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ORIGINAL ARTICLE

O-Ethoxycarbonylmethoxy esters of homocalix[*n*]naphthalenes: synthesis and recognition behaviour towards alkali cations

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Abstract The condensation of 1,2-bis(3-hydroxy-2-naphthyl)ethane and formaldehyde under basic conditions was successfully employed for the synthesis of two new large-ring *n*-homocalixnaphthalenes **5** and **6**. The synthetic yields using a relatively larger reaction scale were higher than those obtained by the sulphur extrusion approach. *O*-Alkylation of these homocalixnaphthalenes afforded the corresponding hexa- and octa-*O*-ester derivatives **5a** and **6a** respectively. The new naphthalene-ring based macrocycle **5a** demonstrated high extraction capability for K^+ under the conditions studied.

Keywords Calixarenes · Homocalixarenes · Calixnaphthalenes · Homocalixnaphthalenes · Alkali metal complexation

Introduction

Homocalixarenes such as **1–3** (Fig. 1) belong to a general class of calixarenes [1] in which the methylene bridges which link the phenyl rings are partly, or completely, replaced by ethano or larger bridges [2, 3]. Such compounds (which can also be considered as belonging to the class of $[2]_n$-metacyclophanes) have significantly different properties to those of their corresponding calixarene analogues. Both "one-pot" and convergent synthesis of several different homocalixarenes have been reported and some of these approaches, as well as their conformational and ionophoric properties, were recently reviewed by Nakamura et al. [4, 5].

Homocalixarenes have been shown to be useful hosts for different cationic guests including uranyl ions, [6] various transition metal ions, [2, 3, 7, 8] alkali earth ions [9] and alkali ions [9, 10]. We have been interested in the synthesis of calixnaphthalenes [11] e.g. **4**, which are naphthalene ring-based calixarenes, and their analogous homocalixnaphthalenes in order to study their potential host-guest properties. Herein, we describe the synthesis and their complexation behaviour toward alkali metal ions, of the ethoxycarbonylmethoxy esters **5a** and **6a**, of two new homocalixnaphthalenes, namely, trihomocalix[6]- and tetrahomocalix[8]naphthalenes **5** and **6**, respectively (Fig 2).

Experimental

General methods

All experiments with moisture- or air-sensitive compounds were carried out in anhydrous solvents under Ar or N_2 atmosphere unless indicated otherwise. Organic solvents were evaporated under reduced pressure using a rotary evaporator. All synthetic products were dried overnight on a vacuum pump, unless otherwise indicated. Flash chromatography was performed on silica gel, particle size 32–63 μm pore size 60 Å. Preparative thin-layer chromatography plates (PLC) were made from F-254 silica gel for TLC (particle size 5–15 μm). Thin-layer chromatography

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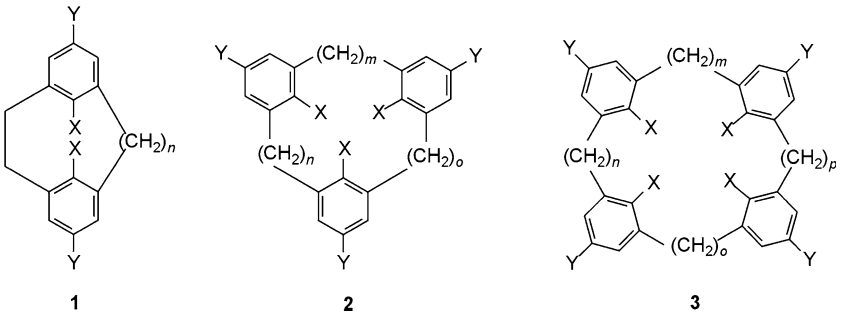


Fig. 1 Some general structures of homocalixarenes (X = OH or OR; Y = H or R where R = alkyl) which have been reported by others [4]

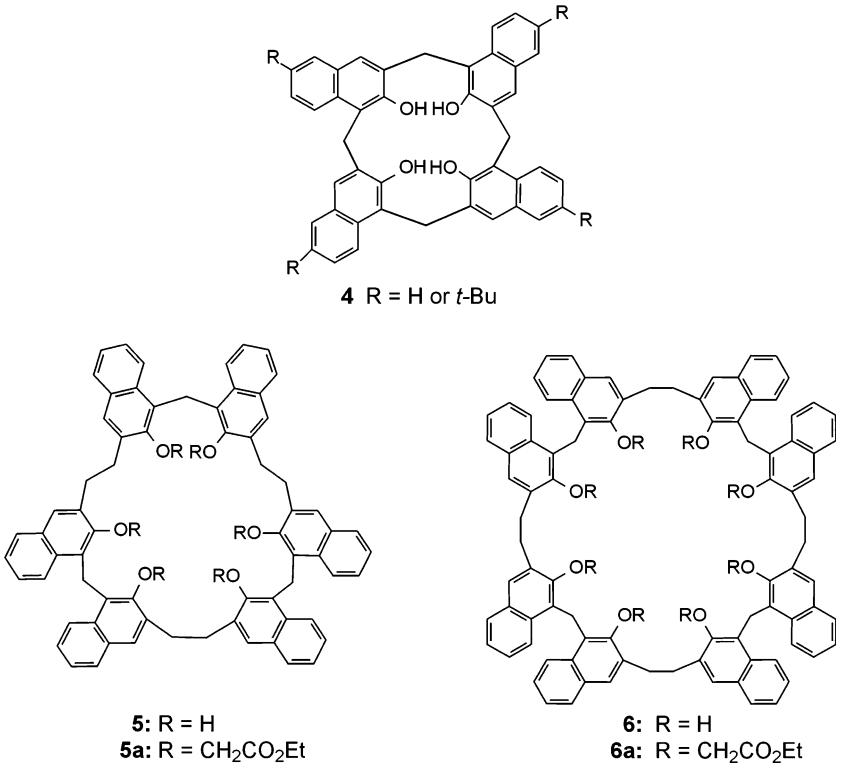


Fig. 2 Structures of calix[4]naphthalenes **4**; trihomocalix[6]naphthalenes **5**, and tetrahomo-[8]naphthalenes **6** and their respective *O*-ethoxycarbonylmethoxy esters **5a** and **6a**

was performed using precoated plastic-backed 200 μm F-254 silica gel plates. All chemical reagents were purchased from Aldrich or Fluka. Solvents purchased from Fisher with ACS grade were dried and distilled according to standard procedures. All melting points (mp) were uncorrected. MS data were presented as follows: *m/z* (relative intensity), assignment (when appropriate), calculated mass (calcd.) for corresponding formula. Unless otherwise indicated, ^{1}H and ^{13}C NMR spectra were conducted using $CDCl_3$ with the internal standard TMS and recorded at either 500 or 300 MHz. Data are presented as follows: chemical shift, multiplicity (s = singlet, br = broad, d = doublet, t = triplet, m = multiplet, sept = septet), coupling constant (*J*, Hz), integration (# of H), and assignment (when appropriate). Reported multiplicities are apparent. Chemical shifts in the ^{13}C NMR are relative to solvent shifts (δ 77.23 ppm for $CDCl_3$).

1,2-Bis(2-methoxy-3-naphthyl)ethane (**12**)

To a stirred solution of **11** (0.51 g, 2.0 mmol) in dry THF (20 mL) at –78 °C was added 1.6 M *n*-BuLi in *n*-hexane (0.62 mL, 1.0 mmol) over 30 min. The reaction mixture was stirred for a further 9 h, then quenched at 0 °C by the addition of cold water (30 mL) and aqueous 10% HCl (10 mL). The resulting colourless precipitate was filtered, washed several times with deionized water and dried at 60 °C overnight to yield **12** (0.32 g, 94%) as a colourless powder: mp 209 °C ($CHCl_3$–MeOH) ((lit. [14]) 184–185.5 °C); ^{1}H NMR δ 3.13 (s, 4H), 3.93 (s, 6H), 7.10 (s, 2H), 7.30 (t, J = 7.5, Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.59 (s, 2H), 7.68–7.72 (m, 4H); ^{13}C NMR δ 31.1, 55.5, 104.9, 123.6, 125.7, 126.5 127.3, 128.3, 129.1, 132.7, 133.7, 156.9; GCMS *m/z* (relative intensity) 342 (M^+, 30), 171 (100), 141 (60), 115 (40), 77 (30).

1,2-Bis(2-hydroxy-3-naphthyl)ethane (**9**)

To a suspension of **12** (3.42 g, 10.0 mmol) in anhydrous CH_2Cl_2 (95 mL) at room temperature, BBr_3 (3.8 mL, 40 mmol) was added dropwise over 30 min. The reaction mixture was stirred for a further 7 h, and then quenched by the addition of cold water (50 mL) at 0 °C. The resulting colourless precipitate was filtered, washed several times with deionized water and dried at 60 °C overnight to yield **9** in quantitative yield as a light yellow powder: mp 229–230 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 3.06 (s, 4H), 7.15 (s, 2H), 7.22 (t, J = 7.3 Hz, 2H), 7.32 (t, J = 7.3 Hz, 2H), 7.63–7.64 (m, 4H), 7.70 (d, J = 9.0 Hz, 2H), 9.83 (s, 2H, OH, disappears upon D_2O addition); ^{13}C NMR (300 MHz, acetone-d_6) δ 30.8, 108.5, 122.7, 125.2, 125.5, 127.0, 128.2, 128.8, 131.3, 133.7, 154.0; LCMS *m/z* (relative intensity) 314 (M^+, 59), 158 (50), 157 (100).

Trihomocalix[6]naphthalene (**5**) and tetrahomocalix[8]naphthalene (**6**)

A mixture of **9** (1.26 g, 4.00 mol), aqueous 37% CH_2O (formalin) (0.4 mL) and K_2CO_3 (0.66 g, 4.8 mol) in DMF (40 mL) was heated at 80 °C with stirring for 1 h. After the solvent was removed under reduced pressure, water (10 mL) was added. The resulting solution was acidified with aqueous 6 M HCl (until the pH reached 1–2) and then treated with $CHCl_3$ (20 mL). The resulting precipitate was isolated by suction filtration. The filtrate was then evaporated to dryness and the residue was treated with another 20 mL $CHCl_3$, and the newly formed precipitate was also isolated by suction filtration. The precipitates were combined, washed several times with water, and then dried at a 50 °C overnight to yield a mixture of **5** and **6** (1.04 g) as a yellow powder, which was used for the next synthetic step without further purification.

Due to the low solubilities of the two isomers in most of the common organic solvents, a small amount of the mixture was dissolved in $CHCl_3$ and purified by PLC (1:1 $CHCl_3$:petroleum ether) to yield **5** as a pale yellow solid: mp 205–210 °C (dec.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.21 (s, 2H), 4.84 (s, 1H), 7.04–7.09 (m, 1H), 7.18–7.23 (m, 1H), 7.54–7.57 (m, 2H), 8.16 (d, J = 8.6 Hz, 1H), 9.28 (s, br, 1H, OH); ^{13}C NMR (300 MHz, DMSO-d_6) δ 22.1, 30.4, 119.9, 122.7, 123.4, 125.1, 126.5, 127.8, 128.8, 131.3, 132.0, 150.7; (-)-APCI MS *m/z* (relative intensity) 978.3 (M^+, 15) calcd.: 979.4 for $C_{69}H_{54}O_6$, 651.2 (100); and **6** as a pale yellow solid: mp 228–230 °C (dec.); ^{1}H NMR (300 MHz, DMSO-d_6) δ 3.19 (s, 2H), 4.81 (s, 1H), 7.03–7.08 (m, 1H), 7.16–7.22 (m, 1H), 7.55 (s, br, 2H), 8.15 (d, J = 8.4 Hz, 1H), 9.26 (s, br, 1H, OH); ^{13}C NMR (300 MHz, DMSO-d_6) δ 22.6, 31.1, 119.4, 123.2, 123.4, 126.0, 127.0, 128.6, 129.4, 131.8, 132.4, 151.8; (–)–APCI MS: *m/z* (relative intensity) 1304.2 (M^+, 7) calcd.: 1,304.5 for $C_{92}H_{72}O_8$, 977.3 (55), 651.2 (100).

Hexaester **5a** and octaester **6a**

The crude mixture of homocalixnaphthalenes **5** and **6** (0.66 g, 1.0 mmol estimated to be a 2:1 mixture) obtained in the previous reaction, K_2CO_3 (1.12 g, 8.08 mmol) and ethyl bromoacetate (0.90 mL, 8.0 mmol) in anhydrous acetone (95 mL) were heated at reflux with stirring for 3 days. After the solvent and excess ethyl bromoacetate were removed under reduced pressure, the resulting residue was mixed with water (20 mL), neutralized with aqueous 3 M HCl and extracted with $CHCl_3$ (3 × 60 mL). The organic layers were combined and washed with deionized water (1 × 50 mL) and brine (1 × 50 mL), dried over $MgSO_4$ and filtered. After the solvent was removed under reduced pressure, the resulting yellow residue was purified by flash chromatography (5:19:76 $CHCl_3$–EtOAc–hexane) to yield hexaester **5a** (0.24 g, 35%) as a pale yellow solid; mp 110–112 °C; ^{1}H NMR ($CDCl_3$) δ 0.88 (s, br, 3H), 3.11 (s, br, 2H), 3.82 (s, br, 2H), 4.19 (s, br, 2H), 4.91 (s, br, 1H), 7.28 (s, br, 2H), 7.62 (s, br, 2H), 8.11 (s, br, 1H); ^{13}C NMR ($CDCl_3$) δ 14.0, 24.0, 29.9, 60.9, 70.4, 124.1, 124.7, 125.6, 127.6, 128.2, 128.7, 131.5, 132.3, 134.3, 153.7, 168.7; (+)–ES MS *m/z* (relative intensity): 1517.55 (M^+Na^+, 13) calcd.: 1,517.50 for $C_{93}H_{90}O_{18}Na$, 1512.55 ($M^+ + H_2O$, 9) calcd.: 1512.62 for $C_{93}H_{90}O_{18}.H_2O$, 1496.7 (M^+, 100) calcd.: 1,495.73 for $C_{93}H_{90}O_{18}$. Further elution with 5:29:66 $CHCl_3$–EtOAc–hexane yielded octaester **6a** (82 mg, 18%) as a pale yellow solid: mp 130–132 °C; ^{1}H NMR ($CDCl_3$) δ 1.02 (s, br, 3H), 3.25 (s, 2H), 4.09 (q, J = 6.5 Hz, 2H), 4.52 (s, 2H), 4.99 (s, 1H), 6.83 (s, br, 1H), 6.99 (s, br, 2H), 7.17 (s, br, 1H), 8.19 (d, J = 8.5, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.9, 23.5, 31.0, 61.0, 71.1, 124.3, 124.5, 125.4, 127.6, 128.4, 128.7, 131.1, 132.0, 133.3, 152.9, 168.9; (+)-ES MS *m/z* (relative intensity) 1994.6 (M^+, 60) calcd.: 1994.3 for $C_{124}H_{120}O_{24}$.

Metal picrate extraction

Extractions of alkali metal picrates (Li, Na, K, Cs and Rb) from their aqueous solutions (deionized water) into chloroform (spectrograde) (Figure 4.9 and 4.10) were performed according to the following typical procedure: 5 mL of an aqueous 1.00×10^{-4} M solution of the metal picrate and 5 mL of a 1.00×10^{-4} M solution of **5a** (or **6a**) in $CHCl_3$ were mechanically shaken in a Teflon®-lined stoppered glass tube for 24 h. The mixture was then equilibrated in a thermostated water bath at 25.0 ± 0.1 °C

for 2 h in order to achieve a good phase separation. The absorbance of the metal picrate remaining in the aqueous phase was then determined spectrophotometrically at 358 nm using a Unicam UV2 UV–vis spectrophotometer. The percentage extraction (*%E*) for each solution was calculated from the expression $\%E = 100(A_o–A)/A_o$. Where A_o is the initial absorbance of the pure metal picrate aqueous solution; and A is the absorbance of the same aqueous solution after extraction. The results are summarized in Table 1.

Results and discussion

The synthesis of dihomocalix[4]naphthalenes, **7** and **8** has previously been reported [11, 12] using a photochemical extrusion of sulphur atoms from the relatively-easily synthesized precursors, tetrahomodithiacalix[4]naphthalenes **7a** and **8a**, respectively. The photochemical approach however suffers from the disadvantage that it could only be carried out on a small scale, and with other dithia precurors which we examined, afforded either only low yields, or none of the desired products (Scheme 1).

Table 1 *%E* values for two-phase solvent extraction of alkali metal picrates from aqueous solution by esters **5a** and **6a** in $CHCl_3$ at 25 °C

Entry	Metal picrate / homocalix-naphthalene	Run #1			Run #2			Average
		A_o	A	*%E*	A_o	A	*%E*	
1	Li^+/**5a**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	Na^+/**5a**	2.5	2.4	2.3	2.5	2.4	2.4	2.4 ± 0.1
3	K^+/**5a**	1.6	0.47	71.0	1.6	0.45	72.0	71± 1
4	Rb^+/**5a**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
5	Cs^+/**5a**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
6	Li^+/**6a**	1.6	1.5	2.9	1.6	1.6	2.4	2.6 ± 0.4
7	Na^+/**6a**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	K^+/**6a**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9	Rb^+/**6a**	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	Cs^+/**6a**	0.0	0.0	0.0	0.0	0.0	0.0	0.0

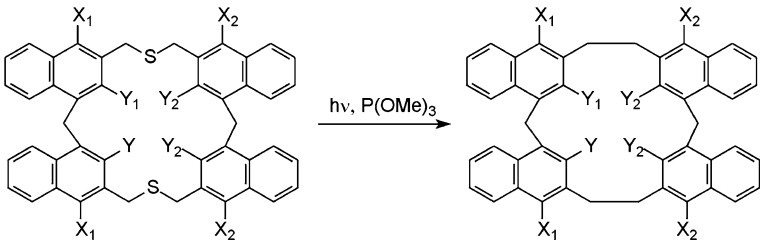
The condensation of 1,2-bis(3-hydroxy-2-naphthyl)ethane (**9**) and formalin, as outlined in Scheme 2 was therefore employed instead, to synthesize trihomocalix[6]naphthalene **5** and tetrahomocalix[8]naphthalene **6**. These new macrocyclic compounds, **5** and **6**, were obtained in synthetically useful amounts, but as a mixture which, as described below, could not be separated without further modification. The reactions leading to **5** and **6** involved a sequential series of functional group interchanges, including methylation of commercially-available 3-hydroxy-2-naphthoic acid (**10**), followed by hydride reduction and subsequent bromination, to form 3-bromomethyl-2-methoxynaphthalene (**11**). *n*-Butyllithium-mediated homocoupling of **11** produced **12** conveniently and in excellent yields, and importantly, it was found that the purity of **11** strongly influenced both the purity and yields of the coupling product, **12**. BBr_3 demethylation of **12** afforded **9**. Condensation of **9** with aqueous 37% formaldehyde in DMF under basic conditions produced the mixture of homocalixnaphthalenes **5** and **6**.

Characterization of homocalixnaphthalenes **5** and **6**

Due to its low solubility in organic solvents, a small amount only of the crude product was purified by preparative-layer chromatography (1:1 $CHCl_3$:petroleum ether) for characterization purposes. The ^{1}H NMR spectra of two products, **5** and **6** which were isolated were very similar, each revealing two singlets at approximately δ 3.2 and 4.8 ppm, corresponding to the ethylene and methylene bridges, respectively. (–)–APCI MS analysis showed the molecular ion peak of trihomocalix[6]naphthalene **5** at *m/z* = 978.3 and that of tetrahomocalix[8]naphthalene **6** at *m/z* = 1304.2, respectively. As revealed by its ^{1}H NMR spectrum, the larger ring compound **6** was the more flexible of the two.

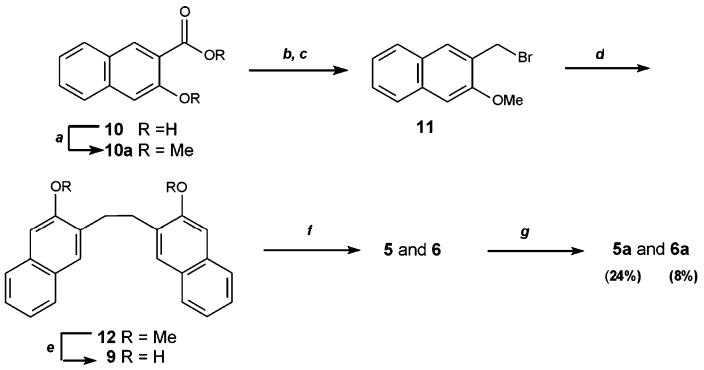
It is well-known that ethoxycarbonylmethoxy ester derivatives ("*O*-esters") of calixarenes [13], homocalixarenes [7, 8] or calixnaphthalenes [14] exhibit ionophoric properties. Compounds **5** and **6** were therefore converted to their corresponding ethoxycarbonylmethoxy ester derivatives **5a** and **6a** (Scheme 2) in order to both enhance

Scheme 1 Synthesis of dihomocalix[4]naphthalenes **7** and **8** via sulphur extrusion



7a X_1, Y_1 = OMe; X_2, Y_1 = H
8a X_1, X_2 = H; Y_1,Y_2 = OMe

7 X_1, Y_1 = OMe; X_2, Y_1 = H
8 X_1, X_2 = H; Y_1,Y_2 = OMe



Reaction conditions: ***a***: **10**, Me_2SO_4, aq NaOH, Adogen, CH_2Cl_2, 0 °C , 10 h, 96%. ***b***: **10a**, $LiAlH_4$, THF, 0 °C - rt , 6.5 h, quant. ***c***: PBr_3, CH_2Cl_2, rt, 2.5 h, 60-90%. ***d***: BuLi, THF, -78 °C - rt , 9.5 h, 60-90%. ***e***: **12**, BBr_3, CH_2Cl_2, rt, 7.5 h, quant. ***f***: **9**, 37% CH_2O, K_2CO_3, DMF, 80 °C, 1H, 79%. ***g***: Mixture of **5** and **6**, $BrCH_2CO_2Et$, K_2CO_3, acetone, reflux, 3d.

Scheme 2 Synthesis of trihomocalix[6-] and tetrahomocalix[8]naphthalenes, **5** and **6** and their *O*-ethoxycarbonylmethoxy esters **5a** and **6a**, respectively

their solubility in organic solvents, and to also evaluate their potential affinities towards alkali cations. Alkylation of the crude reaction product mixture with excess ethyl bromoacetate under basic conditions in acetone afforded the corresponding hexa-*O*-ester **5a** and octa-*O*-ester **6a**, which indeed were more soluble in $CHCl_3$ and could be chromatographically purified in synthetically more useful scales. The two ester derivatives **5a** and **6a** were isolated from the crude reaction mixture, as pale yellow solids, in 24 and 8% yields, respectively. Their (+)–APCI MS spectra clearly showed the presence of the molecular ion peaks at *m/z* = 1,495.8 for **5a** and at *m/z* = 1,994.6 for **6a**, respectively. The ambient temperature ^{1}H NMR spectra revealed **5a** to be conformationally less flexible than **6a** as evidenced by its broader ^{1}H NMR signals. High-temperature VT ^{1}H NMR of both compounds revealed sharpening and better resolved signals for all of their protons.

Solution complexation studies

Preliminary complexation tests of **5a** and **6a** with neutral guests such as C_{60} and C_{70} in toluene, or carbon disulfide solutions, failed to indicate any complexation between either of the hosts with C_{60} and C_{70}, either by ^{1}H NMR or UV–vis spectroscopy. It is possible that the high conformational flexibility of the large annulus, as was noted in an earlier similar study, could partly account for these findings [15]. In order to evaluate their potential ionophoric and extraction capabilities therefore, two-phase solvent extraction experiments of metal picrates were conducted with **5a** or **6a**. The percentage extraction (%*E*) values for these compounds towards alkali metal picrates [14], are shown in Table 1 and Fig. 3.

It is obvious that **6a** is not an efficient receptor for alkali metal ions under the conditions studied, since it slightly extracted from aqueous solutions only Li^+ (%*E* = 2.6) and none of the other cations studied, while in contrast, **5a** proved to be a good receptor for K^+ (%*E* = 71.4) and only a weak one (%*E* = 2.3) for Na^+ (Fig. 3). The selectivity towards K^+ by **5a** can be compared to values reported in the literature for other ionophores such as 18-crown-6 (**13**), homocalix[*n*]arenes **14** and **16**, the ester derivatives of calix[*n*]arenes (**17–22**), and homocalix[*n*]arenes **15** and **23** (Fig. 4 and Table 2) [13]. It should be noted however that compounds **14–16** had been tested with $CHCl_3$ as the extractant solvent.

Macrocycle **6a** demonstrated a low but possibly significant, selectivity towards Li^+. This is a counterintuitive result whose explanation however can only be conjectured upon at the present time. The question is not so much why **6a** binds Li^+, but why **5a** does not, as would be anticipated if π-cation interactions [16, 17] alone were responsible. We note that in the gas phase, $\Delta G°$ for Li^+ binding to benzene

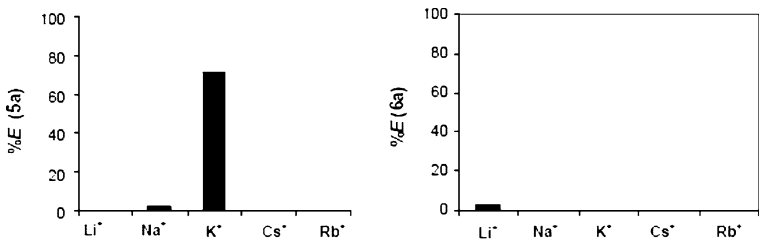


Fig. 3 %*E* values for **5a** (*left*) and **6a** (*right*) with alkali metal picrates

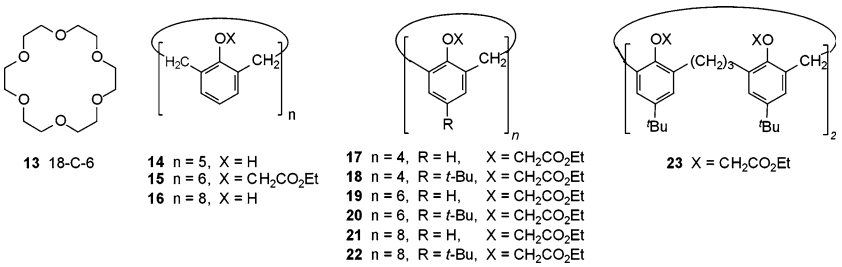


Fig. 4 Structures of **13–23** which have been reported in the literature (see Table 2)

Table 2 *%E* values for two-phase solvent extraction of alkali metal picrates from aqueous solution by various receptors in chloroform or dichloromethane solvents

Receptors	Solvents	Li^+	Na^+	K^+	Rb^+	Cs^+
13[13c]	CH_2Cl_2	8.7	23.1	77.9	77.3	62.9
14[2]	$CHCl_3$	2.0	1.7	2.0	0.3	–
15[2]	$CHCl_3$	–	2.9	–	–	–
16[2]	$CHCl_3$	–	0.2	–	1.3	–
17[13c]	CH_2Cl_2	1.8	60.4	12.9	4.1	10.8
18[13c]	CH_2Cl_2	15.0	94.6	49.1	23.6	48.9
19[13c]	CH_2Cl_2	4.7	10.4	51.3	94.1	94.6
20[13c]	CH_2Cl_2	11.4	50.1	85.9	88.7	100.0
21[13c]	CH_2Cl_2	0.8	7.5	20.2	28.9	30.1
22[13c]	CH_2Cl_2	1.1	6.0	26.0	30.2	24.5
23[8]	CH_2Cl_2	7.6	9.1	11.6	72.0	19.1

is reported to be in the 200 kJ mol^{-1} (exothermic) range [16].[1] On this basis, therefore, Li^+ extraction should have been expected with **5a** as well, the caveat being that solvation and counterion effects play a significant role whose exact role cannot be precisely determined on the basis of only the observations made in this study alone. Conformational flexibility in this host however, could result in suitable orientation(s) of the *O*-ester podands which may allow some small π-cation contribution in the case of the Li^+ binding, but as noted by Gokel et al. [17] "relatively few calixarene candidates for alkali metal cation-π interactions remain once the cases of fortuitous contact have been eliminated".

Conclusions

The base-induced condensation reaction of 1,2-bis (3-hydroxy-2-naphthyl)ethane (**12**) and formaldehyde was successfully employed for the synthesis of two new large-ring *n*-homocalixnaphthalenes **5** and **6**. The synthetic yields were higher than those obtained by the sulphur extrusion approach, on a relatively larger reaction scale. *O*-Alkylation of these homocalixnaphthalenes gave the corresponding hexa-**5a** and octa-*O*-ester derivatives **6a** which had, as expected, higher solubilities than those of their parent homocalixnaphthalenes and which could more easily be separated. Macrocycle **5a** demonstrated a high selectivity towards potassium ions, under the conditions studied.

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