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Alkali and alkaline-earth metal cation complexation and transport properties by tetraphenyl ketone of *p-tert*-butyldihomooxacalix[4]arene

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ABSTRACT: The tetraphenyl ketone of *p-tert*-butyldihomooxacalix[4]arene (**2**) was synthesized for the first time. This derivative possesses the cone conformation in solution at room temperature, which was confirmed by NMR measurements (^{1}H, ^{13}C and NOE 1D). Extraction studies with metal picrates from neutral aqueous solution into dichloromethane, transport experiments with metal picrates through a dichloromethane membrane and stability constant measurements by UV absorption spectroscopy in methanol and acetonitrile were performed to evaluate the binding ability of ketone **2** towards alkali and alkaline earth metal cations. The tetraphenylketone of *p-tert*-butylcalix[4]arene (**3**) was also studied, and the results for the two derivatives were compared. Compound **2** shows a preference for K^+ and Ba^{2+} cations, being selective only in the alkaline earth metal cation series. Compound **3** is a stronger binder than **2**, but is a weaker extractant. Both show transport rates that are not proportional to complex stability or to extraction efficiency. Ketone **2** can be characterized as a selective receptor. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: *p-tert*-butyldihomooxacalix[4]arene tetraphenyl ketone; alkali metal cations; alkaline earth metal cations; complexation; transport properties

INTRODUCTION

One of the most important feature of the calixarenes[1,2] is undoubtedly their ability to bind selectively a large variety of metal cations.

A large number of calix[*n*]arenes (mainly $n = 4$, 5 and 6) chemically modified at the lower rim with ester,[3–10] amide,[6,9–12] ketone,[5,6,13,14] carboxylic acid,[15] crown ether[16–20] and thioamide[21,22] groups as substituents have been synthesized and their cation binding and transport properties studied. The ionophoric activity of these calixarene derivatives has especially been analysed towards alkali and alkaline earth metal cations. Extraction studies, transport experiments through a liquid membrane and stability constant measurements are the techniques used to assess the binding ability of these calixarenes.

The conformation of a calixarene is an important factor for its cation binding selectivity. Calix[4]- and calix[5]-arene derivatives exist in the cone conformation, with the functional groups forming a cavity suitable for cation inclusion.

In the course of the synthesis and NMR conformational analysis of dihomooxacalix[4]arene derivatives,[23] we have started the preparation of dihomooxa compounds with substituents containing the carbonyl group at the lower rim. These derivatives also possess the cone conformation and, compared with the analogous calix[4]-arenes, they are potential host molecules for the larger cations owing to the bigger size of their cavities.

In this work, the tetraphenyl ketone derivative **2** was synthesized for the first time from *p-tert*-butyldihomooxacalix[4]arene (**1**). Its NMR conformational analysis was performed and its binding ability towards alkali and alkaline earth metal cations determined. This property was established by extraction studies with metal picrates from neutral aqueous solution into dichloromethane and stability constant measurements by UV absorption spectroscopy in methanol and acetonitrile. Transport experiments with metal picrates through a dichloromethane membrane were also performed.

The tetraphenyl ketone of *p-tert*-butylcalix[4]arene (**3**) was also studied and the results for the two derivatives were compared.

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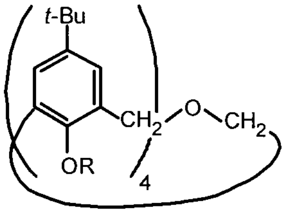
RESULTS AND DISCUSSION

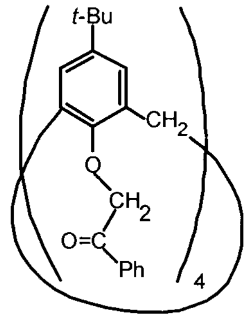
Synthesis and conformational analysis

Treatment of compound **1** with 2-bromoacetophenone, potassium iodide and potassium carbonate in dry acetone under reflux furnished the tetraketone **2**. The ketone **3** was prepared in the same way, according to Arnaud-Neu *et al.*[5]



1 R = H

2 R = CH_2COPh



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Proton and carbon-13 NMR studies were carried out with compound **2** to establish its conformation. The ^1H NMR spectrum displays, in chloroform at room temperature, three AB quartets for the CH_2 bridge protons. Two of them correspond to four protons each and the other to only two protons. Beyond the signals of the ketone group, the spectrum also exhibits two singlets for the *tert*-butyl groups and two pairs of doublets for the aromatic protons. The ^{13}C NMR spectrum indicates the cone conformation,[24] showing one Ar*C*H$_2$Ar resonance at δ 32.4 corresponding to one carbon atom and another at δ 31.7 corresponding to two carbon atoms.

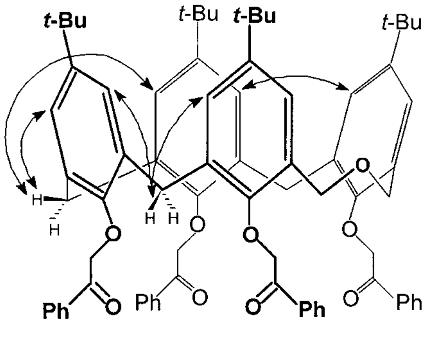

Figure 1. Relevant NOE enhancements for compound **2**

These spectral data established that **2** exists in the cone conformation, which was also confirmed by NOE 1D difference experiments (Fig. 1).

Extraction of alkali and alkaline earth metal cations

The results of phase transfer were obtained by the technique of picrate extraction devised by Pedersen.[25] These data, expressed as a percentage of cation extracted (% *E*), for tetraketones **2** and **3** are given in Table 1 and shown graphically in Fig. 2.

The results obtained with compound **2** range from 26 to 70% for the alkali metal picrates and from 10 to 57% for the alkaline earth metal picrates. These percentages are higher than those for derivative **3** for all cations studied. Ketone **2** shows a high extraction level, with a preference for cations such as K^+ (70%) and Ba^{2+} (57%).

In the alkali metal cation series, **2** displays a plateau selectivity with little discrimination between K^+ and Na^+. This behaviour is consistent with the larger cavity size compared with **3**. Tetramer **3**, being more rigid, gives a sharp peak selectivity for Na^+, like the majority of the calix[4]arene derivatives. Lehn and Sauvage[26] observed that rigid ligands exhibit selectivity peaks, whereas the more flexible ones display plateau selectivity.

The extraction of alkali metal cations with ketone **3** had already been carried out by Arnaud-Neu *et al.*,[5] but with basic metal picrates. Therefore, the comparison with our data is not correct.

In the alkaline earth metal cation series, the most significant characteristic of **2** is the very high extraction level for Ba^{2+}, compared with the low levels for Mg^{2+}, Ca^{2+} and Sr^{2+} and for all alkaline earth metal cations with ketone **3**. Derivative **2** shows a high extraction efficiency towards Ba^{2+}, only compared with the amide derivatives[11] of *p*-*tert*-butylcalix[4]arene: the pyrrolidinamide with 67% and the diethylamide with 74% extraction. However, these amides do not show any selectivity ($S = \% E_{M_1^{n+}} / \% E_{M_2^{n+}}$) for that ion, whereas ketone **2** displays a strong peak selectivity. To our

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

	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Ionic radius (Å)[b]	0.78	0.98	1.33	1.49	1.65	0.78	1.06	1.27	1.43
2	62	68	70	55	26	14	9.6	17	57
3	15	55	27	26	17	7.2	6.8	8.4	6.0

[a] Values with uncertainties less than 5%.

[b] V. M. Goldschmidt, *Skr. Norske Videnskaps-Akad. Oslo I, Mat.-Naturv. Kl.* (1926); data quoted in I. Marcus, *Ion Properties*, pp. 46–47. Marcel Dekker, New York (1997).

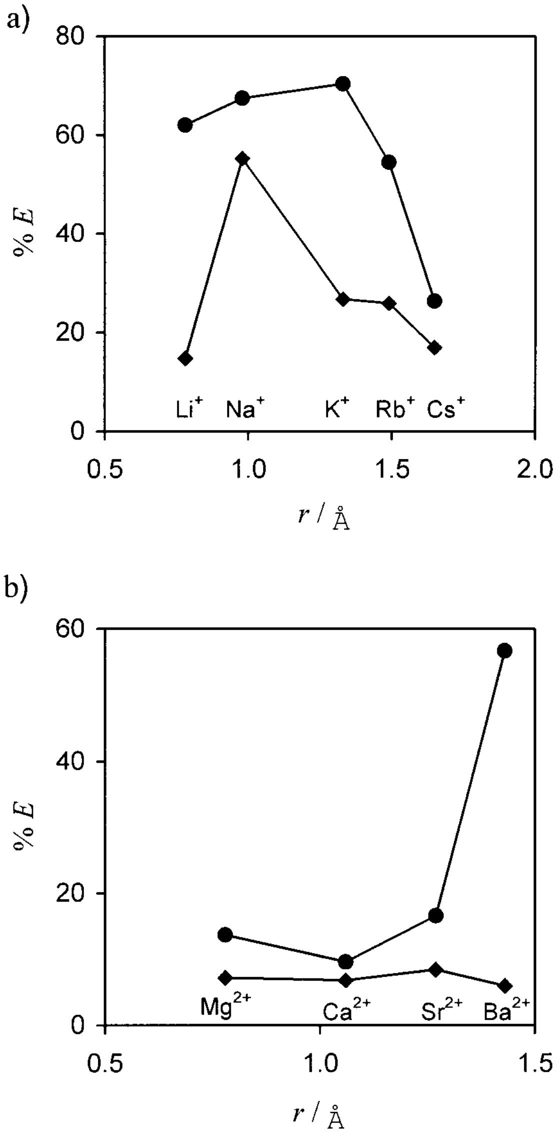

Figure 2. Percentage extraction (% *E*) of metal picrates into CH_2Cl_2 at 25 °C vs the cation ionic radius (*r*) for tetraketones **2** (●) and **3** (◆). (a) Alkali and (b) alkaline earth metals

knowledge, this is the highest selectivity reported for a calixarene towards Ba^{2+}: $S_{Ba^{2+}/Sr^{2+}} = 3.4$; $S_{Ba^{2+}/Mg^{2+}} = 4.1$; $S_{Ba^{2+}/Ca^{2+}} = 5.9$.

These results suggest a good fit between the size of the cation and the cavity size, which appears to be the main factor in selectivity in this cation series.

Determination of stability constants

The stability constants, as log β, for tetraketone **2** in methanol and acetonitrile and for tetraketone **3** in acetonitrile[5] are collected in Table 2. In all cases, the experimental data are consistent with the formation of only 1:1 complexes.

In methanol. The values of log β for the alkali metal series in methanol range from about 2 to 4 with tetraketone **2**. This complexation profile, shown in Fig. 3, is almost the same as that observed in extraction. This ketone shows also a plateau selectivity for cations Na^+, K^+ and Rb^+ with a small maximum for K^+. Owing to the flexibility of this compound, the conformational changes present in the complexation process are easier and the resulting stability of the Na^+ and Rb^+ complexes is the same. However, **2** discriminates clearly between this triad of cations and the smaller Li^+ and the larger Cs^+.

In the alkaline earth metal series, although **2** shows a low extraction level for Mg^{2+}, Ca^{2+} and Sr^{2+}, its complexing ability is much higher (log $\beta \geq 4.0$). These β values are even higher than those found for the alkali metal cations. In this respect, ketone **2** resembles tetrahomodioxacalix[4]arene tetraethyl ester,[27] which does not extract Ca^{2+} and Ba^{2+} ions (ca 1% *E*), but forms very strong complexes (log $\beta > 6$) with these cations. Towards Ba^{2+}, its log β (4.9) is the highest value determined in this work, and agrees with the preference shown by **2** in extraction.

As summarized in Table 3, there is no clear selectivity of **2** within the alkali and the alkaline earth metal series, but a more substantial bivalent/monovalent cation selectivity is observed. For each pair of cations with similar ionic radii, ketone **2** displays a preference for divalent cations. The same was observed with the amide derivatives[11] of *p-tert*-butylcalix[4]arene and some cryptands.[26]

In acetonitrile. The stability constants of derivative **2** were also determined in acetonitrile for comparison with the log β values of **3**, which were obtained in this solvent.[5] Acetonitrile is a dipolar aprotic solvent very different from water, which makes the comparison between extraction and stability data more difficult. Nevertheless, it is possible to make some comments about the results obtained.

Table 2. Logarithms of the stability constants (β) of alkali and alkaline earth metal complexes at 25 °C[a]

Solvent	Ketone	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
MeOH	**2**	2.3	3.7	4.0	3.7	2.2	4.0	4.0	4.5	4.9
MeCN	**2**	3.6	3.2	3.4	3.9	4.1	4.4	—	—	5.0
	3[b]	6.3	6.1	5.1	4.5	5.6	—	—	—	—

[a] Standard deviation of the mean of 2–4 independent series: $\sigma_{n-1} = 0.2$–0.3 log unit.

[b] Data taken from Ref. 5.

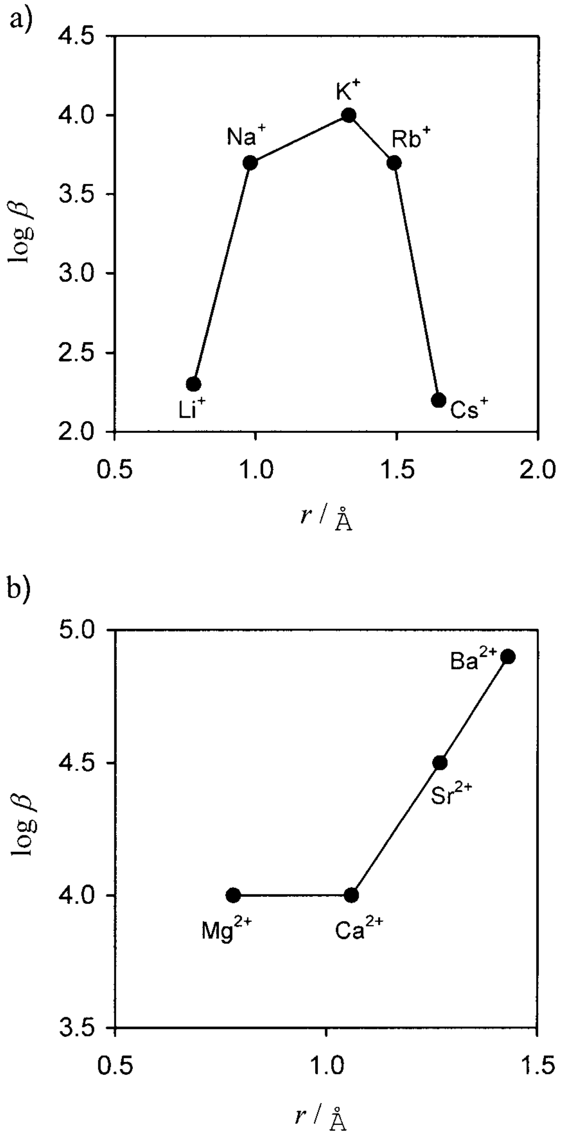

Figure 3. Logarithms of the stability constants (β) of metal cation complexes of tetraketone **2** in methanol vs the cation ionic radius (r). (a) Alkali and (b) alkaline earth metals

In acetonitrile the cations and ligands are less solvated than in methanol, according to Gutmann's donicity scale[28] (14.1 and 23.5, respectively).[12] This means that the competition for solvation becomes less significant and, consequently, the cation–ligand interactions are favoured over the cation–solvent and ligand–solvent interactions. It is then expected that the stability constants in acetonitrile will be higher than those in methanol, mainly for the smallest cations.

The Li^+ complex shows an increase in stability constant of 1.3 log units from methanol to acetonitrile, which is mainly due to a solvent effect, as discussed above. For Na^+ an increase was also expected, although lower than for Li^+, but a slight decrease was observed. In the case of K^+, Rb^+ and Cs^+, they are slightly more solvated in acetonitrile than in methanol,[29] and therefore a decrease in log β value is expected. This is true for K^+, but for the other two cations an increase of log β is observed, mainly for Cs^+. As suggested by Arnaud-Neu *et al.*,[12] this result may indicate that the lower solvation of the ligand in acetonitrile should be the main factor in the higher stability of the complexes in this solvent. Moreover, molecular dynamics (MD) simulations[30] indicate that in water the carbonyl groups have a significant degree of hydration, leading to 'open-type' conformers where the carbonyl groups have a weak involvement in the cation binding. However, in acetonitrile the C=O groups are less solvated and adopt more convergent orientations, where the cation is shielded from the solvent. These studies have not been made in methanol, but the similarity between this solvent and water allows those results to be transposed to methanol. The solvation of the complex[12] should also be an important factor to consider, and according to the previous MD simulations, it will increase with the size of the cation (from Li^+ to Cs^+).

In conclusion, it is possible that there exists a difference in the conformation of ketone **2** in methanol and in acetonitrile, which may be unfavourable to Na^+ and K^+ complexation in acetonitrile.

The log β values obtained for the alkaline earth metal cations Mg^{2+} and Ba^{2+} in acetonitrile can be understood in terms of solvation effects as discussed above.

Ketone **3** is a stronger binder (Table 2) than ketone **2** for all the alkali metal cations, but is a weaker extractant. This is probably due to its higher lipophilicity, which decreases its extraction efficiency.[5] In fact, derivative **2** is more soluble than derivative **3** in methanol.

Ion transport

The studies of ion transport across a liquid membrane were carried out using an apparatus similar to that employed by Lamb and co-workers.[31] The transport rates V, in μmol h^{-1} for compounds **2** and **3**, are presented in Table 4 and Fig. 4.

Ketone **2** shows a transport rate sequence the reverse of that for the stability constants and for the efficiency of

Table 3. Complexation selectivities, $S = \beta_{LM_1}{}^{n+}/\beta_{LM_2}{}^{n+}$, for compound **2**

K^+/Na^+	Ba^{2+}/Sr^{2+}	Mg^{2+}/Li^+	Ca^{2+}/Na^+	Sr^{2+}/K^+	Ba^{2+}/Rb^+
2	2.5	50	2	3.2	16

Table 4. Transport rate [V (μmol h^{-1})] of alkali and alkaline earth metal picrates through a CH_2Cl_2 liquid membrane at 25 °C[a]

Ketone	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
2	1.8	0.17	0.21	0.8	2.7	0.06	1.5	0.7	0.15
3	0.39	0.07	1.5	0.18	0.05	0.01	0.04	0.06	0.09

[a] Reproducibility of ±10%, except for Sr^{2+}–**2** and Ba^{2+}–**3** systems (± 15%).

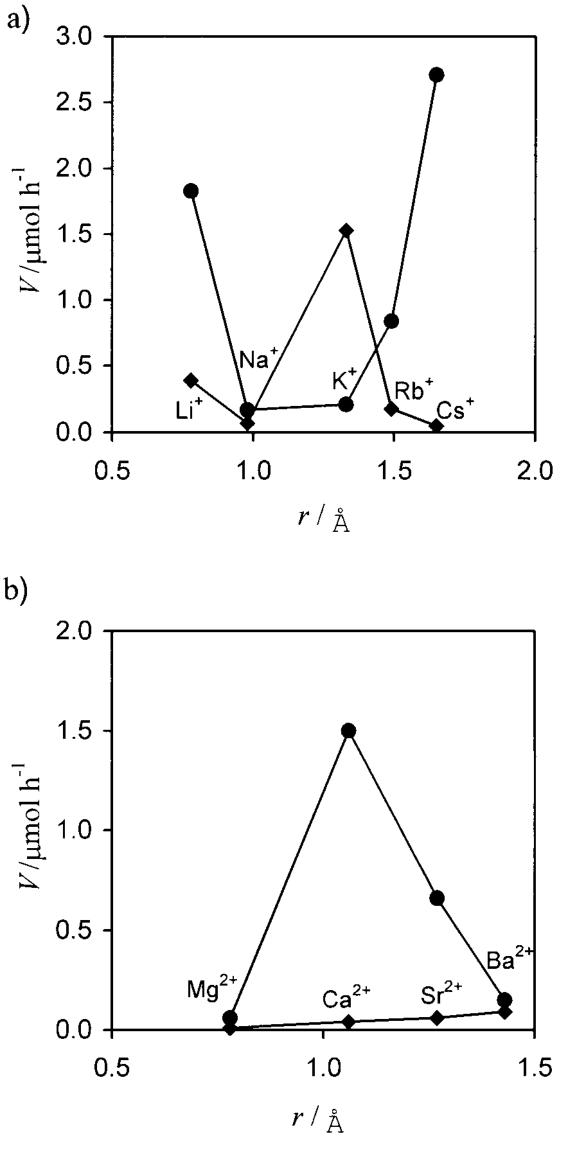

Figure 4. Transport rate [V (μmol h^{-1})] of metal picrates through a CH_2Cl_2 liquid membrane vs the cation ionic radius (r) for tetraketones **2** (●) and **3** (◆). (a) Alkali and (b) alkaline earth metals

extraction. Whereas K^+ and Na^+ are the most extracted and efficiently complexed cations, they become the most slowly transported ones. The opposite is observed with Cs^+, which being the least bound cation is the fastest transported one. Derivative **2** displays good Cs^+/K^+ and Cs^+/Na^+ transport selectivities (Table 5).

Kirch and Lehn[32a] observed that for some cryptands, such as [2.2.2], the transport rates were not proportional to either the complex stability or the extraction efficiency. Lamb *et al.*[31b] also found similar situations with some crown ethers, and the *p-tert*-butylcalix[5]arene pentaethyl ester, and the *p-tert*-butylcalix[4]arene pyrrolidinamide and diethylamide behave in the same way.[9]

This behaviour is due to the extent of the carrier saturation.[32b] The ligands that form more stable complexes extract their preferred cations efficiently, but have slow dissociation rates. This results in saturation of the carrier, so that little carrier stays free for back-diffusion. Hence, the total transport rate will mainly depend on cation dissociation rate.

Towards alkaline earth metal cations a similar situation is observed. Ketone **2** extracts and complexes Ba^{2+} very well, but transports it inefficiently, whereas with Ca^{2+} an opposite behaviour was found. This derivative even displays a very selective transport for Ca^{2+} with respect to Mg^{2+} (Table 5).

Ketone **3** seems to behave like its homologous derivative **2**. It displays a high extraction (55%) and complexation ($\log \beta = 6.1$ in MeCN)[5] level for Na^+, but shows one of the smallest transport rates for this cation (0.07 μmol h^{-1}). For K^+ the transport rate is the highest (1.53 μmol h^{-1}) and the **3**–K^+ complex has a $\log \beta$ value in acetonitrile of 5.1.[5]

Kirch and Lehn[32a] showed for the first time the existence of a relationship between the transport rates and the stability constants. The transport rates for alkali metal picrates by cryptands were maximum when the $\log \beta$ value in methanol was about 5. With calixarenes Arnaud-Neu *et al.*[9] found a similar $\log \beta$ value (5.1 ± 0.7) in methanol. Interestingly, the $\log \beta$ value obtained in

Table 5. Transport selectivities, $S = V_{M_1}{}^{n+}/V_{M_2}{}^{n+}$, for derivatives **2** and **3**

Ketone	Cs^+/K^+	Cs^+/Na^+	Ca^{2+}/Mg^{2+}	K^+/Na^+	K^+/Cs^+
2	12.9	15.9	25	—	—
3	—	—	—	21.9	30.6

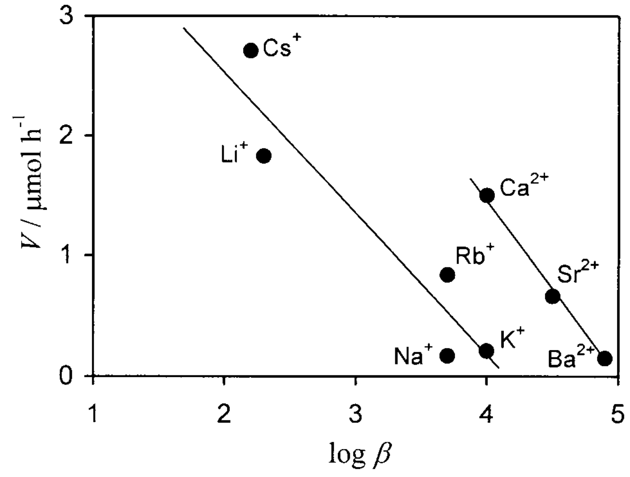

Figure 5. Transport rate [V (μmol h^{-1})] of metal picrates vs log β for tetraketone **2** in methanol

acetonitrile for the **3**–K$^+$ complex is the same as that obtained in methanol for a maximum transport rate.

Ketone **3** is a good selective neutral carrier for K$^+$, with a K$^+$/Na$^+$ selectivity of 21.9, higher than that of pyrrolidinamide (S = 12.8) and diethylamide (S = 13.8) of *p-tert*-butylcalix[4]arene,[9] but near to that of 18-crown-6 (S = 24.8).[31b] The K$^+$/Cs$^+$ selectivity is even higher (Table 5). Derivative **3** is an inefficient carrier towards alkaline earth metal cations, with transport rates ranging from 0.01 μmol h^{-1} for Mg^{2+} up to 0.09 μmol h^{-1} for Ba^{2+}.

CONCLUSIONS

According to the different behaviours of the ligands, Lehn[32b] characterized them as selective carriers or selective receptors. For a selective carrier the most efficiently bound cation is also the fastest transported, whereas for a selective receptor the best bound cation is the most slowly transported one. Hence it is possible to distinguish from a plot of transport rates versus stability constants whether a ligand is a receptor (negative slope) or a carrier (positive slope).

The plot shown in Fig. 5 indicates that ketone **2** is a selective receptor. For ketone **3** such a conclusion cannot be drawn, because the β values were measured in acetonitrile (as mentioned before). If these results were transposed to methanol, derivative **3** could also be considered as a selective receptor.

EXPERIMENTAL

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. ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded on a Varian Unity 300 spectrometer with TMS as internal reference. Coupling constants J are given in Hz. The NOE 1D difference spectra were acquired with a saturation delay of 5 s and 256 transients. Fast atom bombardment (FAB) 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.

*Tetraphenyl p-tert-butyldihomooxacalix[4]arene tetraketone (**2**).* A mixture of *p-tert*-butyldihomooxacalix[4]arene **1** (1 g, 1.48 mmol), potassium iodide (1 g, 6 mmol), potassium carbonate (0.83 g, 6 mmol), 2-bromoacetophenone (1.2 g, 6 mmol) and dry acetone (70 ml) was refluxed in an atmosphere of N_2 for 48 h. After cooling, the reaction mixture was poured into 150 ml of water. The precipitated material was removed by filtration, taken up in dichloromethane and successively washed with 5% aqueous sodium metabisulphite, water, 1 M hydrochloric acid and water and dried with anhydrous Na_2SO_4. Evaporation of the solvent gave a deep-yellow solid, which was boiled in methanol (70 ml) and filtered. Recrystallization from propan-2-ol furnished 0.68 g (40%) of **2** as white needles: m.p. 146–148 °C; IR (KBr), ν_{max} 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$), δ 7.86, 7.83, 7.81, 7.79 (4d, 8H COArH), 7.46–7.20 (m, 12H, COArH), 7.06 (d, 2H, ArH), 6.92 (2d, 4H, ArH), 6.89 (d, 2H, ArH), 5.70 (d, 2H, OCH$_2$CO, J = 17.2), 5.64 (d, 2H, OCH$_2$CO, J = 17.6), 5.45 (d, 2H, OCH$_2$CO, J = 17.6), 5.19 (d, 2H, OCH$_2$CO, J = 17.2), 5.08 (d, 2H, ArCH$_2$Ar, J = 13.6), 5.06 (d, 2H, CH$_2$OCH$_2$, J = 12.2), 5.03 (d, 2H, ArCH$_2$Ar, J = 13.7), 4.54 (d, 2H, CH$_2$OCH$_2$, J = 12.2), 3.39 (d, 2H, ArCH$_2$Ar, J = 13.7), 3.38 (d, 2H, ArCH$_2$Ar, J = 13.6), 1.12, 1.05 [2s, 36H, C(CH$_3$)$_3$]; ^{13}C NMR (CDCl$_3$), δ 195.8, 195.4 (CO), 153.4, 153.2, 145.3, 145.0, 135.1, 134.9, 133.2, 133.1, 132.7, 130.9 (Ar), 132.9, 132.8, 128.41 (2C), 128.36 (2C), 127.82 (2C), 127.78 (2C), 126.9, 126.1, 126.0, 124.8 (ArH), 76.1, 75.9 (O*C*H$_2$CO), 68.8 (CH$_2$OCH$_2$), 34.0, 33.9 [*C*(CH$_3$)$_3$], 32.4, 31.7 (ArCH$_2$Ar), 31.5, 31.4 [C(*C*H$_3$)$_3$]; MS, *m/z* 1150. Analysis: calculated for $C_{77}H_{82}O_9$; C, 80.32; H, 7.18. Found: C, 80.20; H, 7.16.

Tetraketone **3** was prepared as described by Arnaud Neu *et al.*[5] using 2-bromoacetophenone as the alkylating agent.

Extraction studies. The metal picrates were prepared *in situ* by stepwise addition of an aqueous picric acid solution to an aqueous metal hydroxide solution, until neutralization was reached, determined by potentiometry with a glass electrode. The final concentration of the metal picrates was obtained by dilution. This method was used in all cases, except for Mg(OH)$_2$, the solubility of which in water is very low. Magnesium picrate was obtained by addition of the metal hydroxide in excess to an aqueous solution of picric acid. The mixture was stirred for 2–3 days and its pH was measured after filtration. Neutralization was reached by addition of picric acid.

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 shaken vigorously 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 ($\lambda_{max} = 354$ nm). For each cation–calixarene system, the absorbance measurements were repeated four times. Blank experiments without calixarene were also performed, yielding a negligible absorbance.

Determination of stability constants. The stability constants β were determined at 25 °C and at a constant ionic strength (0.01 M) in methanol and acetonitrile by spectrophotometry in the wavelength range 250–300 nm. The spectral changes induced by stepwise addition of the cation salts (0.1 ml aliquots up to 1 ml) to the calixarene solution (2 ml) directly in the measurement cell (1 cm pathlength), were recorded at several significant wavelengths, with a Hitachi Model U-2000 double-beam spectrophotometer equipped with a thermostated cell compartment. For each cation, the experiments were repeated at least twice and a minimum of 120 experimental values were obtained. These data were treated with a non-linear least-squares program developed in our laboratory (adapted to spectrophotometric or potentiometric data) incorporating the algorithm of Marquardt[33] to ensure convergence.

In methanol (Merck, Uvasol) the concentration of ketone **2** was 6×10^{-5} M. The ionic strength (0.01 M) was provided by Et_4NCl (Fluka, purum, $\geq$98%) and the salts used were chlorides: LiCl, CsCl (Riedel-de Haën, p.a.), RbCl (Aldrich, +99%), NaCl, KCl and all the alkaline earth metal chlorides (Merck, p.a.). In acetonitrile (Merck, Uvasol) the concentration of **2** was 8×10^{-5} M, the ionic strength (0.01 M) provided by Et_4NClO_4 (Fluka, purum, >99%) and the salts were perchlorates: $LiClO_4$ (Agros, p.a.), $RbClO_4$ (Sigma), $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ (Aldrich, 99%, ACS reagent) or nitrates ($CsNO_3$, Sigma).

Transport experiments. The ion transport across a liquid membrane was carried out using an apparatus similar to that employed by Lamb *et al.*[31] The membrane phase, 50 ml of CH_2Cl_2 containing the calixarene derivative (7×10^{-5} M), was placed at the bottom of a thermostated vessel (height 10.5 cm, diameter 6.5 cm) with a 3.5 cm magnetic stirring bar inside. An open glass cylinder (diameter 4 cm) was inserted into the membrane. The receiving phase, 25 ml of doubly distilled water, was placed outside the cylinder and the source phase, 7 ml of aqueous metal picrate solution (5×10^{-3} M), was added very slowly to the inside. The apparatus was maintained at 25 °C and the phases were 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. For each system a series of 8–10 experimental points were obtained. For the slower systems, the transport experiments were followed during a 10 h maximum period. 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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