Pentaalkyl ester derivatives of *p*-benzylcalix[5]arene and *p-tert*-octylcalix[5]arene: synthesis, crystal structure and metal ion complexation

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We report the synthesis of two pentamethyl ester derivatives of the *p*-benzyl- (**1**) and *p-tert*-octylcalix[5]arenes (**2**) in the cone conformation. The detailed structure of the already known pentaethyl ester derivative of **1**, established by X-ray crystallography, shows the 1,2-alternate conformation of this compound. The binding properties of the three pentaalkyl esters have been assessed by liquid–liquid extraction and complexation of alkali and silver metal ions in methanol and acetonitrile. These ligands display high selectivities within the alkali series, which depend on different factors such as the conformation, the substituents on the *para*-positions and the functional groups, and the solvent.

Introduction

The base-induced condensation of *p*-substituted phenols and formaldehyde produces the calixarene series,[1] macrocyclic compounds available in a variety of ring sizes, which constitute highly attractive platforms for more elaborate host molecules by chemical modification. Because of their ready accessibility, the *even*-numbered members of the series, in particular calix[4]arenes, have been converted into a wide variety of derivatives designed for the selective complexation of different metal ions.[2,3] In contrast, the chemistry of calix[5]arenes is seldom investigated because the *odd*-numbered calixarenes are obtained in very low yields. The isolation of the first calix[5]arene was reported by Kämmerer *et al.*[4] from *p*-cresol by a stepwise procedure leading to very low yields because of the great number of steps. Subsequently, Ninagawa and Matsuda[5] reported the first one-step synthesis of *p-tert*-butylcalix[5]arene in *ca.* 6% yield. From a different work-up procedure, which involved column chromatography, Markowitz *et al.*[6] reported the isolation of the same compound in a similar yield. This yield was increased to 15% by Stewart and Gutsche[7] following a new synthetic procedure which, while still low, allowed workable amounts of *p-tert*-butylcalix[5]arene to be obtained. Following a quite similar strategy Iwamoto *et al.*[8] reported the synthesis of *p-tert*-butylcalix[5]arene in *ca.* 22% yield. This highest yield arose from the use of HPLC techniques, since these authors showed that even-numbered calixarenes are less soluble in tetralin than odd-numbered ones and are, therefore, easier to isolate. More recently, Haino *et al.*[9] described a stepwise synthesis for the calix[5]arene containing two different *para* substitutents with *ca.* 19% yield. A similar procedure was used by No and Kwon[10] to synthesize four calix[5]arenes containing three different *para* substituents with yields of 27–32%.

We have already described[11] the treatment of *p*-benzyl phenol with formaldehyde in the presence of KOH leading to the calix[5]-, calix[6]- and calix[8]arenes. *p*-Benzylcalix[5]arene **1** was produced in 33% yield, allowing conformational studies. As seen for other calixarenes, the calix[5]arenes present conformational isomerism and can exist in the four discrete forms "cone", "partial cone", "1,2 alternate" and "1,3 alternate". The cone conformation of **1** was evidenced by ^{1}H NMR at low temperature, the ArCH_2Ar displaying a pair of doublets at −30 °C.[11] A distorted cone conformation has recently been evidenced for **1** by single crystal X-ray diffraction.[12] We also introduced *n*-alkyl substituents with increasing length onto the OH groups of **1** in order to gain information on conformational inversion.[13] We demonstrated that the conformational inversion of **1** is inhibited at room temperature when substituents are greater than *n*-propyl. More particularly the pentaethyl ester derivative **1**-CH_2CO_2Et was shown to be in a *fixed* conformation which could not be determined at that time.

In this paper we report our new results on conformational and complexing properties of pentaalkyl derivatives of *p*-benzylcalix[5]arene **1** and of related *p-tert*-octylcalix[5]arene **2**. We first present the synthesis of the pentamethyl ester **1**-CH_2CO_2Me and the pentamethyl ester **2**-CH_2CO_2Me in cone conformation (see Chart 1). Then, we report the determination of the conformation of **1**-CH_2CO_2Et (see Chart 1) by single-crystal X-ray diffraction. This conformation was shown to be 1,2-alternate. The binding properties of **1**-CH_2CO_2Et in the 1,2-alternate conformation and of **1**-CH_2CO_2Me and **2**-CH_2CO_2Me in the cone conformation, towards alkali metal and silver cations have been assessed by extraction experiments from water into dichloromethane and by determination of the stability constants in methanol and acetonitrile. Comparison is made with related pentaalkyl ester derivatives of *p-tert*-butylcalix[5]arene **3** described in the literature.

Results and discussion

Synthesis of the ligands

The treatment of calixarenes with $BrCH_2CO_2R$, as alkylating agents, has been shown to be a useful method for introducing ester groups onto the OH groups.[14,15] In a general manner calix[5]arenes **1** and **2** were reacted with an excess of $BrCH_2CO_2R$ (R = Me or Et) in the presence of K_2CO_3 (also in excess) by refluxing in dry acetone for 6 h. After filtration and washings with acetone and dichloromethane, the crude residues were precipitated with methanol to afford **1**-CH_2CO_2Me (92%) and **2**-CH_2CO_2Me (85%) as white solids. ^{1}H NMR indicated a *cone conformation* for both molecules. Only singlets at 6.57 ppm and 6.85 ppm were detected for the Ar*H* aromatic protons of the calixarenes moieties and at 4.45 ppm and 4.61 ppm for the ArOCH_2CO_2R. Characteristic AB systems were observed at 4.68, 3.15 ppm with J = 14.0 Hz and 4.61, 3.34 ppm with J = 14.2 Hz for the ArCH_2Ar methylenic protons in the macroring respective to **1**-CH_2CO_2Me and **2**-CH_2CO_2Me.

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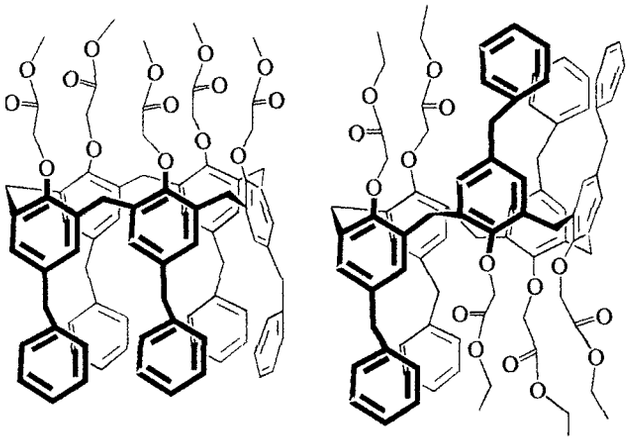
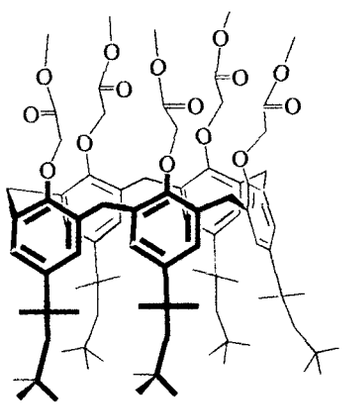


1-CH_2CO_2Mc **1**-CH_2CO_2Et



2-CH_2CO_2Mc

Chart 1 The ligands studied.

Crystal structure of 1-CH_2CO_2Et

The molecule **1**-CH_2CO_2Et,[13] which has no crystallography-imposed symmetry, is represented in Fig. 1. The conformation appears to be 1,2-alternate, as indicated by the torsion angles φ and χ generally used to characterize calixarene conformations,[16] with the angle signs sequence $+-$ $++$ $-+$ $--$ $-+$, in which the $++$ and $--$ pairs correspond to an upside-down reversing of a ring with respect to its neighbour (Table 1). However, apart from their sign, these torsion angles are far from their ideal value, which indicates a distorted conformation. The representation of calix[5]arene conformations proposed by Stewart *et al.*[17] is not easy to use here since the five methylene carbon atoms do not define a proper plane (root mean square (rms) deviation of fitted atoms: 0.45 Å), which prevents us from determining unambiguously the inward or outward canting of the phenolic rings. The conformational description proposed by Thondorf and Brenn[18] is of more practical use in the present case. Among the five planes defined by four methylene carbon atoms, the one with the lowest rms deviation (0.14 Å) is considered as the 'major plane'. This plane corresponds to the rings bonded to O(1), O(4) and O(7). The 'minor plane', defined by the remaining methylene carbon atom and the two adjacent ones, corresponds to the rings bonded to O(7) and O(10). The conformation of the molecule is finally characterized by the arrangement of the lower rim substituents with respect to the concave region defined by these two planes with the notation 'T' or 't' to indicate that the substituent (in the 'major' and 'minor' planes, respectively) is pointing towards this region and 'A' or 'a' if it points away from it. In the present case, the conformation is AATta, which is one of the ten possibilities (out of a total of 32) associated with the 1,2-alternate geometry. Molecular dynamics simulations indicate that this conformation is one of the low energy ones for *p*-methylcalix[5]arene pentamethyl ester.[18] It is notable in our case that one phenolic ring (bonded to O(1)) is very close to the 'major plane', with a dihedral angle of 17.4(1)°. The conformation of the benzyl substituents appears extremely irregular and is probably determined by packing constraints, without inclusion in any calixarene cavity.

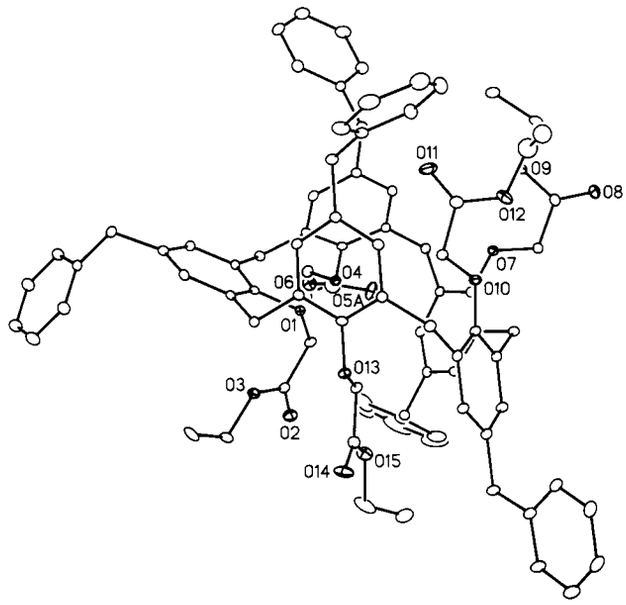


Fig. 1 Molecular unit in **1**-CH_2CO_2Et. For clarity, the main component only is represented in the disordered parts. Hydrogen atoms omitted for clarity.

Table 1 Selected torsion angles (°)

Rings	ϕ	χ
1–2	122.4	−41.2
2–3	100.6	91.0
3–4	−45.6	84.6
4–5	−119.7	−124.8
5–1	−110.4	42.1

Extraction studies

The extraction percentages of alkali picrates with the pentaalkyl esters derivatives reported in Table 2 provide some first indications on the binding abilities of the ligands toward this family of cations. These data show that the three pentaalkyl esters studied, as the two related *p-tert*-butylpentaalkyl esters previously studied by Barrett *et al.*,[19] present a plateau selectivity for the larger alkali cations K^+, Rb^+ and Cs^+ with, however, little but significant discrimination between them. With the cone derivative **1**-CH_2CO_2Me, Cs^+ is slightly better extracted ($\%E = 30.7$) than Rb^+ ($\%E = 29.4$) and K^+ ($\%E = 24.8$). With the 1,2 alternate derivative **1**-CH_2CO_2Et, as with the cone **2**-CH_2CO_2Me, the selectivity is in favour of Rb^+ ($\%E = 40.4$ and 61.7, respectively). Li^+ and Na^+ are always poorly extracted, except Na^+ by ligand **2**-CH_2CO_2Me, for which $\%E = 23.1$.

The order of efficiency of the different ligands decreases in the series: **3**-$CH_2CO_2Bu^t$ > **2**-CH_2CO_2Me > **3**-CH_2CO_2Et > **1**-CH_2CO_2Et > **1**-CH_2CO_2Me. It is clear that there is a dependence upon the nature of the substituents on the functional groups and the *para*-positions. Although it is difficult to evaluate the former effect in compounds **1**-CH_2CO_2Me and **1**-CH_2CO_2Et because of their conformational difference, the comparison of ligands **3**-CH_2CO_2Et and **3**-$CH_2CO_2Bu^t$

Table 2 Percentage extraction of alkali picrates by calix[5]arene esters from H_2O into CH_2Cl_2 at 20 °C

	Extraction (%)				
Cations	**1**-CH_2CO_2Me	**1**-CH_2CO_2Et	**2**-CH_2CO_2Me	**3**-CH_2CO_2Et[a]	**3**-$CH_2CO_2Bu^t$[a]
Li^+	2.4 ± 0.2	2.60 ± 0.07	7.6 ± 0.4	8.0	25
Na^+	4.8 ± 0.2	7.04 ± 0.08	23.1 ± 0.8	32.7	68.7
K^+	24.8 ± 0.1	36.31 ± 0.08	55.5 ± 0.1	46.6	74
Rb^+	29.4 ± 0.2	40.34 ± 0.08	61.66 ± 0.08	51	72.0
Cs^+	30.7 ± 0.3	32.11 ± 0.08	54.4 ± 0.2	51.2	68.0

[a] From ref. 19.

Table 3 Extraction selectivity of calix[5]arene esters

	S[a]				
Cations	**1**-CH_2CO_2Me	**1**-CH_2CO_2Et	**2**-CH_3CO_2Me	**3**-CH_2CO_2Et[b]	**3**-$CH_2CO_2Bu^t$[b]
K^+/Na^+	6.5	4.6	2.4	1.4	1.1
Rb^+/Na^+	6.2	5.7	2.7	1.6	1.0
Cs^+/Na^+	5.22	5.2	2.3	1.6	1.0
Rb^+/Li^+	12.3	15.5	8.1	6.4	2.9

[a] $S(M_1/M_2) = \%E(M_1)/\%E(M_2)$. [b] From ref. 19.

Table 4 Stability constants ($\log \beta \pm 2\sigma_{n-1}$)[a] of alkali complexes in methanol and acetonitrile, at 25 °C, $I = 0.01$ mol dm^{-3} (Et_4NCl or Et_4NClO_4)

	MeOH					AN[d]		
Cations	**1**-CH_2CO_2Me	**1**-CH_2CO_2Et	**2**-CH_2CO_2Me	**3**-CH_2CO_2Et[c]	**3**-$CH_2CO_2Bu^t$[c]	**1**-CH_2CO_2Me	**1**-CH_2CO_2Et	**2**-CH_2CO_2Me
Li^+	[b]	2.49 ± 0.01[d]	2.28 ± 0.01[d]	1.0	1.5	3.50 ± 0.05	3.46 ± 0.06	3.92 ± 0.06
Na^+	2.6 ± 0.1[d]	3.7 ± 0.2[d]	4.5 ± 0.1[d]	4.4	5.1	4.20 ± 0.1	4.77 ± 0.01	5.0 ± 0.1
K^+	5.15 ± 0.08[d]	5.22 ± 0.02[d]	5.29 ± 0.05[e]	5.31	6.1	5.66 ± 0.02	5.52 ± 0.01	6.2 ± 0.1
Rb^+	5.5 ± 0.1[d]	5.3 ± 0.1[d]	5.7 ± 0.2[d] 5.7 ± 0.2[e]	5.56	5.75	5.63 ± 0.01	5.79 ± 0.01	6.50 ± 0.06
Cs^+	5.26 ± 0.02[d]	5.3 ± 0.2[d]	5.55 ± 0.04[d] 5.45 ± 0.01[e]	5.5	5.26	5.3 ± 0.1	5.21 ± 0.04	6.08 ± 0.05
Ag^+	3.87 ± 0.04[d]	—	3.82 ± 0.01[d] 3.97 ± 0.01[e]	4.0	4.33	5.5 ± 0.3	5.50 ± 0.09	4.10 ± 0.06

[a] Arithmetic means of n experiments ($n \geq 3$); the precision corresponds to $\pm\sigma_{n-1}$, σ_{n-1} = standard deviation on the means. [b] No spectral change observed. [c] From ref. 19. [d] Spectrophotometric measurements. [e] Potentiometric measurements.

studied before showed an important increase in $\%E$ values when replacing ethyl by *tert*-butyl groups, (*i.e.* $\Delta\%E = 27.4$ for K^+). The nature of the *para*-substituent has even a greater influence as seen from the comparison between **1**-CH_2CO_2Me and **2**-CH_2CO_2Me ($\Delta\%E = 32.26$ for Rb^+).

It can also be seen from the values in Table 3 that the *p*-benzyl derivatives **1**-CH_2CO_2Me and **1**-CH_2CO_2Et are more selective than their *p*-*tert*-octyl (**2**-CH_2CO_2Me) and *p*-*tert*-butyl (**3**-CH_2CO_2Et and **3**-$CH_2CO_2Bu^t$) counterparts. This can be accounted for by an increase in rigidity of the molecules caused by the presence of the benzyl substituents, thus preventing a good complementarity with the smaller cations.

Complexation studies

Complexation studies were then undertaken in methanol and acetonitrile by UV absorption spectrophotometry. The spectra of ligand solutions (2.0×10^{-5} mol $dm^{-3} \leq C_L \leq 7.0 \times 10^{-5}$ mol dm^{-3}) containing increasing amounts of metal ion (up to $C_M/C_L = 238$ in the case of Li^+ with **2**-CH_2CO_2Me) have been recorded between 250 and 300 nm. Complexation induces a decrease of the intensity of the absorption bands of the ligands, with, in some cases, a hypsochromic shift. The interpretation of these spectral changes using the numerical programs Sirko[20] and/or Letagrop–Spefo[21] shows the formation of complexes of 1:1 stoichiometry exclusively. When the complexes were very stable, as in the case of the larger K^+, Rb^+ and Cs^+ cations with **2**-CH_2CO_2Me, the spectrophotometric values were confirmed by competitive potentiometry using Ag^+ as auxiliary cation. The logarithms of the corresponding stability constants $\log \beta$ are given in Table 4, as well as literature data for compounds **3**-CH_2CO_2Et and **3**-$CH_2CO_2Bu^t$.

The three ligands studied display in both solvents a preference for the larger alkali cations with very little discrimination between these cations, which mirrors the extraction data.

Influence of ester substituents and the conformation. When going from the methyl ester **1**-CH_2CO_2Me (cone) to the ethyl ester **1**-CH_2CO_2Et (1,2-alternate), a significant increase in stability is observed in methanol for the complexes with the smaller cations Li^+ and Na^+. For instance, the Li^+ complex, which could not be detected with **1**-CH_2CO_2Me, has a stability constant of 2.49 log units with **1**-CH_2CO_2Et. Such a difference is not observed with the larger cations, both ligands forming complexes of similar stability with K^+, Rb^+ and Cs^+. The same trends are observed in acetonitrile, but the effects are much weaker than in methanol. It thus seems that, for pentaalkyl esters, the 1,2-alternate conformation favours the complexation of the smaller cations with respect to the cone conformation, although, as said before for extraction results, it is difficult to ascribe the differences observed with the two ligands to either the nature of the ester substituents or the conformation, as both vary in the ligands. However, on the basis of previous results on the pentaalkyl ester derivatives **3**,[19] the substituent effect does not lead to such differences in stability and the conformational effect should thus be predominant.

Table 5 Comparison of the complexation selectivities $S(M^+/Na^+)$ of calix[5]arene esters in methanol and acetonitrile

Ligands	Solvents	Selectivities		
		K^+/Na^+	Rb^+/Na^+	Cs^+/Na^+
1-CH_2CO_2Me	MeOH	347	976	447
	CH_3CN	29	27	13
1-CH_2CO_2Et	MeOH	33	40	33
	CH_3CN	5.6	10	2.7
2-CH_2CO_2Me	MeOH	5.9	16	8.5
	CH_3CN	14	32	12

Influence of the para-substituents. One of our goals was to study the influence of the *para*-substituents on the complexing properties of calix[5]arene esters. The *p-tert*-octyl derivative **2**-CH_2CO_2Me is a stronger binder than its *p*-benzyl homologue **1**-CH_2CO_2Me in both methanol and acetonitrile. In methanol, the difference in the complexing abilities is particularly important for the smaller cations (Li^+ and Na^+). As said before, no complexation was detected with Li^+ and **1**-CH_2CO_2Me. However, its *p-tert*-octyl counterpart forms a stable complex with the latter cation ($\log \beta = 2.28$). As regards the Na^+ complex, $\log \beta$ value increases from 2.6 to 4.5 when going from **1**-CH_2CO_2Me to **2**-CH_2CO_2Me. Such an increase in stability was not observed for the complexes of the larger cations K^+, Rb^+ and Cs^+ (maximum $\Delta \log \beta = 0.2$ for Rb^+).

These observations suggest that the *p-tert*-octyl substituents allow a greater flexibility than the *p*-benzyl ones, leading to a better complementarity between the hydrophilic part of the molecule and the smaller cations and hence the better complexation of these cations by **2**-CH_2CO_2Me. The high selectivity of **1**-CH_2CO_2Me for the larger cations can therefore be ascribed to the higher rigidity of this ligand preventing efficient complexation of the smaller cations.

Solvent effect. In agreement with the cation solvation properties of the two solvents (MeOH and CH_3CN), the stability constants observed with the three pentaalkyl esters increase from MeOH to CH_3CN. The influence of the solvent is generally more important for the smaller alkali cations Li^+ and Na^+ than for the larger ones. For example, the stability constants of the Li^+ complexes with **1**-CH_2CO_2Et and **2**-CH_2CO_2Me increase by more than 1 log unit on going from methanol to acetonitrile. But the most important variation is for the Li^+ complex with **1**-CH_2CO_2Me. Whereas no complexation was observed in methanol, a value of $\log \beta = 3.5$ is found in acetonitrile. However the stability constant of the Na^+ complex of **2**-CH_2CO_2Me increases only by a value of 0.5 log unit when going from methanol to acetonitrile. The higher stabilization of Li^+ complexes in acetonitrile can be explained in terms of solvation of the cation, since Li^+ is less solvated in acetonitrile than in methanol as shown by the value of its transfer activity coefficient between the two solvents ($\log \gamma_{MeOH \rightarrow CH_3CN} = 4.5$, instead of $-1 \leq \log \gamma \leq 1$ for the other alkali cations).[22] Similar results have already been observed with calix[4]arene esters and amides.[23,24]

With the two *p*-benzyl derivatives **1**-CH_2CO_2Me and **1**-CH_2CO_2Et, the increase in the stability constants from methanol to acetonitrile, more important for the smaller alkali cations than for the larger ones, induces a decrease in the selectivity of these two ligands for the larger cations with respect to Li^+ and Na^+. The selectivities $S(M^+/Na^+)$ (with $M^+ = K^+$, Rb^+, Cs^+), expressed as the ratio of the corresponding stability constants, are summarized in Table 5 for both solvents. The higher decreases in selectivity are found for ligand **1**-CH_2CO_2Me for which the values of $S(Rb^+/Na^+)$ and $S(Cs^+/Na^+)$ are respectively 36 and 34 times smaller in acetonitrile than in methanol. However, this ligand remains the most selective in the two solvents. In the case of **2**-CH_2CO_2Me the selectivities increase from methanol to acetonitrile because of the increase in stability of Rb^+ and Cs^+ complexes, which is higher than the increase in stability of the Na^+ complex.

Silver complexes. The three pentaalkyl esters **1**-CH_2CO_2Me, **1**-CH_2CO_2Et and **2**-CH_2CO_2Me form stable complexes with Ag^+ in both solvents. These complexes have the same stability or are less stable than their homologues with K^+, the cation of the same size as Ag^+. In methanol, their stability also compares with that of their homologues with the *p-tert*-butyl esters **3**-CH_2CO_2Et and **3**-$CH_2CO_2Bu^t$. In this solvent, the complexation does not seem to depend on the *para*-substituent, whereas in acetonitrile the replacement of *p*-benzyl by *para-tert*-octyl groups induces a significant decrease in stability ($\Delta \log \beta = 1.4$ between **1**-CH_2CO_2Me and **2**-CH_2CO_2Me complexes). Contrary to the expectations based on the very high solvation of Ag^+ in acetonitrile, an increase in stability is observed on going from methanol to acetonitrile, in particular with **1**-CH_2CO_2Me ($\Delta \log \beta = 1.63$).

Experimental

Materials

In both synthesis and physico-chemical studies, commercial grade solvents (methanol [Carlo Erba], acetonitrile [SDS, purex for Analyses], acetone [SDS], dichloromethane [SDS, synthesis grade]) were used without purification. Ligand **1**-CH_2CO_2Et was prepared as already described.[13]

Analytical procedures

The melting points (mps) were taken on a Büchi 500 apparatus in capillaries sealed tubes. ^{1}H-NMR spectra were recorded at 200 MHz on a Bruker SY200 spectrometer. In all cases the samples were dissolved in $CDCl_3$, which was used as internal standard at 7.26 ppm. Mass spectra were recorded on a ZAB HF VG-Analytical or a LKB 9000 S spectrometer. Analytical TLC was carried out with glass plates Kieselgel Merck 5515. Elemental analysis were determined at the Service de Microanalyse of the Institut de Chimie de Strasbourg.

Crystal structure determination

The data were collected on a Nonius Kappa-CCD area detector diffractometer[25] using graphite monochromated MoK_α radiation (0.71073 Å). The crystal was introduced in a Lindemann glass capillary with a protecting 'Paratone' oil (Exxon Chemical Ltd.) coating. The data were processed with the HKL package.[26] The structure was solved by direct methods with SHELXS-86[27] and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-93.[28] Two parts of ester groups, comprising two atoms each, are disordered over two positions, which were refined with occupancies constrained to sum up to unity. All non-hydrogen atoms were refined anisotropically, except the disordered ones. The hydrogen atoms were introduced at calculated positions (except those in the disordered parts) as riding atoms with a displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. Crystal data and structure refinement parameters are given in Table 6. The molecular drawing was done with SHELXTL.[29] All calculations were performed on a Silicon Graphics R4000 workstation.

CCDC reference number 188/211. See http://www.rsc.org/suppdata/p2/a9/a908336g for crystallographic files in .cif format.

Picrate extraction experiments

The percentages of alkali picrates extracted from water into dichloromethane have been determined at 20 °C according to

Table 6 Crystal data and structure refinement details

Empirical formula	$C_{90}H_{90}O_{15}$
M/g mol^{-1}	1411.62
T/K	123(2)
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	38.065(2)
b/Å	15.1021(4)
c/Å	26.538(1)
β/°	100.147(1)
V/Å^3	15017(3)
Z	8
μ/mm^{-1}	0.084
Reflections collected	44818
Independent reflections	10531
Observed reflections [$I > 2\sigma(I)$]	6723
R_{int}	0.13
Number of parameters	970
R_1	0.088
wR_2	0.175

Pedersen's procedure.[30] The experimental details and the preparation of the metal picrates have already been reported.[31]

Stability constant determinations

The stability constants equal to the concentration ratio $\beta = [ML^+]/[M^+][L]$ have been determined in methanol and acetonitrile. The measurements were performed by UV absorption spectrophotometry according to the procedure already described.[23] Potentiometric measurements with Ag^+ as an auxiliary cation have been performed in methanol, according to procedure already described[24] to check the very high stability constants found in the case of larger alkali cations. The data were treated by the programs Sirko[20] and/or Letagrop-Spefo.[21] The metallic salts used were the following chlorides in methanol: LiCl (Fluka, purum), NaCl (Merck, pa), KCl (Merck, Pa), RbCl (Fluka, puriss), CsCl (Merck, pa), and the following perchlorates or nitrate in acetonitrile: $LiClO_4$ (Fluka, purum), $NaClO_4$ (Merck, pa), $KClO_4$ (Prolabo, normapur), $RbClO_4$ (Sigma), $CsNO_3$ (Fluka, purum). The silver cation was used as the perchlorate: $AgClO_4 \cdot H_2O$ (Fluka, puriss). In all solutions, the ionic strength was maintained at 0.01 mol dm^{-3} by use of the supporting electrolytes Et_4NCl in methanol and Et_4NClO_4 in acetonitrile. All these salts were dried under vacuum for 24 hours before use.

Preparation of 1-CH_2CO_2Me and 2-CH_2CO_2Me

5,11,17,23,29-Pentabenzylcalix[5]arene-31,32,33,34,35-pentaethanoate pentamethyl ester 1-CH_2CO_2Me. A mixture of 5,11,17,23,29-pentabenzyl-31,32,33,34,35-pentahydroxycalix-[5]arene (500 mg, 0.51 mmol), potassium carbonate (3.70 g, 26.77 mmol) and methyl bromoacetate (3.70 g, 24.18 mmol) were refluxed in dry acetone (50 ml) for 6 h under an inert N_2 atmosphere. Upon cooling to room temperature the mixture was filtered and the inorganic residue was washed with acetone and methylene chloride. The combined organic solutions were concentrated under high vacuum. The residue was precipitated with methanol to afford 5,11,17,23,29-pentabenzylcalix[5]-arene-31,32,33,34,35-pentaethanoate pentamethyl ester: Yield 92% (627 mg), mp 74–75 °C; δ_H(200 MHz; $CDCl_3$) 7.25–6.98 (m, 25H, ArH), 6.57 (s, 10H, ArH), 4.68 (d, 5H, J = 14.0 Hz, Ar-CH_2-Ar), 4.45 (s, 10H, ArOCH_2CO$_2$CH$_3$), 3.75 (s, 15H, OCH$_2$CO$_2$CH_3), 3.49 (s, 10H, Ar-CH_2-Ar), 3.15 (d, 5H, J = 14.0 Hz, Ar-CH_2-Ar); MS(FAB), m/z 1341.5 (M + H$^+$) (Found: C, 76.36; H, 6.09. $C_{85}H_{80}O_{15}$ requires C, 76.10; H, 6.01%).

The following calixarene ester was prepared according to the same procedure.

5,11,17,23,29-Penta-*tert*-octylcalix[5]arene-31,32,33,34,35-pentaethanoate pentamethyl ester 2-CH_2CO_2Me. Yield 85%, mp 163–164 °C; δ_H(200 MHz; $CDCl_3$) 6.85 (s, 10H, ArH), 4.72 (d, 5H, J = 14.2 Hz, Ar-CH_2-Ar), 4.61 (s, 10H, OCH_2CO$_2$CH$_3$), 3.78 (s, 15H, OCH$_2$CO$_2$CH_3), 3.34 (d, 5H, J = 14.2 Hz, Ar-CH_2-Ar), 1.34 (s, 10H, C(CH$_3$)$_2$CH_2C(CH$_3$)$_3$), 1.00 (s, 30H, Ar-C(CH_3), 0.68 (s, 45H, CH$_2$C(CH_3)$_3$); MS(FAB), m/z 1475.0 (M + Na$^+$) (Found: C, 83.16; H, 11.10. $C_{95}H_{150}O_5$ requires C, 83.15; H, 11.01%).

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