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Synthesis, NMR conformational analysis, complexation and transport studies of an inherently chiral dihomooxacalix[4]arene triester

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Abstract—The synthesis of the inherently chiral triethyl ester monomethyl ether of *p-tert*-butyldihomooxacalix[4]arene (**3**) is reported. A distorted cone conformation in solution at room temperature has been established for triester **3** by NMR measurements (^{1}H, ^{13}C, NOE 1D and 2D). The extracting and complexing properties of **3** towards the entire alkali and alkaline earth cation series have been assessed by picrate extraction and stability constant determinations. Transport experiments with metal picrates through a CH_2Cl_2 membrane have also been performed. Comparison is made with tetraethyl ester of *p-tert*-butylcalix[4]arene (**4**) described in literature and also studied by us. **3** is a poor phase transfer agent and binder. In contrast, it is a good carrier, mainly for the alkali cations and displays a selective transport for Ba^{2+}.

1. Introduction

In the last decade the interest in calixarenes[1,2] increased nearly in an exponential way. The parent compounds are readily available and their frameworks can, then, be chemically modified by the introduction of functional groups either at upper or lower rims. Thus, calixarenes have been used as starting materials for the construction of more and more elaborate host molecules of various types of guests.

Lower rim functionalised calix[*n*]arenes (mainly $n = 4$, 5 and 6) with ester groups[3–13] are one of the earliest and more studied families of derivatives towards their ionophoric properties. This binding ability has especially been analysed towards alkali and alkaline earth metal cations and has been assessed by extraction studies, transport experiments and stability constant measurements.

In recent years we have started the synthesis of dihomooxacalix[4]arene derivatives with substituents containing the carbonyl group at the lower rim[14,15] and the study of their binding properties. As calix[4] and calix[5]arenes, those derivatives also possess the cone conformation and fall between these two groups of calixarenes.

In the present work we report the synthesis and conformational and the complexing properties of triethyl ester monomethyl ether of *p-tert*-butyldihomooxacalix[4]arene (**3**). This compound has mixed functionalities at the lower rim (two different substituents) and therefore it is inherently chiral.[16] The binding properties of **3** towards alkali and alkaline earth metal cations have been established by extraction studies with metal picrates from neutral aqueous solution into dichloromethane and by determination of stability constants in methanol. Transport experiments with metal picrates through a dichloromethane membrane have also been performed.

The tetraethyl ester of *p-tert*-butylcalix[4]arene (**4**) is also studied, and the results of the two derivatives are compared.

2. Results and discussion

2.1. Synthesis and NMR conformational analysis

Compound **3** was synthesized by the reaction of *p-tert*-butyldihomooxacalix[4]arene monomethyl ether (**2**)[16] with ethylbromoacetate and potassium carbonate in refluxing acetone for two days. Tetraester **4** was prepared in the same way, according to Ref. 17, and compound **2** had already been obtained from *p-tert*-butyldihomooxacalix[4]arene (**1**).

Keywords: calixarenes; metal cations; extraction; complexation; transport properties.
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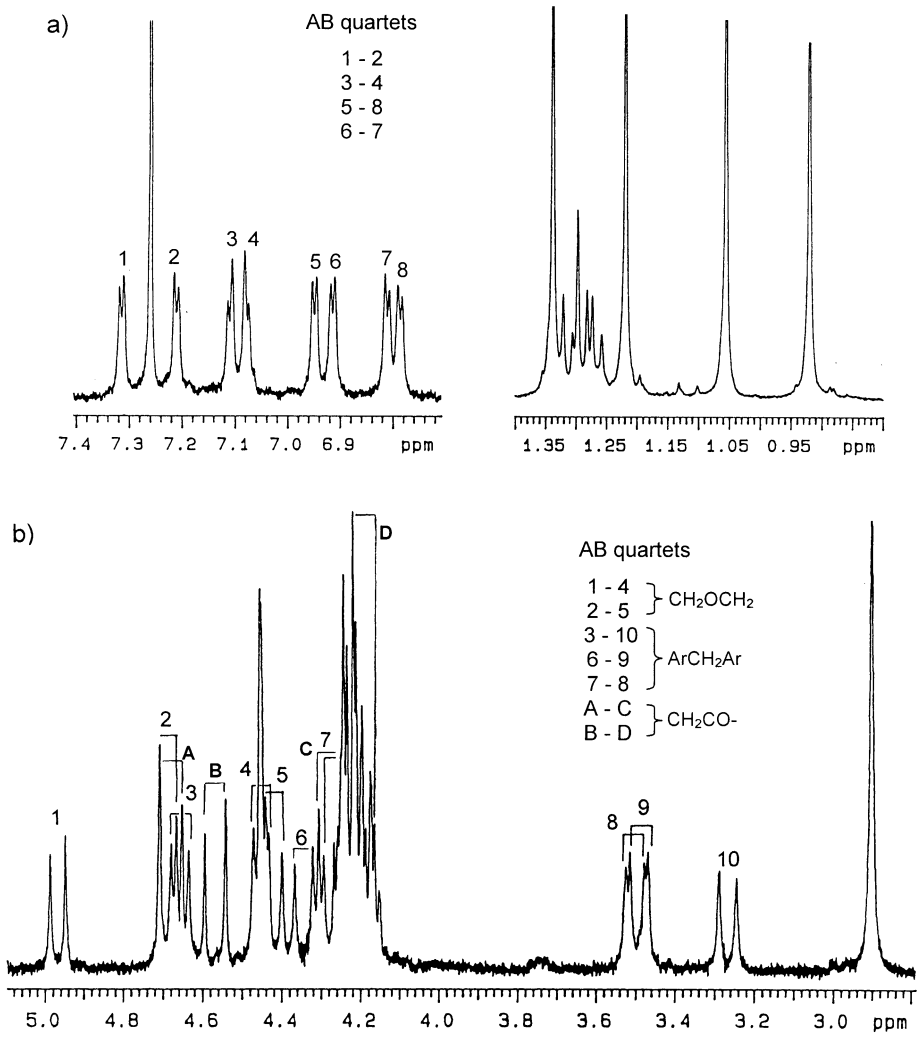
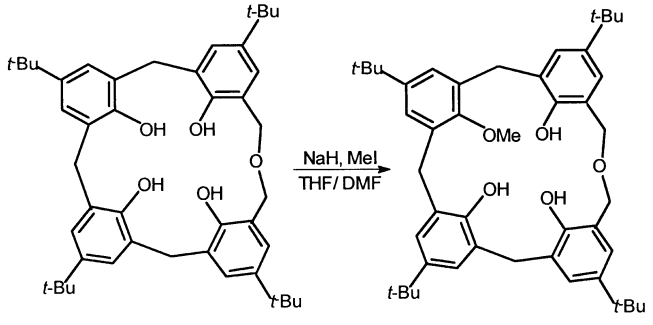
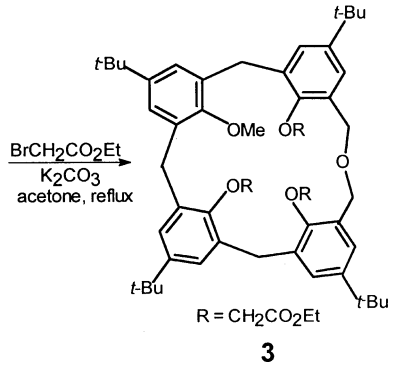
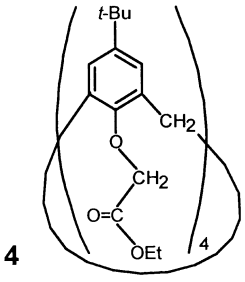


Figure 1. 300 MHz ^{1}H NMR spectrum of triester **3**, in $CDCl_3$ at 22°C. (a) Aromatic protons and CH_3 groups, (b) CH_2 and methoxy groups.







Proton, carbon-13, COSY, NOE 1D and 2D NMR experiments were carried out in chloroform at room temperature with compound **3** to establish its conformation.

The ^{1}H NMR spectrum (Fig. 1) displays four singlets for the *tert*-butyl groups, one singlet for the methoxy group, two triplets (one with the double of the intensity) and two or three quartets for the ester groups, CH_3 and CH_2, respectively, five AB quartets for the CH_2 bridge protons, two AB quartets and two singlets or a large singlet for the $-OCH_2CO-$ groups and four pairs of doublets for the aromatic protons.

The ^{13}C NMR spectrum shows three Ar*C*H_2Ar resonances at

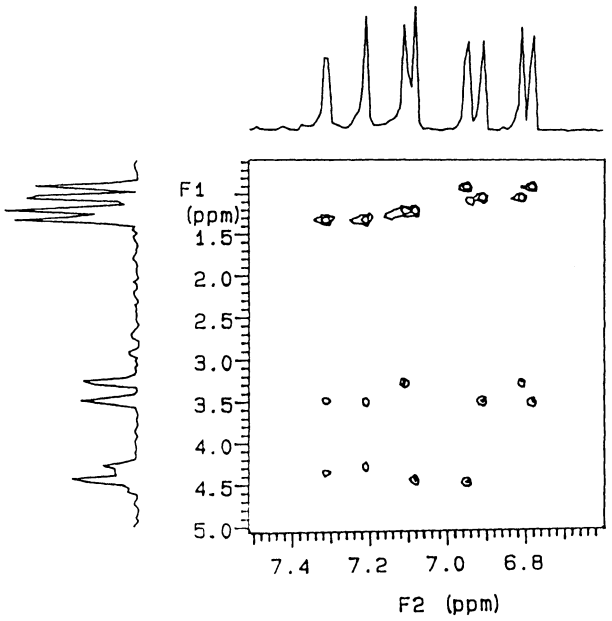


Figure 2. NOESY spectrum of **3** in $CDCl_3$ at 22°C and 500 MHz, showing the correlations of the aromatic protons.

δ 31.1, 33.4 and 33.5, indicating a cone conformation[18] for this compound. This conformation was also confirmed by NOE 1D experiments and a NOESY spectrum (Fig. 2). The more relevant NOE enhancements are shown in Fig. 3.

Beyond these characteristic effects of a cone conformation, it is also possible to observe in ring C NOE effects between the aromatic proton at 7.21 ppm and the axial methylene proton 7, and between the aromatic proton at 7.32 ppm and the proton 6. These effects suggest that ring C is in a distorted position, forming a larger angle with the mean plane of the methylene bridges.

These dihomooxacalix[4]arene derivatives in the cone conformation with only two different substituents at the lower rim are inherently chirals.[16] This chirality was demonstrated by the addition of an excess of Pirkle's reagent, (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol, to a $CDCl_3$ solution of compound **3**, causing duplication of proton signals. For example, the splitting pattern for the aromatic protons is shown in Fig. 4.

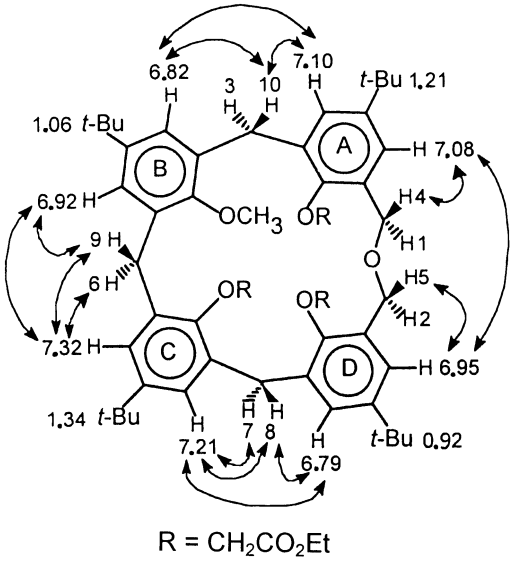


Figure 3. Relevant NOE enhancements for triester **3**.

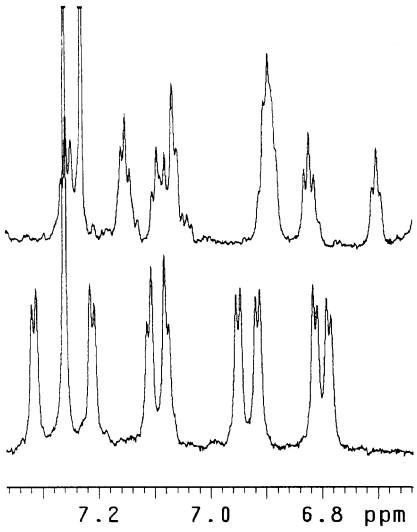


Figure 4. Partial 300 MHz ^1H NMR spectra in $CDCl_3$ at 22°C in the absence (bottom) or in the presence (top) of Pirkle's reagent for compound **3**.

2.2. Extraction studies

The ionophoric properties of compound **3** towards alkali and alkaline earth metal cations were first evaluated by the picrate extraction method developed by Pedersen.[19] The results, for derivatives **3** and **4**, are reported in Table 1 and shown graphically in Fig. 5. Relatively to compound **4**, these values are the published data for the alkali series and the alkaline earth Ca^{2+} and Ba^{2+} cations,[20] and those obtained by us for Mg^{2+} and Sr^{2+}.

For compound **3** the extraction percentage (% *E*) ranges from 8 to 16% for the alkali metal cations and is less than 7% for all the alkaline earth metal cations. These values are similar to those for derivative **4**,[20] mainly in the case of the alkaline earth cations. However, triester **3** due to its larger cavity size compared to that of **4**, displays a plateau selectivity with little discrimination between K^+ and Na^+, contrary to **4** that shows a sharp peak selectivity for Na^+. More relevant, perhaps, is the fact that **3** possesses only three ester groups and consequently only six donating sites, contrary to derivative **4** with eight sites. The efficiency of interaction with the cations also depends on the number of donor sites.[21] Therefore, **3** surrounds the cations in a less efficient way.

The lower percentages found for the alkaline earth metal cations relative to the alkali metal cations can be connected with the lower number of donor sites of the ligand. As the hydration number is 6 for the alkali cations and 8 for the alkaline earth[22] (except Mg^{2+}), the lack of donor sites in triester **3** will have a greater effect on divalent cations.

This compound is a more flexible molecule and therefore can undergo more pronounced conformational changes,

Table 1. Percentage extraction of alkali and alkaline earth metal picrates into CH_2Cl_2 at 25°C

	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ionic radius (Å)[a]	0.78	0.98	1.33	1.49	1.65	0.78	1.06	1.27	1.43
3	9.3	13	16	9.1	8.3	6.7	5.1	5.7	4.4
4[b]	7.2	29	4.7	3.6	5.6	6.5	4.3	8.0	5.1

Values with uncertainties less than 5%.
[a] Goldschmidt, V. M. *Skrifter Norske Videnskaps-Akad. Oslo, I, Mat.-Naturv. Kl,* **1926**; data quoted in Marcus, I. *Ion Properties*, Marcel Dekker: New York, 1997; pp 46–47.
[b] Data taken from Ref. 20, except for Mg^{2+} and Sr^{2+}, whose values were obtained in this work.

being able to receive the smallest cation (Li^+) as much as the larger ones (Rb^+ and Cs^+).

Triester **3** exists in a distorted cone conformation in solution as mentioned above, which can also contribute to its weak extracting ability.

The extraction of alkali metal cations with the analogous *p-tert*-butylcalix[4]arene triester was done by Nam et al.,[10] but with basic metal picrates. Therefore, it is not correct to establish a comparison between the two triesters.

2.3. Determination of stability constants

The stability constants (log β) for triester **3** in methanol are reported in Table 2 and Fig. 6, which also contain the published data for tetraester **4**.[23] These data were obtained by UV absorption spectrophotometry measurements.

Table 2. Stability constants (log β) of alkali and alkaline earth complexes in methanol at 25°C

	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
3	2.6	3.1	2.6	2.7	3.0	4.1	3.1	3.0	3.2
4[a]	2.6	5.0	2.4	3.1	2.7	≤1	≤1	≤1	≤1

Standard deviation on the mean of 2–4 independent series: σ_{n-1}=0.2–0.3 log unit.
[a] Data taken from Ref. 23.

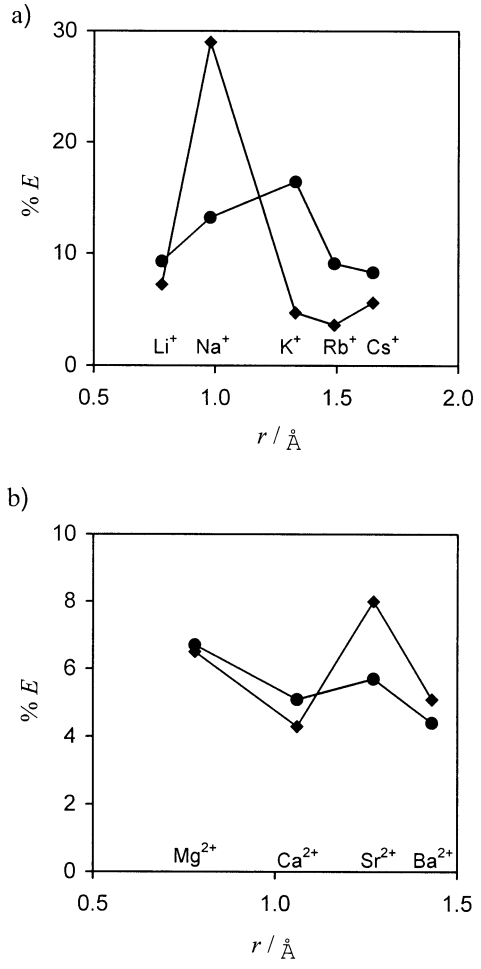


Figure 5. Percentage extraction (% *E*) of metal picrates into CH_2Cl_2 at 25°C vs the cation ionic radius (*r*) for compounds **3** (●) and **4** (◆). (a) Alkali and (b) Alkaline earth metals.

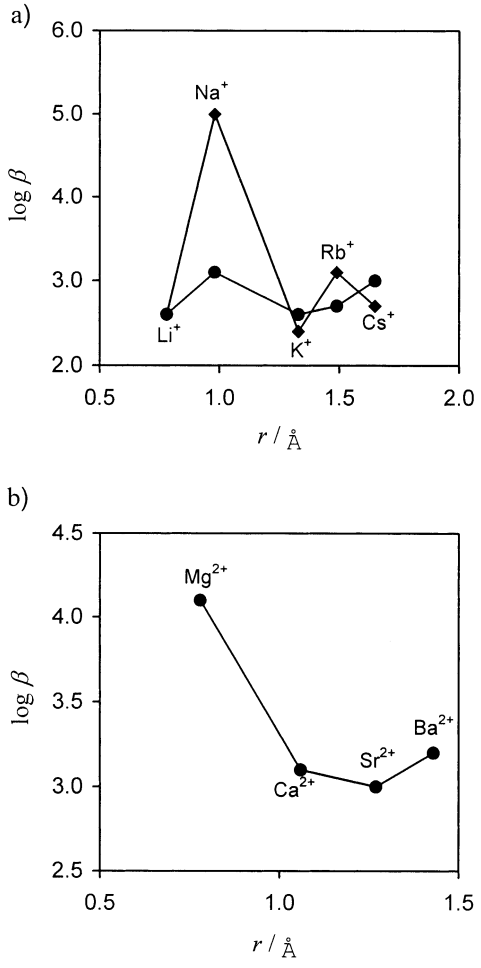


Figure 6. Stability constants (log β) for complexes of metal cations and derivatives **3** (●) and **4** (◆) in methanol vs the cation ionic radius (*r*). (a) Alkali and (b) Alkaline earth metals.

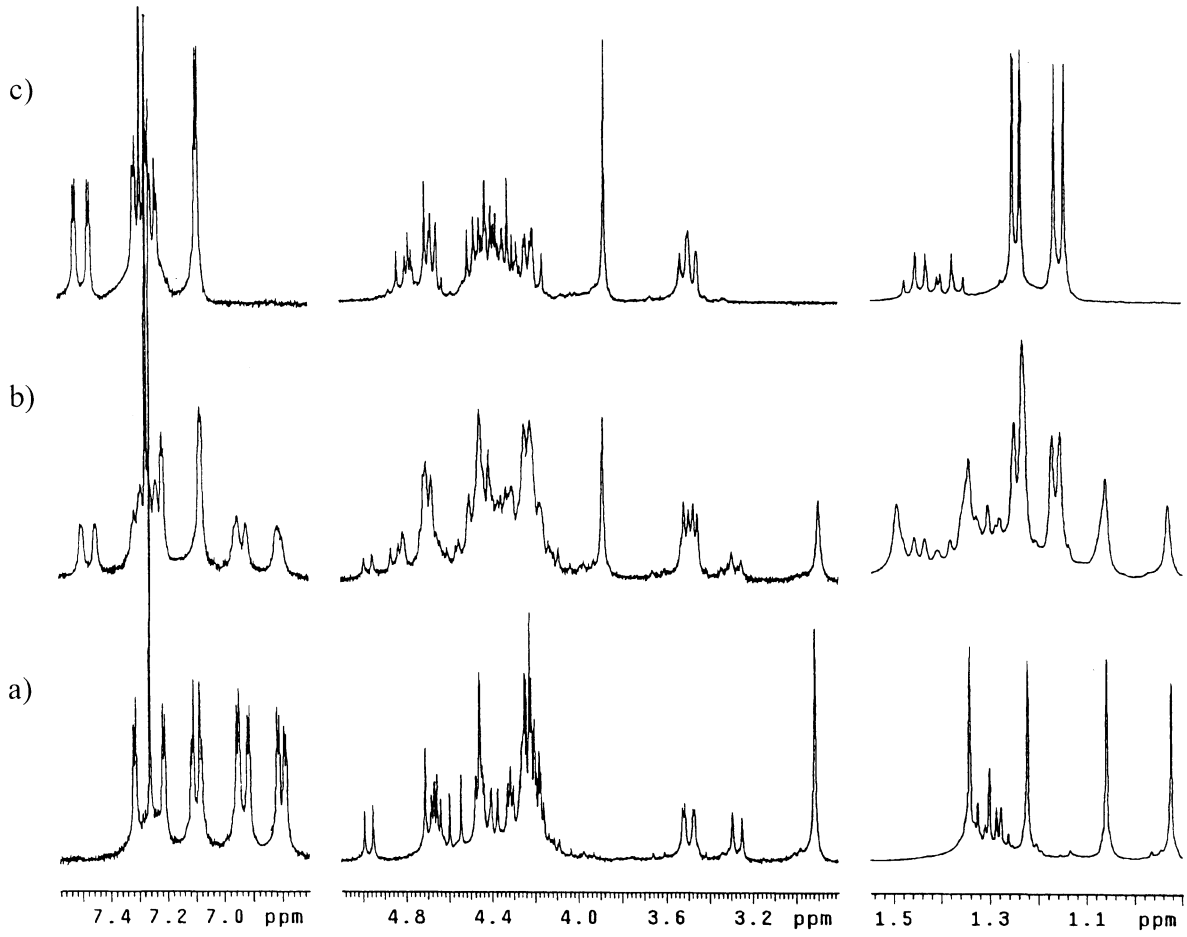


Figure 7. 300 MHz ^{1}H NMR spectra of ligand **3** in $CDCl_3$ at 22°C. (a) free ligand, (b) upon addition of 0.4 and (c) 1 equiv. of NaSCN.

In all cases the experimental data are consistent with the formation of only 1:1 complexes. This was confirmed, for sodium cation, by ^{1}H NMR titration experiments.

Variable amounts of NaSCN (up to 3 equiv.) in CD_3OD were added to a $CDCl_3$ solution of triester **3** directly in the NMR tube and the proton spectra were registered after each addition. Titration of **3** with NaSCN initially induces duplication and broadening of most signals until the [salt]/[ligand] ratio reaches the unity value, when the signals become sharp (Fig. 7). For lower values of this ratio both signals of the complexed and uncomplexed ligand broaden and are present in the spectrum, indicating that on the NMR time scale the exchange rate between the two species is intermediate at room temperature. These results show not only the complexation of Na^+, but also a relatively weak affinity of **3** towards this cation. The ^{1}H NMR titration experiment indicates a 1:1 stoichiometry for the NaSCN complex with ligand **3**, since all signals remain unchanged after subsequent additions of the salt.

Triester **3** is a poor binder for all the alkali series, showing log β values between 2.6 and 3.1. This ligand has a very small preference for Na^+ (log β=3.1) and Cs^+ (log β=3.0) cations, quite closely followed by the other three ($Rb^+ > K^+ = Li^+$). Compound **3** practically does not discriminate between the alkali cations, evidencing its larger conformational mobility compared with that of tetraester **4**. For **3**, slight flexing movements of its ligating groups allow the inclusion of the smaller Na^+ or the larger Cs^+, without significant energy cost resulting from contraction or expansion of the cavity. This leads to just stable complexes.

In the alkaline earth metal cation series the stability constants are higher than those obtained for the alkali metal cations, with log β values between 3.0 and 4.1. Triester **3** is a stronger binder than tetraester **4** for all the alkaline earth metal cations. **3** exhibits a plateau selectivity for Ca^{2+}, Sr^{2+} and Ba^{2+} cations, but shows a clear preference for Mg^{2+} (log β=4.1). This preference may be due to the relatively lower hydration number of Mg^{2+} than the other alkaline earth cations. Compound **3**, although a weaker binder, shows a similar behaviour as that of tetrahomodioxacalix[4]arene tetraethyl ester,[20] which does not extract Ca^{2+} and Ba^{2+} (ca 1% *E*), but forms very strong complexes (log β>6) with these cations.

For triester **3** the stabilities of its complexes are expected to be mainly controlled by the number of donor sites of the ligand.

2.4. Transport studies

The experiments of ion transport across a liquid membrane were carried out using an apparatus similar to that employed

Table 3. Transport rate ($V/\mu mol\ h^{-1}$) of alkali and alkaline earth picrates through a CH_2Cl_2 liquid membrane at 25°C

	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
3	1.2	2.7	3.1	3.4	2.3	0.01	0.04	0.8	2.4
4	0.24	1.8	1.0	0.08	0.06	0.01	0.03	0.03	0.04
4[a]	0.07	3.9	0.50	0.06	0.03	–	–	–	–

Reproducibility of ±10%.
[a] Data taken from Ref. 8.

by Lamb et al.[24]. Table 3 and Fig. 8 present the transport rates V, in $\mu mol\ h^{-1}$, for compounds **3** and **4**.

Triester **3** is a better carrier than tetraester **4** for all the cations studied. In the alkali series, **3** shows a preference for Rb^+ (3.4 $\mu mol\ h^{-1}$) and again a plateau selectivity, in this case increasing from Na^+ to Rb^+.

The transport rate is determined either by diffusion of the species or by the rate of complexation and decomplexation at both interfaces.[25]

As discussed above, this flexible ligand is a poor phase transfer agent and binder, showing a weak affinity for the cations. Hence, it is expected that compound **3** rapidly releases the cations at the interface with the receiving phase, being a better carrier than receptor. As an example, comparing the cases of K^+ and Na^+ cations, it is shown that the former is extracted more than the latter and therefore its capture rate should be bigger, at the first interface. Admitting that both carrier-cation complexes diffuse with similar speeds across the membrane, K^+ should be released more quickly than Na^+ to the receiving phase, mainly due to the lower stability of **3**–K^+ complex (log β=2.6) relative to that of **3**–Na^+ complex (log β=3.1).

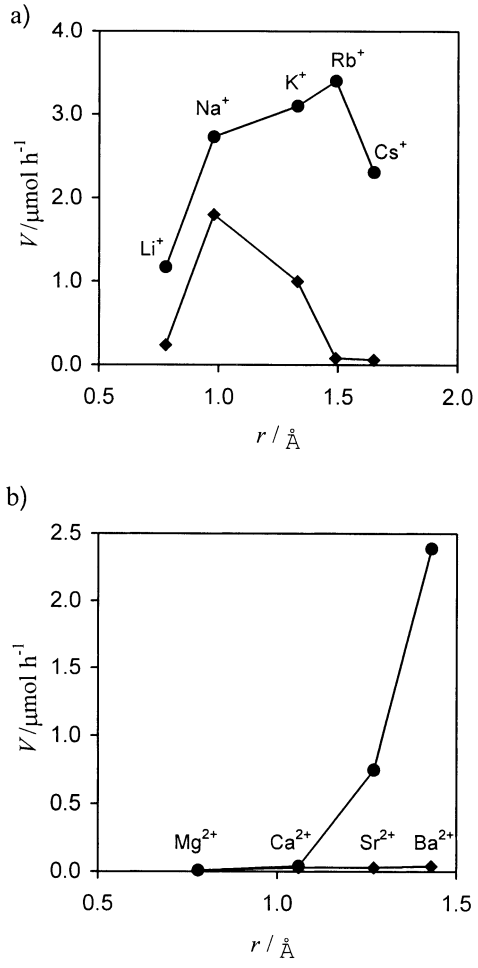


Figure 8. Transport rate ($V/\mu mol\ h^{-1}$) of metal picrates through a CH_2Cl_2 liquid membrane vs the cation ionic radius (r) for derivatives **3** (●) and **4** (◆). (a) Alkali and (b) ALkaline earth metals.

The sequence of transport rates for compound **4** is $Na^+ > K^+ > Li^+ > Rb^+ > Cs^+$. Although this selectivity order is the same found in literature,[8] we did not obtain such a sharp selectivity peak for Na^+ (Table 3). However, the conditions and the experimental apparatus used in both cases were different, as well as the anions (picrate and thiocyanate).

In the alkaline earth cation series, Mg^{2+}, Ca^{2+} and Sr^{2+} are transported by **3** to a very low extent. The transport rate value for Mg^{2+} (0.01 $\mu mol\ h^{-1}$) is even similar to that found for transport without ligand. This cation, despite being less extracted by **3**, is fairly well complexed (log β=4.1) and this should provoke a slower decomplexation rate to the receiving phase.

The most significant aspect towards these divalent cations is the very selective transport shown for Ba^{2+}.

Compound **4** exhibits very small transport rates for all the alkaline earth cations.

3. Conclusions

Triester **3** has been obtain in a distorted cone conformation in solution at room temperature and possesses only three ester groups with only six donating sites. This makes it a more flexible molecule, leading to its weak extracting and complexing ability. Nevertheless, this derivative is a good carrier, mainly for the alkali cations, and shows a selective transport towards Ba^{2+} cation. The trend found in transport seems, to some extent, to follow that of extraction and complexation. However, the characterization[26] of compound **3** is ambiguous, being probably more close to a selective carrier.

4. Experimental

4.1. Syntheses

All chemicals were reagent grade and were used without further purification. Melting points were measured on an Electrothermal 9200 apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer Model 1760 FTIR spectrophotometer. ^1H- and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer with TMS as internal reference. The NOE 1D difference spectra were acquired with a saturation delay of 5 s and 256 transients. The conventional COSY 45 and the phase sensitive NOESY

experiments were collected as a 256×2K complex points. The NOESY spectrum was acquired on a Varian Unity 500 spectrometer with a mixing time of 1 s. Fast atom bombardment mass spectra were obtained on a VG Trio 2000 quadrupole instrument, using *m*-nitrobenzyl alcohol as a matrix. Elemental analyses were determined on a Fisons EA 1108 microanalyser.

4.1.1. 7,13,19,25-Tetra-*tert*-butyl-28-methoxy-27,29,30-tri-ethylacetate-2,3-dihomo-3-oxacalix-[4]arene (3). A mixture of *p-tert*-butyldihomooxacalix[4]arene monomethyl ether **2** (1 g, 1.45 mmol), potassium carbonate (0.9 g, 6.5 mmol), ethyl bromoacetate (1 ml, 9 mmol) and dry acetone (100 ml) was refluxed in an atmosphere of N_2 for 48 h. After cooling, the reaction mixture was filtered, and the solid residue was washed several times with dichloromethane. The combined organic solutions were concentrated to an oily residue, which was dissolved in ethanol. After standing at 0°C for ca. 3–4 days, **3** was obtained as a crystalline product in 55% (0.75 g) yield: mp 139–140°C; IR (KBr), ν_{max} 1775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32, 7.21, 7.10, 7.08, 6.95, 6.92, 6.82, 6.79 (8d, 8H, ArH), 4.97 (d, 1H, CH_2OCH_2, J=11.8 Hz), 4.69 (d, 1H, CH_2OCH_2, J=12.2 Hz), 4.68 (d, 1H, OCH_2CO, J=16.5 Hz), 4.66 (d, 1H, $ArCH_2Ar$, J=13.1 Hz), 4.57 (d, 1H, OCH_2CO, J=16.0 Hz), 4.46 (d, 1H, CH_2OCH_2, J=11.8 Hz), 4.45 (s, 2H, OCH_2CO), 4.42 (d, 1H, CH_2OCH_2, J=12.2 Hz), 4.35 (d, 1H, $ArCH_2Ar$, J=13.7 Hz), 4.29 (d, 1H, OCH_2CO, J=16.5 Hz), 4.28 (d, 1H, $ArCH_2Ar$, J=14.1 Hz), 4.27–4.16 (3q, 6H, OCH_2CH_3), 4.19 (d, 1H, OCH_2CO, J=16.0 Hz), 3.50 (d, 1H, $ArCH_2Ar$, J=14.1 Hz), 3.49 (d, 1H, $ArCH_2Ar$, J=13.7 Hz), 3.27 (d, 1H, $ArCH_2Ar$, J=13.1 Hz), 2.90 (s, 3H, OCH_3), 1.34 (s, 9H, $C(CH_3)_3$), 1.30 (t, 6H, OCH_2CH_3), 1.28 (t, 3H, OCH_2CH_3), 1.21, 1.06, 0.92 (3s, 27H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 170.6, 169.61, 169.60 (CO), 155.4, 153.2, 152.7, 152.4, 146.0, 145.6, 145.3, 134.7, 133.9, 133.2, 132.8, 132.5, 130.7, 130.5 (Ar), 127.6, 127.3, 127.1, 126.9, 125.9, 125.6, 125.6, 125.5, 124.5 (ArH), 71.4, 70.9 (CH_2OCH_2), 69.9, 69.3, 68.9 (OCH_2CH_3), 61.3 (OCH_3), 60.79, 60.75, 60.4 (OCH_2CO), 34.1, 33.9 ($C(CH_3)_3$), 33.5, 33.4 ($ArCH_2Ar$), 31.6, 31.5, 31.3, 31.2 ($C(CH_3)_3$), 31.1 ($ArCH_2Ar$), 30.9 (OCH_2CH_3), 14.2 (OCH_2CH_3); MS, *m/z* 950. Anal. Calcd for $C_{58}H_{78}O_{11}$: C, 73.23; H, 8.26. Found: C, 73.28; H, 8.28.

p-tert-Butylcalix[4]arene tetraethylacetate **4** was prepared as described by Arnaud Neu et al.[17]

4.2. Extraction studies

Equal volumes (5 ml) of neutral aqueous solution of metal picrates (2.5×10^{-4} M) and solutions of calixarene derivatives (2.5×10^{-4} M) in CH_2Cl_2 were vigorously shaken for 2 min, and then thermostated in a water bath with mechanical stirring, at 25°C for 15 h. After complete phase separation, the concentration of picrate ion in the aqueous phase was determined spectrophotometrically (λ_{max}= 354 nm). The details of metal picrates preparation have already been described.[14] For each cation–calixarene system, the absorbance measurements were repeated four times. Blank experiments showed that no picrate extraction occurred in the absence of a calixarene derivative.

4.3. ^1H NMR titration experiments

From a solution of NaSCN (1 M) in CD_3OD and with a 25 μl syringe, several aliquots (up to 3 equiv.) were added to a $CDCl_3$ solution (2×10^{-2} M) of the ligand **3** directly in the NMR tube. The spectra were registered after each addition of the salt.

4.4. Determination of stability constants

The stability constants β were determined at 25°C and at a constant ionic strength (0.01 M) in methanol (Merck, Uvasol) by spectrophotometry in the wavelength range 250–300 nm. The concentration of the ligand solution was 2×10^{-4} M. The ionic strength (0.01 M) was provided by Et_4NCl (Fluka, purum≥98%) and the salts used were chlorides: LiCl, CsCl (Riedel-de Haen, p.a.), RbCl (Aldrich, +99%), NaCl, KCl and all the alkaline-earth chlorides (Merck, p.a.).

The spectrophotometric technique has already been described in detail elsewhere.[14]

4.5. Transport experiments

The ion transport across a liquid membrane was done using an apparatus similar to that employed by Lamb et al.[24] The membrane phase, 50 ml of CH_2Cl_2 containing the calixarene derivative (7×10^{-5} M), the receiving phase, 25 ml of doubly distilled and deionized water and the source phase, 7 ml of aqueous metal picrate solution (5×10^{-3} M), were placed in a thermostated vessel. The apparatus was maintained at 25°C and the phases stirred at 150 rpm. The experiments were repeated, at least, three times. The appearance of the picrate ion in the receiving phase was followed by UV spectrophotometry at regular time intervals. The experimental procedure has already been described elsewhere,[14] as well.

In all cases, the plots of the number of moles transported to the receiving phase vs time, were linear, with correlation coefficients of at least 0.997. The slope of these straight lines represents the transport rate values. Experiments with no carrier present were performed, indicating no transport of metal picrates.

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