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First Synthesis of 1,3-Alternate 25,27-Dialkyloxy-5,17-diarylcalix[4]arenes-crown-6 as New Cesium Selective Extractants by Suzuki Cross-coupling Reaction

JEAN GUILLON[a,*], JEAN-MICHEL LEGER[a], CECILIA DAPREMONT[a], LOU APOLLONIA DENIS[a], PASCAL SONNET[b], STÉPHANE MASSIP[a] and CHRISTIAN JARRY[a]

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The synthesis of new 25,27-dialkyloxy-5,17-diaryl-calix[4]arenes-crown-6 1a–f in 1,3-alternate conformation by Suzuki cross-coupling reaction is reported. Their conformation was determined using ^{1}H, ^{13}C, 2D NMR and ROESY analysis, and X-ray crystallography. Extraction experiments using a two-phase solvent method involving sodium, potassium or cesium picrate showed good extraction of the cesium cation. The X-ray crystal structures of 1,3-alternate 25,27-dipropoxy-5,17-diphenyl-calix[4]arene-crown-6 ether 1a and its cesium picrate complex were established. Solid-state data were used to determine the complexation behavior of these new ligands. The efficiency of calixarenes 1a–f for cesium ion extraction could be ascribed to the rigidity and flatness linkages caused by the aryl groups at the lower rim of the aromatic moieties in the calixarene skeleton. In addition, the introduction of these aromatic moieties in positions 5 and 17 enhanced the solubility of the metal complexes in organic media.

Keywords: Calix[4]arene-crown-6; Cesium extraction; Cesium complexation; Conformation; Suzuki reaction

INTRODUCTION

Calix[4]arenes belong to the class of compounds known as [1_n]metacyclophanes and are cyclic tetramers composed of four phenolic and four methylene moieties [1,2]. Of all the known calix[*n*]arenes ($n = 4–20$) [3], calix[4]arenes are by far the most studied and applied [4]. Their popularity as hosts in the area of supramolecular chemistry is due, in part, to the structural and functional diversity of the four possible conformational isomers known as the cone, partial cone, 1,2-alternate and 1,3-alternate isomers [1]. Binding studies have demonstrated a correlation between the conformation of calix[4]arene and its molecular recognition properties [1,4,5]. Therefore, synthetic methods for the selective formation of each conformer are highly desirable. Calixarene-crowns, or calixcrowns, are macrocyclic compounds that combine calixarene and polyether units and are being studied intensively as hosts for selective ion recognition [6]. Calix[4]arenes-crown-6 in the 1,3-alternate conformation [6–10] have attracted intense interest in recent years as selective extractants for large alkali metal cations for possible applications such as nuclear-waste remediation [11,12], sensing [13] and radiopharmacy [14]. In particular, significant efforts have been directed towards the use of 1,3-dialkyloxycalix[4]arenes-crown-6 (i.e. di-Oct calix C6 and di-*n*-Pr calix C6) in the remediation of $^{137}Cs^{+}$, a fission product found in radioactive liquid nuclear wastes [15,16]. These calix[4]arenes-crown-6 were found to be exceptionally selective ionophores for the cesium cation over other alkali metal ions due to complexation of the cesium ion not only with the crown ether moiety but also with the two rotated aromatic nuclei (cation–π-interaction) when they are fixed in the 1,3-alternate conformation [6–8].

In terms of molecular diversity designed to develop powerful and highly selective ionophores for cesium metal cation, many variations of 1,3-alternate

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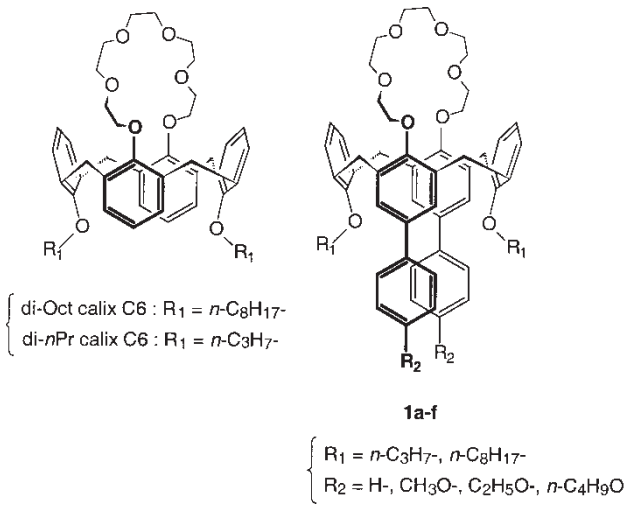


FIGURE 1 1,3-Alternate di-Oct calix C6, di-*n*-Pr calix C6 and 25,27-dialkyloxy-5,17-diarylcalix[4]arenes-crown-6 **1a–f**.

1,3-dialkyloxycalix[4]arene-crown-6 have been reported by subtle changes in the calix[4]arene skeleton, as distinguished by choosing different alkyl chain lengths and structures [6–8,17–19], and by inserting 1,3-dioxybenzene moieties in the crown ether [6,10,16,20]. Introduction of various substituted aromatic rings connected to the calix[4]arene skeleton in positions 5 and 17 could result in an optimized conformational structure for metal ion encapsulation due to the potential rigidity and flatness of linkages caused by electronic and steric interactions. The incorporation of such aromatic moieties is designed to enhance the complex solubility in organic media, and partially to improve the selectivity for cesium ions. Such an approach was based on structure–activity considerations related to the influence of the ligands lipophilicity towards extraction solvents [21,22]. With this in mind, we aimed to synthesize a series of 1,3-alternate 25,27-dialkyloxy-5,17-diarylcalix[4]arene-crown-6 **1** to investigate their complexation behavior towards cesium metal ions through solvent extraction (Fig. 1).

A complete spectrometric study was undertaken using ^{1}H, ^{13}C, 2D NMR and ROESY analysis and X-ray crystallography. The X-ray crystal structures of **1a** and its cesium picrate complex were established. Solid-state data were used to determine the complexation behavior of these new ligands in relation to their use in the field of nuclear waste treatment, which of great importance given current environmental concerns.

RESULTS AND DISCUSSION

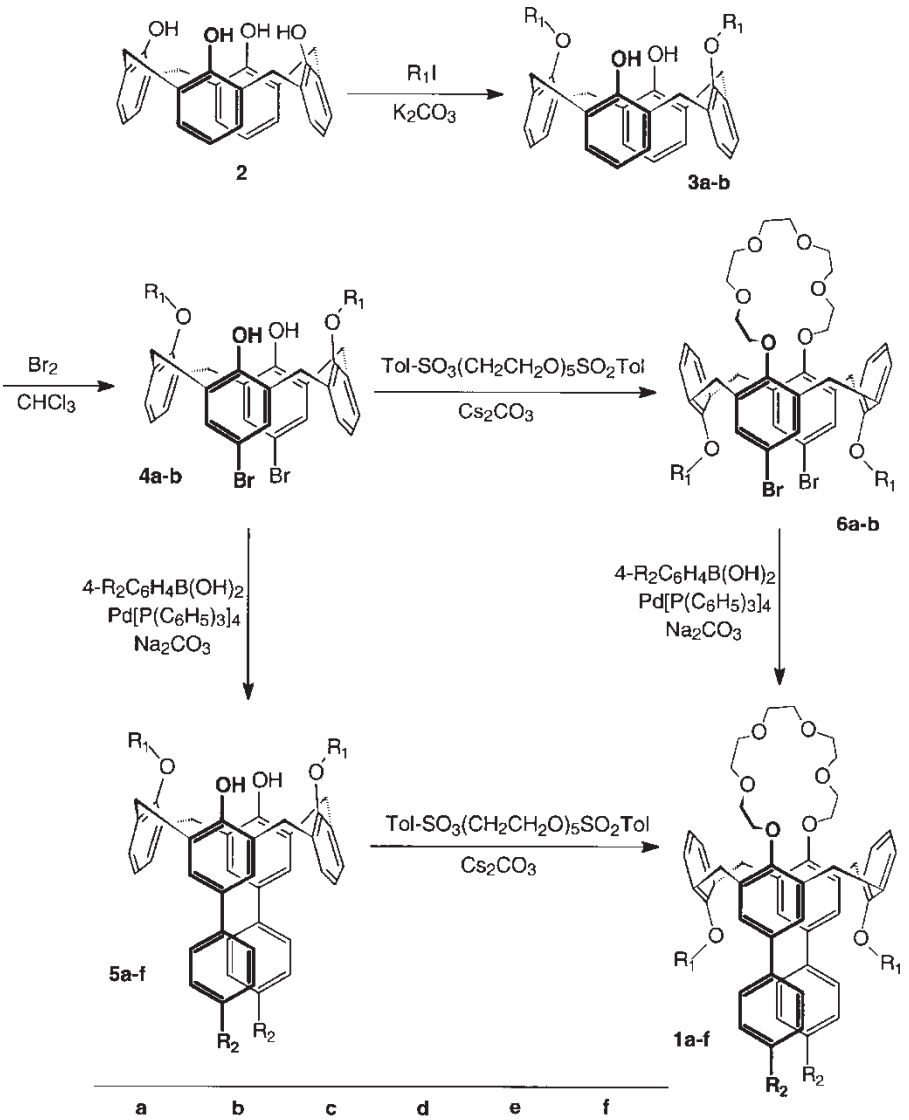
Synthesis

The 1,3-alternate 25,27-dialkyloxy-5,17-diarylcalix[4]arenes-crown-6 **1a–f** were prepared by two alternative routes (Scheme 1). The first was a four-step procedure from commercially available calix[4]arene **2** and involved dipropylation, bromination, Suzuki cross-coupling reaction and etherification.

The reaction of **2** with 1-iodoalkane in K_2CO_3–CH_3CN gave mainly the well-known diametrically substituted cone 25,27-dialkyloxycalix[4]arenes **3a** and **3b** [8,18,19]. The 5,17-dibromo-25,27-dialkyloxycalix[4]arene derivatives **4a** and **4b** were then prepared by regioselective bromination of the calixarene dialkyl ethers **3a** and **3b** [23–25]. Both **4a** and **4b** were characterized as being in the cone conformation at room temperature by the presence of two doublets ($J \approx 13$ Hz) in their ^{1}H NMR spectra for the bridging methylenes at $\delta \sim 3.35$ and 4.28 ppm. 25,27-Dialkyloxy-5,17-diarylcalix[4]arenes **5a–f** were prepared in fairly good yield (54–82%) by a Suzuki cross-coupling reaction of calixarenes **4a** and **4b** with various substituted arylboronic acids in the presence of $Pd(PPh_3)_4$ as a catalyst and a 2 M aqueous solution of sodium carbonate [25–27]. This reaction selectively led to diametrically 5,17-substituted calix[4]arenes **5a–f** in the cone conformation, as substantiated by the characteristic chemical shift ($\delta = 3.47$–3.50 and 4.39–4.42 ppm) and coupling constants ($J = 12.90$–13.05 Hz) of the two types of diastereotopic proton signals of the methylene bridges. The 3D structure of **5a** was established by X-ray crystallography and confirmed the cone conformation in the solid state as anticipated on the basis of ^{1}H NMR data (Fig. 2).

Reaction of **5a–f** with pentaethylene glycol ditosylate in DMF using Cs_2CO_3 as a base (and template) gave 1,3-alternate calix[4]arenes-crown-6 **1a–f** in 19–28% yields. The singlet at 3.86–3.88 ppm is highly characteristic for the methylene bridge protons of 1,3-alternate calix[4]arene-crown-6. The ^{13}C NMR spectra show one signal around 38 ppm, specific for *anti*oriented nuclei. In the ROESY spectrum, strong through-space correlations of some crown ether protons with the doublet at 7.15 ppm and the triplet at 6.89 ppm indicate that these signals belong to the aromatic rings bearing the alkyl groups. ROESY also clearly corroborate the 1,3-alternate conformation because the singlet of aromatic protons in the *meta* position of the crown ether nuclei (7.27 ppm) are correlated with the alkyloxy protons. In addition, the methylene protons $ArCH_2Ar$ correlate with the aromatic *meta* proton bearing the crown ether. This 1,3-alternate conformation was also proved by the X-ray crystal structure as shown in Fig. 3 for **1a**, which presents two independent molecules (designated as A and B) in the asymmetric unit.

The second investigated route to **1a–f** first involved the bridging of dibromocalixarenes **4a** and **4b** with pentaethylene glycol ditosylate with Cs_2CO_3



	a	b	c	d	e	f
R_1	*n*-C_3H_7-	*n*-C_8H_{17}-	*n*-C_3H_7-	*n*-C_8H_{17}-	*n*-C_3H_7-	*n*-C_3H_7-
R_2	H-	H-	CH_3O-	CH_3O-	C_2H_5O-	*n*-C_4H_9O-

SCHEME 1 Synthesis of 1,3-alternate 25,27-dialkyloxy-5,17-diarylcalix[4]arenes-crown-6 **1a–f**.

as the base to produce **6a** and **6b** in the 1,3-alternate conformation [28]. This was then followed by the Suzuki-type cross-coupling of **6a** and **6b** with arylboronic acids to introduce aromatic rings in positions 5 and 17 of the calixarene moiety (Scheme 1). All the NMR spectra confirmed the proposed structure.

Extraction of Cesium

A first estimation of the ionophoric properties of ligands **1a–f** was achieved with sodium, potassium and cesium picrate, according to the extraction method developed by Pedersen [29–31]. The results, expressed as extraction percentage (Ex%), are reported in Table I.

High extraction percentages towards Cs^+ (Ex% = 51.5–55.0) were measured for **1a–f**. A strong preference for Cs^+ was found in comparison with that for Na^+ and K^+ (Ex% = 2.0–2.8 and 14.4–15.2, respectively). The cesium extraction results are readily explained by the preorganization of the ligand and by the fact that the less polar 1,3-alternate conformation allows the interaction of the cesium ion with the π-electron cloud of the arene rings [7,8].

Under these experimental conditions, it may be seen that the introduction of various substituted aryl rings at the lower rim of the aromatic moieties in the calixarene skeleton slightly increases their cesium picrate extraction ability with respect to di-Oct calix C6 and di-*n*-Pr calix C6, used as references.

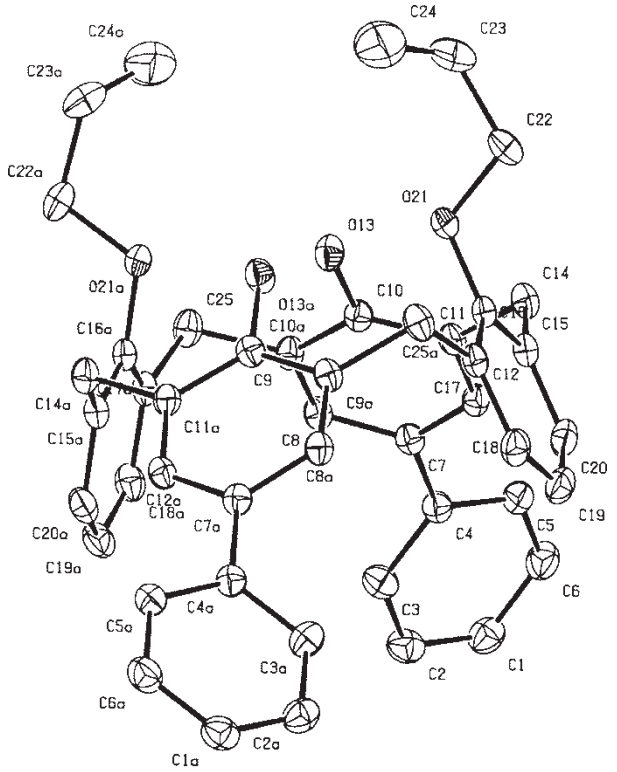


FIGURE 2 A view of **5a** with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, H atoms are omitted for clarity.

The efficiency of **1a**–**f** for cesium ion extraction may be ascribed to the rigidity and flatness of the calixarene framework, enabling it to easily encapsulate the cesium ion, and also to the presence of the aromatic moieties in positions 5 and 17, which enhance the solubility of the complexes in organic media [21,22].

TABLE I Extraction percentage (Ex%) of sodium, potassium and cesium picrate by calix-crowns **1a**–**f**, from water to dichloromethane, at 20°C*

Ligand	Na^+	K^+	Cs^+
di-Oct calix C6	2.2 ± 0.3	14.1 ± 0.3	51.1 ± 0.5
di-nPr calix C6	2.0 ± 0.4	14.6 ± 0.4	50.7 ± 0.5
1a	2.0 ± 0.3	15.1 ± 0.5	51.5 ± 0.7
1b	2.6 ± 0.5	14.8 ± 0.6	55.0 ± 0.4
1c	2.2 ± 0.5	15.2 ± 0.5	53.9 ± 0.5
1d	2.8 ± 0.6	14.4 ± 0.4	53.1 ± 0.5
1e	2.6 ± 0.4	14.6 ± 0.6	52.5 ± 0.7
1f	2.3 ± 0.3	14.5 ± 0.4	52.7 ± 0.3

*Standard deviation σ_{n-1} on the mean of $n = 4$ experiments.

Solid-state Structure

Crystals of **1a** and its cesium picrate complex **1a**·CsPic were studied by X-ray crystallography (Figs. 3 and 4). The structure of **1a** can be compared to that of 1,3-alternate dioctyloxycalix[4]arene benzocrown-6 [32], the only previously published structure of an uncomplexed 1,3-alternate dialkyloxycalix[4]arene crown-6 ether (Table II).

Two molecules (designed as A and B) were found in the asymmetric unit, each with a distinct crown conformation. In both molecules, the crown cavity is collapsed in on itself, as typically observed for large uncomplexed crown-ether molecules [33]. In molecules A and B, the O49–O64 distances were

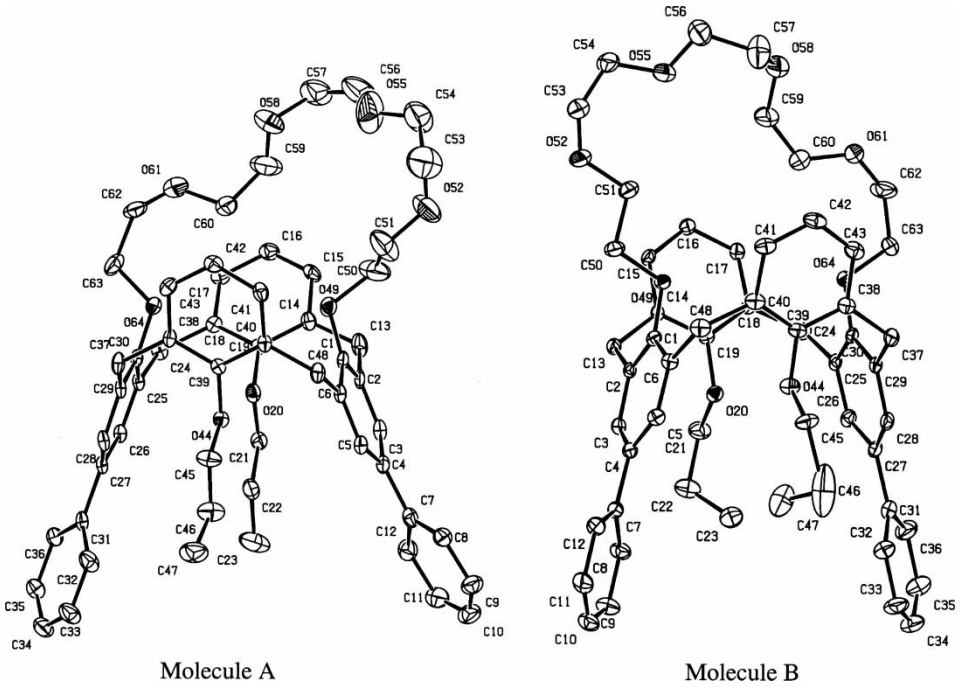


FIGURE 3 A view of **1a** (molecules A and B) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, H atoms are omitted for clarity.

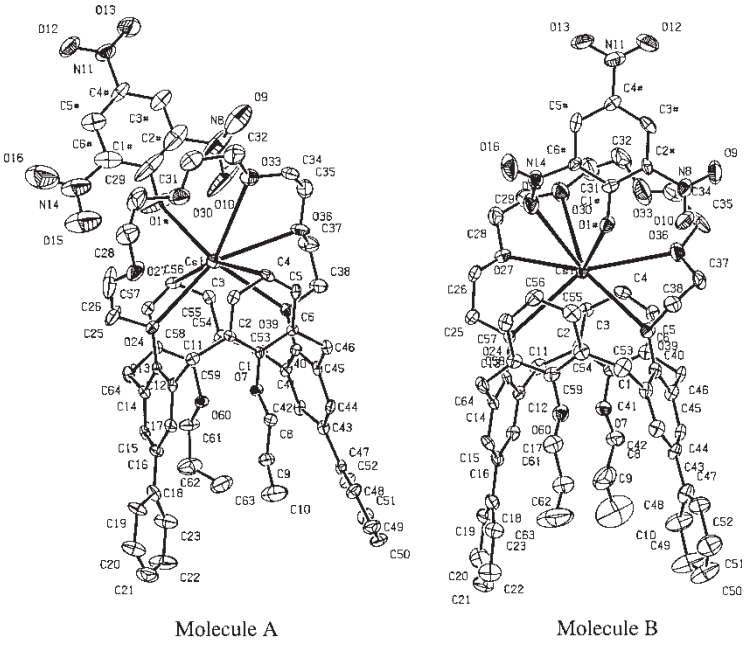


FIGURE 4 A view of **1a**·CsPic complex (molecules A and B) with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, H atoms are omitted for clarity.

4.790(8) and 4.491(8) Å, respectively, and the distances between the two phenyl rings bearing the alkyloxy moieties (C16–C42) were 6.619(9) and 7.425(9) Å, respectively. Similar O_{phenyl}–O_{phenyl} distances in the previously described 1,3-alternate dioctyloxycalix[4]arene benzocrown-6 [32] were found at 4.543 and 4.61 Å, while the homologous C–C distances range from 7.05 to 7.07 Å.

The X-ray crystal structure of **1a**·CsPic is depicted in Fig. 4. As previously reported for the free ligand **1a**, two independent molecules (designated A and B), were found in the crystal unit. The structure of **1a**·CsPic (Fig. 4) shows the ligand around the cation, with the latter encapsulated in the polar cage created by the oxygen atoms of the crown-6 and the two inverted aromatic rings C1–C6 and C54–C59 of the calix[4]arene. The cation was found positioned between the two aromatic rings.

By reference to **1a**, the O24–O39 distance in **1a**·CsPic increases by about 0.1–0.6 Å to 4.890(10)–5.092(12) Å in molecules A and B (Table III).

TABLE II Relevant interatomic distances (Å) observed in calixarene **1a**

	Molecule A	Molecule B
C1–C30	5.286(8)	5.264(7)
O49–O64	4.790(8)	4.491(8)
O52–O61	6.984(7)	6.720(8)
C16–C42	6.619(9)	7.425(9)
C19–C39	5.180(7)	5.043(8)
C4–C27	6.687(8)	7.099(6)
C7–C31	7.530(9)	8.273(7)
C10–C34	9.042(9)	10.687(10)

In **1a**·CsPic, the Cs–O24 and Cs–O39 distances are 3.154(6) and 3.273(6) Å for molecule A, and 3.380(6) and 3.089(8) Å for molecule B, respectively. The remaining Cs–O_{crown} bond lengths in the coordination sphere are spread over a wide range [3.152(9)–3.885(7) Å for molecule A and 3.089(8)–3.506(7) Å for molecule B]. Data appear consistent with the O_{phenyl}–O_{phenyl} distances for previously reported Cs·calix[4]arene-crown-6 structures, which range from 4.7 to 4.9 Å, and with typical Cs–O_{phenyl} distances observed between 3.2 and 3.3 Å [7,8,32,34,35]. In both A and B molecules, the crown-6 moiety is bent to allow the participation of the picrate ion in the coordination sphere of the cation via its phenoxy oxygen [d(Cs–O1Pic) = 2.958(14) and 3.111(8) Å, respectively]. Only in molecule B is one

TABLE III Relevant interatomic distances (Å) and angles (°) observed in **1a**·CsPic

	Molecule A	Molecule B
O24–O39	5.092(12)	4.890(10)
Cs1–O24	3.154(6)	3.380(6)
Cs1–O39	3.273(6)	3.089(8)
Cs1–O27	3.885(7)	3.167(9)
Cs1–O30	3.536(6)	3.343(7)
Cs1–O33	3.152(9)	3.506(7)
Cs1–O36	3.173(10)	3.193(9)
Cs1–C3	3.464(6)	3.563(11)
Cs1–C4	3.397(11)	3.456(9)
Cs1–C5	3.577(10)	3.685(7)
Cs1–C55	3.711(9)	3.695(9)
Cs1–C56	3.433(12)	3.649(12)
Cs1–C57	3.621(8)	4.021(8)
Cs1–O1(Pic)	2.958(14)	3.111(8)
Cs1–O15(Pic)	–	3.295(10)
C4–Cs1–C56	158.0(2)	152.5(4)

TABLE IV Cation–arene centroid distances, d (Å), and tilt angles, Ψ (°)

		Cs^+	
Arene	Source	d (Å)	Ψ (°)
1,3-Alternate diisopropoxycalix[4]arene-crown-6	X-ray [32]	3.80	20
		3.52	14
1,3-Alternate dimethoxycalix[4]arene-crown-6	MM [32]	3.75	22
		3.43	15
1,3-Alternate dihydrocalix[4]arene-benzocrown-6	X-ray [32]	3.88	12
		3.42	8
1a·CsPic (molecule A)	X-ray	3.91	23
		3.66	12
1a·CsPic (molecule B)	X-ray	4.01	17
		3.79	16

X-ray and MM, respectively, denote X-ray crystallography and molecular mechanics.

oxygen atom of the adjacent NO_2 group used as a ligand [d(Cs–O15Pic) = 3.295(10) Å].

In the crystal structure of **1a**·CsPic, cation–π interactions are possible between the metal ion and some carbon atoms of the two rotated benzene rings. Hence, the Cs–C4 and Cs–C56 contacts range from 3.397(11) to 3.456(9) Å in A, and from 3.433(12) to 3.649(12) Å in B. Similar cation–π interactions have been documented previously [7,8,32–34].

In addition, the bond angle of C4–Cs1–C56 (158.0(2)°) in molecule A was observed to be greater than the one in molecule B (152.5(4)°), which could indicate greater cation–π interactions in molecule A than in molecule B.

Examination of the complex structure provided an explanation in terms of the geometric features associated with the π–cation interactions. The bonding interactions between a cation and an arene can be characterized by two geometric parameters: the distance d, between the cation and the centroid of the arene ring, and the tilt angle Ψ defined as the angle between the cation–centroid vector and the normal to the arene plane. The stability of the complexes is related to the minimal values [32]. The calculated distances d are of 3.66 and 3.91 Å for molecule A, and 3.79 and 4.01 Å for molecule B, respectively (Table IV). The angles Ψ are 12° and 23° in molecule A of **1a**·CsPic, and 16° and 17° in molecule B, respectively.

These results are in accordance with the previously published values for calix[4]arene crown-6 complexed with Cs^+, and can explain the stability of **1a**·CsPic.

CONCLUSION

In this work the synthesis of the new 1,3-alternate calix[4]arene-crown-6 ethers **1a–f** designed as potential cesium-selective ionophores was reported. Aromatic groups at positions 5 and 17 were introduced to enhance the complex solubility in organic media and improve the potential rigidity and flatness linkages. A preliminary quantification of their ionophoric properties was achieved by a two-phase solvent extraction followed by a UV spectroscopic procedure, showing high efficiency towards extraction of the cesium cation. Based on the results of the X-ray crystal structure determination of **1a** and its cesium picrate complex **1a**·CsPic, an initial approach to the complexation behavior of these new ligands was proposed. This should be confirmed by a complementary study involving the bulk liquid membrane system [7,8,16,36] to determine the transport rate of the cesium ions and measure their selectivity relative to other alkali metal ions. Nevertheless, the improved solubility of the new calixarenes **1a–f**, which will allow their use in supported liquid membranes, makes them highly attractive for treatment of radioactive waste, an important environmental problem.

MATERIALS AND METHODS

Commercially produced reagents were used as received without additional purification. Melting points were determined with an SM-LUX-POL Leitz hot-stage microscope and are uncorrected. IR spectra were recorded on a Bruker IFS-25 spectrophotometer. Absorption spectra was measured on a Perkin Elmer Lambda 2 UV–Vis scanning spectrophotometer. NMR spectra were recorded with tetramethylsilane as internal standard using a Bruker Avance 300 spectrometer (^{1}H, ^{13}C) or a Bruker Avance 500 spectrometer (^{1}H, ^{13}C, HMQC, HMBC, TOCSY, ROESY). Splitting patterns were designated as follows: s = singlet; d = doublet; t = triplet; q = quartet; qt = quintuplet; sex = sextuplet; m = mutiplet. Analytical TLC was carried out on 0.25 precoated silica gel plates (Polygram SIL G/UV_{254}) with visualization by irradiation with a UV lamp. Silica gel 60 (70–230 mesh) was used for column chromatography. Elemental analyses (C, H) for new

compounds were performed by CNRS (Vernaison, France) and agreed with the proposed structures within ±0.3% of the theoretical values. All solvents and reagents were purchased from Acros and Aldrich Chimie and used without further purification.

In the NMR spectra, the 'Ar' notation indicates the aromatic nuclei of the calixarene backbone, considering the phenol oxygen as the main substituent to which the ipso, ortho, meta and para positions refer.

Synthesis of 25,27-Dialkyloxy-5,17-dibromocalix[4]arene, Cones 4a and 4b (General Procedure)†

To a cooled (0°C), stirred solution of **3a** or **3b** (1.97 mmol) in anhydrous $CHCl_3$ (40 mL) was added a solution of Br_2 (0.20 mL, 3.94 mmol) in anhydrous $CHCl_3$ (40 mL) during 20 min. The solution was stirred at 0°C for 1 h and at RT for 1 h, and then concentrated under reduced pressure. The solid residue was triturated in hexane, filtered, and then washed with methanol to give **4a** and **4b**.

25,27-Dipropyloxy-5,17-dibromocalix[4]arene, Cone 4a

White crystals (97%); mp 371°C [23–25].

25,27-Dioctyloxy-5,17-dibromocalix[4]arene, Cone 4b

White crystals (93%); mp 162°C. IR (KBr) ν 3410 cm^{-1} (OH). ^1H NMR ($CDCl_3$) δ 8.34 (s, 2H, O*H*), 7.18 (s, 4H, Ar-*H* meta), 6.95 (d, J = 7.50 Hz, 4H, Ar-*H* meta), 6.82 (t, J = 7.50 Hz, 2H, Ar-*H* para), 4.27 (d, J = 13.20 Hz, 4H, ArCH_2Ar), 3.99 (t, J = 6.85 Hz, 4H, OCH_2), 3.34 (d, J = 13.20 Hz, 4H, ArCH_2Ar), 2.07 (qt, J = 6.85 Hz, 4H, CH_2), 1.68 (qt, J = 6.85 Hz, 4H, CH_2), 1.49–1.33 (m, 16H, CH_2), 0.91 (t, J = 6.85 Hz, 6H, CH_3). Anal. Calcd for $C_{44}H_{54}Br_2O_4$: C, 65.51; H, 6.75. Found: C, 65.75; H, 6.89.

Synthesis of 25,27-Dialkyloxy-5,17-diarylcalix[4]arene, Cones 5a–f (General Procedure)

A mixture of cones **4a** or **4b** (3.30 mmol), arylboronic acid (8.25 mmol), tetrakis(triphenylphosphine)palladium(0) (0.39 mmol), anhydrous toluene (55 mL) and anhydrous CH_3OH (15 mL) was stirred at 100°C for 15 min and then treated with 2 M aqueous Na_2CO_3 (9 mL). The suspension was stirred at 100°C for 4 h, cooled to room temperature, diluted with CH_2Cl_2 (100 mL), washed 2 M aqueous Na_2CO_3 (50 mL) containing 3 mL of concentrated NH_3 and then with water (50 mL), dried over Na_2SO_4 and concentrated. The residue was triturated in CH_3OH to give **5a–f** as crystals, which were filtered, washed with CH_3OH and dried.

25,27-Dipropyloxy-5,17-diphenylcalix[4]arene, Cone 5a

Pale yellow crystals (64%); mp 302°C. IR (KBr) ν 3405 cm^{-1} (OH). ^1H NMR ($CDCl_3$) δ 8.56 (s, 2H, O*H*), 7.56 (d, J = 7.35 Hz, 4H, Ar′-*H* ortho), 7.43 (t, J = 7.35 Hz, 4H, Ar′-*H* meta), 7.32 (s, 4H, Ar-*H* meta), 7.30 (t, J = 7.35 Hz, 2H, Ar′-*H* para), 7.04 (d, J = 7.55 Hz, 4H, Ar-*H* meta), 6.82 (t, J = 7.55 Hz, 2H, Ar-*H* para), 4.42 (d, J = 12.90 Hz, 4H, ArCH_2Ar), 4.05 (t, J = 6.55 Hz, 4H, OCH_2), 3.50 (d, J = 12.90 Hz, 4H, ArCH_2Ar), 2.14 (sex, J = 6.55 Hz, 4H, CH_2), 1.39 (t, J = 6.55 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 153.1 (Ar ipso),151.9 (Ar ipso), 141.5 (Ar′ ipso), 133.4 (Ar para), 132.2 (Ar′ meta), 129.1 (Ar meta), 128.5 (Ar ortho), 128.4 (Ar′ para), 127.2 (Ar′ ortho), 126.7 (Ar ortho), 126.2 (Ar meta), 125.4 (Ar para), 78.4 (OCH_2), 31.6 (ArCH_2Ar), 23.5 (CH_2), 10.9 (CH_3). Anal. Calcd for $C_{46}H_{44}O_4$: C, 83.60; H, 6.71. Found: C, 83.75; H, 6.82.

25,27-Dioctyloxy-5,17-diphenylcalix[4]arene, Cone 5b

White crystals (72%); mp 51°C. IR (KBr) ν 3400 cm^{-1} (OH). ^1H NMR ($CDCl_3$) δ 8.49 (s, 2H, O*H*), 7.55 (d, J = 7.40 Hz, 4H, Ar′-*H* ortho), 7.42 (t, J = 7.40 Hz, 4H, Ar′-*H* meta), 7.32 (s, 4H, Ar-*H* meta), 7.30 (t, J = 7.40 Hz, 2H, Ar′-*H* para), 7.03 (d, J = 7.55 Hz, 4H, Ar-*H* meta), 6.82 (t, J = 7.55 Hz, 2H, Ar-*H* para), 4.42 (d, J = 12.90 Hz, 4H, ArCH_2-Ar), 4.07 (t, J = 6.70 Hz, 4H, OCH_2), 3.51 (d, J = 12.90 Hz, 4H, ArCH_2Ar), 2.14 (qt, J = 6.70 Hz,4H, CH_2), 1.77 (qt, J = 6.70 Hz, 4H, CH_2), 1.55–1.37 (m, 16H, CH_2), 0.95 (t, J = 6.70 Hz, 6H, CH_3). Anal. Calcd for $C_{56}H_{64}O_4$: C, 83.96; H, 8.05. Found: C, 83.91; H, 8.17.

25,27-Dipropyloxy-5,17-di(4-methoxyphenyl)calix[4]arene, Cone 5c

Pale yellow crystals (61%); mp > 350°C. IR (KBr) ν 3410 cm^{-1} (OH). ^1H NMR ($CDCl_3$) δ 8.47 (s, 2H, O*H*), 7.46 (d, J = 8.00 Hz, 4H, Ar′-*H* ortho), 7.25 (s, 4H, Ar-*H* meta), 7.02 (d, J = 7.65 Hz, 4H, Ar-*H* meta), 6.95 (d, J = 8.00 Hz, 4H, Ar′-*H* meta), 6.83 (t, J = 7.65 Hz, 2H, Ar-*H* para), 4.39

†The name calix[4]arene is used instead of the official *Chemical Abstracts* name: pentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-25,26,27,28-tetrol.

(d, $J = 13.05$ Hz, 4H, ArCH_2Ar), 4.03 (t, $J = 6.50$ Hz, 4H, OCH_2), 3.85 (s, 6H, CH_3O), 3.47 (d, $J = 13.05$ Hz, 4H, ArCH_2Ar), 2.11 (sex, $J = 6.50$ Hz, 4H, CH_2), 1.36 (t, $J = 6.50$ Hz, 6H, CH_3). Anal. Calcd for $C_{48}H_{48}O_6$: C, 79.97; H, 6.71. Found: C, 80.12; H, 6.78.

25,27-Dioctyloxy-5,17-di(4-methoxyphenyl) calix[4]arene, Cone 5d

Pale yellow crystals (54%); mp 310°C. IR (KBr) ν 3410 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$) δ 8.39 (s, 2H, O*H*), 7.49 (d, $J = 8.70$ Hz, 4H, Ar′-*H* ortho), 7.25 (s, 4H, Ar-*H* meta), 7.01 (d, $J = 7.55$ Hz, 4H, Ar-*H* meta), 6.96 (d, $J = 8.70$ Hz, 4H, Ar′-*H* meta), 6.79 (t, $J = 7.55$ Hz, 2H, Ar-*H* para), 4.39 (d, $J = 12.90$ Hz, 4H, ArCH_2Ar), 4.03 (t, $J = 6.85$ Hz, 4H, OCH_2), 3.86 (s, 6H, CH_3O), 3.46 (d, $J = 12.90$ Hz, 4H, ArCH_2Ar), 2.12 (qt, $J = 6.85$ Hz, 4H, CH_2), 1.74 (qt, $J = 6.85$ Hz, 4H, CH_2), 1.50–1.35 (m, 16H, CH_2), 0.93 (t, $J = 6.85$ Hz, 6H, CH_3). Anal. Calcd for $C_{58}H_{68}O_6$: C, 80.89; H, 7.96. Found: C, 80.96; H, 7.73.

25,27-Dipropyloxy-5,17-di(4-ethoxyphenyl) calix[4]arene, Cone 5e

Beige crystals (80%); mp > 300°C. IR (KBr) ν 3400 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$) δ 8.46 (s, 2H, O*H*), 7.48 (d, $J = 8.60$ Hz, 2H, Ar′-*H* ortho), 7.45 (d, $J = 8.60$ Hz, 2H, Ar′-*H* ortho), 7.25 (s, 4H, Ar-*H* meta), 7.02 (d, $J = 7.55$ Hz, 4H, Ar-*H* meta), 6.96 (d, $J = 8.60$ Hz, 2H, Ar′-*H* meta), 6.94 (d, $J = 8.60$ Hz, 2H, Ar′-*H* meta), 6.80 (t, $J = 7.55$ Hz, 2H, Ar-*H* para), 4.40 (d, $J = 12.90$ Hz, 4H, ArCH_2Ar), 4.08 (q, $J = 7.00$ Hz, 4H, OCH_2), 4.03 (t, $J = 6.85$ Hz, 4H, OCH_2), 3.47 (d, $J = 12.90$ Hz, 4H, ArCH_2Ar), 2.11 (sex, $J = 6.85$ Hz, 4H, CH_2), 1.46 (t, $J = 7.00$ Hz, 6H, CH_3), 1.36 (t, $J = 6.85$ Hz, 6H, CH_3). Anal. Calcd for $C_{50}H_{52}O_6$: C, 80.18; H, 7.00. Found: C, 80.24; H, 6.88.

25,27-Dipropyloxy-5,17-di(4-n-buthoxyphenyl) calix[4]arene, Cone 5f

Beige crystals (82%); mp 232°C. IR (KBr) ν 3410 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$) δ 8.45 (s, 2H, O*H*), 7.45 (d, $J = 8.70$ Hz, 4H, Ar′-*H* ortho), 7.25 (s, 4H, Ar-*H* meta), 7.04 (d, $J = 7.55$ Hz, 4H, Ar-*H* meta), 6.94 (d, $J = 8.70$ Hz, 4H, Ar′-*H* meta), 6.81 (t, $J = 7.55$ Hz, 2H, Ar-*H* para), 4.40 (d, $J = 12.90$ Hz, 4H, ArCH_2Ar), 4.04 (t, $J = 7.40$ Hz, 4H, OCH_2), 4.00 (t, $J = 7.00$ Hz, 4H, OCH_2), 3.47 (d, $J = 12.90$ Hz, 4H, ArCH_2Ar), 2.14 (sex, $J = 7.00$ Hz, 4H, CH_2), 1.82 (qt, $J = 7.40$ Hz, 4H, OCH_2), 1.54 (sex, $J = 7.40$ Hz, 4H, OCH_2), 1.37 (t, $J = 7.00$ Hz, 6H, CH_3), 1.01 (t, $J = 7.40$ Hz, 6H, CH_3). Anal. Calcd for $C_{54}H_{60}O_6$: C, 80.56; H, 7.51. Found: C, 80.67; H, 7.65.

Synthesis of 25,27-Dialkyloxy-5,17-dibromocalix[4] arene-crown-6, 1,3-Alternate 6a and 6b (General Procedure)

A mixture of calix[4]arene derivatives **4a** or **4b** (4.13 mmol) and Cs_2CO_3 (62 mmol) in DMF (550 mL) was heated at 80°C for 15 min. Subsequently, pentaethylene glycol ditoluene-*p*-sulfonate (4.54 mmol) was added and the reaction mixture was heated at 80°C for 16 h. Then DMF was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (350 mL), washed with H_2O (2 × 250 mL), and dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/1, then 4/1) to give crude calix[4]arene, which was triturated in hot CH_3OH to give **6a** and **6b**.

25,27-Dipropyloxy-5,17-dibromocalix[4]arene-crown-6, 1,3-Alternate 6a

White crystals (30%); mp 183°C [28].

25,27-Dioctyloxy-5,17-dibromocalix[4]arene-crown-6, 1,3-Alternate 6b

White crystals (28%); mp 41°C; ^{1}H NMR ($CDCl_3$) δ7.19 (s, 4H, Ar-*H* meta), 7.08 (d, $J = 7.35$ Hz, 4H, Ar-*H* meta), 6.86 (t, $J = 7.35$ Hz, 2H, Ar-*H* para), 3.75 (s, 8H, ArCH_2Ar), 3.70 (s, 4H, OCH_2), 3.64 (m, 4H, OCH_2), 3.51 (m, 8H, OCH_2), 3.42 (m, 8H, OCH_2), 1.35 (m, 24H, CH_2), 0.93 (t, $J = 7.10$ Hz, 6H, CH_3). Anal. Calcd for $C_{54}H_{72}Br_2O_8$: C, 64.28; H, 7.19. Found: C, 64.36; H, 7.23.

Synthesis of 25,27-Dialkyloxy-5,17-diarylcalix[4] arene-crown-6, 1,3-Alternate 1a–f (General Procedure)

Method A. A mixture of calix[4]arene derivative **5a–f** (2.12 mmol) and Cs_2CO_3 (31.8 mmol) in DMF (280 mL) was heated at 80°C for 15 min. Subsequently, pentaethylene glycol ditoluene-*p*-sulfonate (2.33 mmol) was added and the reaction mixture was heated at 80°C for 16 h. Then DMF was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (250 mL), washed with H_2O (2 × 180 mL), and dried over Na_2SO_4. Evaporation of the solvent gave a residue that was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/1, then 4/1) to give crude calix[4]arene, which was triturated in hot CH_3OH to give **1a–f**.

25,27-Dipropyloxy-5,17-diphenylcalix[4]arene-crown-6, 1,3-Alternate 1a

White crystals (23%); mp 116°C; ^{1}H NMR ($CDCl_3$) δ 7.47 (d, $J = 7.40$ Hz, 4H, Ar′-*H* ortho), 7.34

(t, $J = 7.40$ Hz, 4H, Ar′-*H* meta), 7.28 (t, $J = 7.40$ Hz, 2H, Ar′-*H* para), 7.27 (s, 4H, Ar-*H* meta), 7.15 (d, $J = 7.45$ Hz, 4H, Ar-*H* meta), 6.89 (t, $J = 7.45$ Hz, 2H, Ar-*H* para), 3.88 (s, 8H, ArCH_2Ar), 3.75 (s, 4H, OCH_2), 3.70 (t, $J = 5.15$ Hz, 4H, OCH_2), 3.68 (t, $J = 6.05$ Hz, 4H, OCH_2), 3.57 (t, $J = 5.15$ Hz, 4H, OCH_2), 3.48 (t, $J = 7.40$ Hz, 4H, OCH_2), 3.41 (t, $J = 6.05$ Hz, 4H, OCH_2), 1.24 (sex, $J = 7.40$ Hz, 4H, CH_2), 0.57 (t, $J = 7.40$ Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 157.4 (Ar ipso), 156.7 (Ar ipso), 141.6 (Ar para), 135.3 (Ar′ ipso), 134.3 (Ar ortho), 134.1 (Ar ortho), 130.1 (Ar meta), 128.9 (Ar′ meta), 128.8 (Ar meta), 127.0 (Ar′ ortho), 126.7 (Ar′ para), 122.6 (Ar para), 72.8 (OCH_2), 71.6, 71.4, 71.3, 70.3, 70.2 (OCH_2), 38.5 (ArCH_2Ar), 23.2 (CH_2), 10.0 (CH_3). Anal. Calcd for $C_{56}H_{62}O_8$: C, 77.93; H, 7.24. Found: C, 78.03; H, 7.36.

25,27-Dioctyloxy-5,17-diphenylcalix[4]arene-crown-6, 1,3-Alternate 1b

White crystals (20%); mp 72°C; ^{1}H NMR ($CDCl_3$) δ 7.51 (d, $J = 7.20$ Hz, 4H, Ar′-*H* ortho), 7.32 (t, $J = 7.20$ Hz, 4H, Ar′-*H* meta), 7.29 (s, 4H, Ar-*H* meta), 7.27 (t, $J = 7.20$ Hz, 2H, Ar′-*H* para), 7.15 (d, $J = 7.40$ Hz, 4H, Ar-*H* meta), 6.90 (t, $J = 7.40$ Hz, 2H, Ar-*H* para), 3.89 (s, 8H, ArCH_2Ar), 3.75 (s, 4H, OCH_2), 3.69 (t, $J = 5.20$ Hz, 4H, OCH_2), 3.66 (t, $J = 6.00$ Hz, 4H, OCH_2), 3.50 (m, 4H, OCH_2), 3.44 (m, 8H, OCH_2), 1.23–0.93 (m, 24H, CH_2), 0.89 (t, $J = 7.00$ Hz, 6H, CH_3). Anal. Calcd for $C_{66}H_{82}O_8$: C, 79.00; H, 8.24. Found: C, 78.85; H, 8.20.

25,27-Dipropyloxy-5,17-di(4-methoxyphenyl) calix[4]arene-crown-6, 1,3-Alternate 1c

White crystals (28%); mp 194°C; ^{1}H NMR ($CDCl_3$) δ 7.39 (d, $J = 8.75$ Hz, 4H, Ar′-*H* ortho), 7.22 (s, 4H, Ar-*H* meta), 7.15 (d, $J = 7.35$ Hz, 4H, Ar-*H* meta), 6.89 (t, $J = 7.35$ Hz, 2H, Ar-*H* para), 6.87 (d, $J = 8.75$ Hz, 4H, Ar′-*H* meta), 3.86 (s, 6H, CH_3O), 3.85 (s, 8H, ArCH_2Ar), 3.75 (s, 4H, OCH_2), 3.71 (t, $J = 5.00$ Hz, 4H, OCH_2), 3.69 (t, $J = 6.20$ Hz, 4H, OCH_2), 3.58 (t, $J = 5.00$ Hz, 4H, OCH_2), 3.47 (t, $J = 7.45$ Hz, 4H, OCH_2), 3.43 (t, $J = 6.20$ Hz, 4H, OCH_2), 1.28 (sex, $J = 7.45$ Hz, 4H, CH_2), 0.60 (t, $J = 7.45$ Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 157.3 (Ar ipso), 156.5 (Ar ipso), 155.1 (Ar′ para), 134.5 (Ar′ ipso), 133.9 (Ar para), 133.8 (Ar′ ortho), 129.7 (Ar meta), 128.0 (Ar ortho), 127.8 (Ar ortho), 127.6 (Ar meta), 122.1 (Ar para), 113.8 (Ar′), 72.8 (OCH_2), 71.5, 71.4, 71.2, 70.0, 69.9 (OCH_2), 55.2 (CH_3O), 38.0 (ArCH_2Ar), 22.8 (CH_2), 10.1 (CH_3). Anal. Calcd for $C_{58}H_{66}O_{10}$: C, 75.66; H, 7.20. Found: C, 75.79; H, 7.25.

25,27-Dioctyloxy-5,17-di(4-methoxyphenyl) calix[4]arene-crown-6, 1,3-Alternate 1d

White crystals (23%); mp 79°C; ^{1}H NMR ($CDCl_3$) δ 7.43 (d, $J = 8.30$ Hz, 4H, Ar′-*H* ortho), 7.23 (s, 4H, Ar-*H* meta), 7.13 (d, $J = 7.30$ Hz, 4H, Ar-*H* meta), 6.91 (t, $J = 7.30$ Hz, 2H, Ar-*H* para), 6.86 (d, $J = 8.30$ Hz, 4H, Ar′-*H* meta), 3.86 (s, 6H, CH_3O), 3.83 (s, 8H, ArCH_2Ar), 3.74 (s, 4H, OCH_2), 3.67 (m, 8H, OCH_2), 3.50–3.44 (m, 12H, OCH_2), 1.26–1.00 (m, 24H, CH_2), 0.88 (t, $J = 6.95$ Hz, 6H, CH_3). Anal. Calcd for $C_{68}H_{86}O_{10}$: C, 76.80; H, 8.15. Found: C, 76.93; H, 8.29.

25,27-Dipropyloxy-5,17-di(4-ethoxyphenyl) calix[4]arene-crown-6, 1,3-Alternate 1e

White crystals (17%); mp 171°C; ^{1}H NMR ($CDCl_3$) δ 7.38 (d, $J = 8.60$ Hz, 4H, Ar′-*H* ortho), 7.21 (s, 4H, Ar-*H* meta), 7.14 (d, $J = 7.45$ Hz, 4H, Ar-*H* meta), 6.89 (t, $J = 7.45$ Hz, 2H, Ar-*H* para), 6.87 (d, $J = 8.60$ Hz, 4H, Ar′-*H* meta), 4.07 (q, $J = 6.95$ Hz, 4H, OCH_2), 3.86 (s, 8H, ArCH_2Ar), 3.75 (s, 4H, OCH_2), 3.71 (t, $J = 4.95$ Hz, 4H, OCH_2), 3.68 (t, $J = 6.15$ Hz, 4H, OCH_2), 3.57 (t, $J = 4.95$ Hz, 4H, OCH_2), 3.47 (t, $J = 7.40$ Hz, 4H, OCH_2), 3.41 (t, $J = 6.15$ Hz, 4H, OCH_2), 1.47 (t, $J = 6.95$ Hz, 6H, CH_3), 1.27 (sex, $J = 7.40$ Hz, 4H, CH_2), 0.59 (t, $J = 7.40$ Hz, 6H, CH_3). Anal. Calcd for $C_{60}H_{70}O_{10}$: C, 75.76; H, 7.42. Found: C, 75.89; H, 7.46.

25,27-Dipropyloxy-5,17-di(4-butoxyphenyl) calix[4]arene-crown-6, 1,3-Alternate 1f

White crystals (19%); mp 128°C; ^{1}H NMR ($CDCl_3$) δ 7.37 (d, $J = 8.45$ Hz, 4H, Ar′-*H* ortho), 7.21 (s, 4H, Ar-*H* meta), 7.14 (d, $J = 7.30$ Hz, 4H, Ar-*H* meta), 6.89 (t, $J = 7.30$ Hz, 2H, Ar-*H* para), 6.87 (d, $J = 8.45$ Hz, 4H, Ar′-*H* meta), 3.99 (t, $J = 7.00$ Hz, 4H, OCH_2), 3.86 (s, 8H, ArCH_2Ar), 3.75 (s, 4H, OCH_2), 3.70 (t, $J = 5.05$ Hz, 4H, OCH_2), 3.68 (t, $J = 6.20$ Hz, 4H, OCH_2), 3.56 (t, $J = 5.05$ Hz, 4H, OCH_2), 3.45 (t, $J = 7.20$ Hz, 4H, OCH_2), 3.40 (t, $J = 6.20$ Hz, 4H, OCH_2), 1.81 (sex, $J = 7.00$ Hz, 4H, CH_2), 1.53 (qt, $J = 7.00$ Hz, 4H, CH_2), 1.25 (sex, $J = 7.20$ Hz, 4H, CH_2), 1.01 (t, $J = 7.00$ Hz, 6H, CH_3), 0.58 (t, $J = 7.20$ Hz, 6H, CH_3). Anal. Calcd for $C_{64}H_{78}O_{10}$: C, 76.31; H, 7.80. Found: C, 76.43; H, 7.93.

Method B. A mixture of 25,27-dialkyloxy-5,17-dibromocalix[4]arene-crown-6, 1,3-alternate **6a** or **6b** (1.1 mmol), arylboronic acid (2.62 mmol), tetrakis (triphenylphosphine)palladium(0) (0.33 mmol), anhydrous toluene (45 mL), and anhydrous CH_3OH (5 mL) was stirred at 100°C for 15 min and then treated with 2 M aqueous Na_2CO_3 (3 mL). The suspension was stirred at 100°C for 4 h, cooled to room temperature, diluted with CH_2Cl_2 (100 mL), washed with 2 M aqueous Na_2CO_3 (70 mL) containing 3 mL of concentrated NH_3 and then with water (50 mL), dried over Na_2SO_4 and concentrated. The oily residue was purified by column chromatography (SiO_2, ethyl acetate/hexane = 1/1, then 4/1)

TABLE V Crystal data and structure refinement for compounds **5a**, **1a** and **1a**·CsPic complex

Compound	**5a**	**1a**	**1a**·CsPic
Formula	$C_{46}H_{44}O_4$, $3.5H_2O$	$2C_{56}H_{62}O_8$	$2C_{56}H_{62}O_8$, $2C_6H_2N_3O_7Cs$
Mol. Wt	723.87	1726.11	2448.21
Crystal system	Trigonal	Monoclinic	Triclinic
Space group	$P_{-3}\,c1$	$P2_1/c$	P_{-1}
Cell parameters at 295 K			
a (Å)	25.276(10)	19.850(7)	10.620(6)
b (Å)	25.276(10)	26.185(7)	17.585(6)
c (Å)	11.501(10)	20.330(2)	31.303(8)
α (deg)	90	90	95.56(2)
β (deg)	90	116.22(2)	94.11(3)
γ (deg)	120	90	91.51(4)
V (Å^3)	6363.3(7)	9480(4)	5800(4)
Z	6	4	2
D_{calc} (mg m^{-3})	1.133	1.209	1.402
$F(000)$	2340	3696	2528
Crystal size (mm^3)	0.30 × 0.15 × 0.10	0.50 × 0.25 × 0.03	0.01 × 0.15 × 0.25
No. of unique reflections measured	2881	7534	9357
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.067	1.033	1.053
R $[I > 2\sigma(I)]$	0.0694	0.0712	0.0583
wR^2 $[I > 2\sigma(I)]$	0.1856	0.1795	0.1351

to give crude calix[4]arene, which was triturated in hot CH_3OH to give **1a**–**f**.

25,27-Dipropyloxy-5,17-diphenylcalix[4]arene-crown-6, 1,3-Alternate 1a

White crystals (39%).

25,27-Dioctyloxy-5,17-diphenylcalix[4]arene-crown-6, 1,3-Alternate 1b

White crystals (23%).

25,27-Dipropyloxy-5,17-di(4-methoxyphenyl) calix[4]arene-crown-6, 1,3-Alternate 1c

White crystals (32%).

25,27-Dioctyloxy-5,17-di(4-methoxyphenyl) calix[4]arene-crown-6, 1,3-Alternate 1d

White crystals (25%).

25,27-Dipropyloxy-5,17-di(4-ethoxyphenyl) calix[4]arene-crown-6, 1,3-Alternate 1e

White crystals (21%).

25,27-Dipropyloxy-5,17-di(4-buthoxyphenyl) calix[4]arene-crown-6, 1,3-Alternate 1f

White crystals (13%).

CRYSTALLOGRAPHIC STUDY

The structure of compounds **1a**, **5a** and complex **1a**·CsPic was established by X-ray crystallography (Figs. 2–4, Table V). Colorless single crystals of **1a** and **5a** and yellow crystals of complex **1a**·CsPic were obtained by slow evaporation from methanol/chloroform (20/80) solution.

The unit cell dimensions were determined using the least-squares fit from 25 reflections ($25° < \theta < 35°$) for **1a** and **1a**·CsPic, and 5875 reflections with $1° < \theta < 23°$ were used for unit cell refinement of **5a**. Intensities were collected with an Enraf-Nonius CAD-4 diffractometer using Cu Kα radiation and a graphite monochromator up to $\theta = 45°$ for **1a** and **1a**·CsPic, and with a Bruker-Nonius κ-CCD diffractometer using Mo Kα radiation for **5a**. The data for all three compounds were collected at relatively low resolution, that is no reflections were observed for $\theta > 45°$ with λ_{Cu}, and for $\theta > 23°$ with λ_{Mo}. The data were corrected for Lorentz and polarization effects and for empirical absorption correction [37]. The structure was solved by direct methods using SHELX86 [38] and refined using SHELX97 [39] suite of programs. Crystallographic data for the structures **1a**, **5a** and **1a**·CsPic reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-218900, CCDC-218901 and CCDC-229582, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

PICRATE EXTRACTION MEASUREMENTS

Picrate extraction experiments (Table I) were performed following Pedersen's procedure [8,19,29–31].

A mixture of 5 mL of a 2.5×10^{-4} M aqueous picrate solution and 5 mL of a 2.5×10^{-4} M solution of calixarene in CH_2Cl_2 was vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water bath at 20 ± 0.1°C for 30 min, and finally left standing for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically described as previously (maximum absorption of the picrate ion at 355 nm, $\varepsilon = 14\,285\ \text{mol}^{-1}\,\text{L}\,\text{cm}^{-1}$). The percentage extraction (Ex%) was calculated from the absorbance A of the aqueous phase measured at 355 nm using the equation $\text{Ex}\% = 100(A_0 - A)/A_0$, where A_0 is the absorbance of the aqueous phase of a blank experiment carried out without calixarene.

The sodium, potassium and cesium picrates were prepared as described elsewhere [8,26] by stepwise addition of a 2.0×10^{-2} M aqueous picric acid solution to a 0.14 M aqueous solution of sodium, potassium or cesium hydroxide until neutralization, which was checked by pH control with a glass electrode. The picrates then rapidly washed with ethanol and diethyl ether before being dried *in vacuo* for 24 h.

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