, and P. Schwinte: *J. Chem. Soc. Perkin Trans. 2*, 1119 (1992).
2. F. Arnaud-Neu, G. Barrett, S. Fanni, D. Marrs, W. McGregor, M. A. McKervey, M. Schwing-Weill, V. Vetrogon, and S. Wechsler: *J. Chem. Soc. Perkin Trans. 2*, 453 (1995).
3. C. D. Gutsche: in F. Stoddart (ed.), *Calixarenes*, The Royal Society of Chemistry, Hertfordshire, UK.
4. A. Ikeda and S. Shinkai: *Chem. Rev.* **97**, 1713 (1997).
5. M. Bocheńska, J. F. Biernat, and J. S. Bradshaw: *J. Incl. Phenom.* **10**, 19 (1991).
6. M. Bocheńska and W. Simon: *Microchim. Acta* **III**, 277 (1990).
7. R. P. Buck and E. Lindner: *Pure Appl. Chem.* **66**, 2527 (1994); Y. Umezawa, K. Umezawa, and H. Sata: *Pure Appl. Chem.* **67**, 507 (1995); E. Bakker, E. Pretsch, and P. Buhlmann: *Anal. Chem.* **72**, 1127 (2000).
8. E. Bakker, R. K. Meruva, E. Pretsch, and M. E. Meyerhoff: *Anal. Chem.* **466**, 3021 (1994).
9. A. Ceresa and E. Pretsch: *Anal. Chim. Acta* **395**, 41-52 (1999); E. Bakker and E. Pretsch: *Anal. Chem.* **70**, 295-302 (1998).
10. A. J. C. Wilson (ed.): *International Tables for Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, 1992; Tables 6.1.14 (pp. 500–502) and 4.2.6.8 (pp. 219–222).
11. G. M. Sheldrick: SHELXS-86. *Acta Crystallogr., Sect. A* **46**, 467 (1990); G. M. Sheldrick: SHELXL-93, *Program for Crystal Structure Refinement*, University of Göttingen, Germany (1993).
12. M. Bocheńska: *J. Mol. Struct*. **450**, 107–115 (1988).
13. (a) Z. Stefanac and W. Simon, *Chimia* **20**, 436 (1966); *Microchim. J.* **12**, 125 (1967); (b) M. Hiraoka, *Studies in Organic Chemistry*, Vol. 12, Elsevier, Amsterdam (1982).
14. M. Bocheńska, V. Ch. Kravtsov, and V. Zavodnik, *J. Incl. Phenom.* **28**, 125 (1997).
15. G. Ferguson, J. F. Gallagher, Y. Li, M. A. McKervey, E. Madigan, J. F. Malone, M. B. Moran, and A. Walker: *Supramol. Chem.* **7**, 223 (1996) and references therein.
16. W. J. Wolfgong, L.K. Talafuse, J. M. Smith, M. J. Adams, F. Adeogba, M. Valenzuela, E. Rodriguez, K. Contreras, D. M. Carter, A. Bacchus, A. R. Mcguffey, and S.G. Bott: *Supramol. Chem.* **7**, 67 (1996).
17. L. C. Groenen, B. H. M. Ruël, A. Casnati, P. Timmerman, W. Verboom, S. Harkema, A. Pochini, R. Ungaro, and D. N. Reinhoudt: *Tetrahedron Lett.* **32**, 2675 (1991).
18. F. N. Allen and O.Kennard: *Chemical Design Automation News* **8**, 131 (1993).
19. G. Ferguson, J. F. Gallagher, and S. Pappalardo: *J. Incl. Phenom.* **14**, 349 (1992).