Mixed "Amide-phosphoryl" Calix[4]arenes. On the Selectivity of Two Conformers Towards Alkali Ion Complexation

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Abstract. The binding properties of *cone*-5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoyl-methoxy)-26,28-bis(diphenylphosphinoylmethoxy)calix[4] arene (*cone*-**1**) towards alkali metals have been compared with those of the corresponding *partial-cone* conformer (*paco*-**1**). Both hybrid ligands form stable complexes with alkali picrates in tetrahydrofuran having a 1 : 1 cation/ligand ratio. Regarding extractability, that presented by *cone*-**1** decreases continually on-going from Li/Na to Cs, while that for *paco*-**1** presents a peak selectivity for Na (with the following order Na > K > Rb > Li > Cs). These selectivities parallel, respectively, results obtained for extraction and transport experiments. The kinetics of the alkali metal thiocyanate transport through a bulk liquid membrane containing these ligands in 1,2-dichloroethane could be rationalised in terms of a simple mathematical model. The lower transfer coefficients found for *paco*-**1** relative to *cone*-**1** reflect the larger size of the diffusing *paco*-complex.

Key words: calixarenes, alkali metals, complexation, extraction

1. Introduction

Many recent publications have illustrated the great potential of *p-tert*-butylcalix[4]arene as a building block for the construction of selective cation receptors [1–6]. The complexation ability of *O*-functionalized calix[4]arenes, i.e., bearing complexing units attached at the lower rim, depends mainly on (i) the number and nature of any pendent binding functions and (ii) the conformation of the macrocyclic platform. In general cone conformers provide access to receptors whose primary binding motif involves only the *O*-tethered substituents, but other conformations, notably the 1,3-alternate form can involve the aryl units of the calixarene in the coordination sphere. This structural versatility controls the shape, size and constitution of the receptor cavity and introduces selectivity for cation
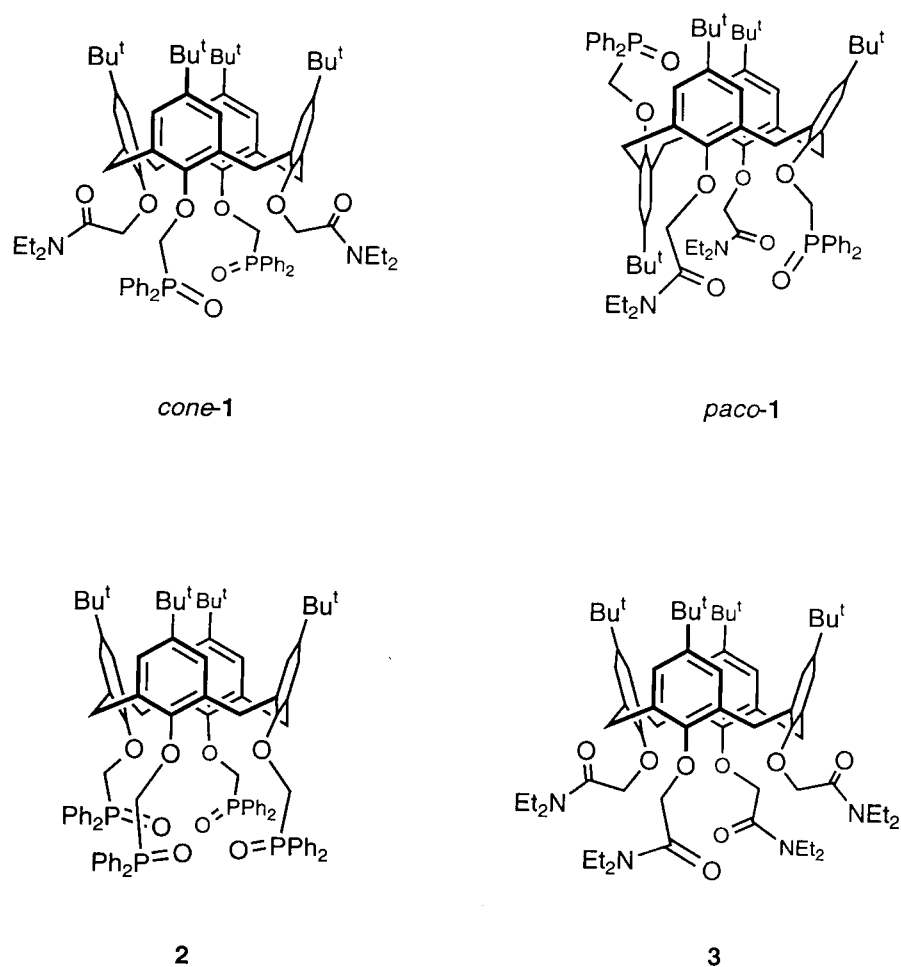
Figure 1. Structure of the calixarenes mentioned in this study.

complexation. We note that comparative studies between tetra-functionalised *cone* and *partial cone* conformers are scarce.

As part of our studies on the extractive properties of phosphorylated calixarenes [7–12], we now report an investigation of the transport properties (i.e., compl- exation, extraction and carrier properties) of *paco-***1**, a partial cone calix[4]arene bearing two phosphoryl and two amide podands (Figure 1). The present work complements a previous study where it was shown that the corresponding cone isomer *cone-***1** presents a marked specificity for binding Li$^+$ and Na$^+$ vs. other alkali cations [11]. This behaviour contrasts with that of the tetraphosphorylated calixarene **2** [11, 13] and tetra-amide **3** [14, 15], which, respectively, display a good selectivity for K$^+$ and Na$^+$.

2. Experimental

2.1. REAGENTS AND INSTRUMENTATION

5, 11, 17, 23-Tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26, 28-bis-(diphenylphosphinoylmethoxy)calix[4]arene (*cone*-**1**) and 25, 27-*syn*-26, 28-*anti*-5, 11, 17, 23-tetra-*tert*-butyl-25, 27-bis(diethylcarbamoylmethoxy)-26, 28-bis(diphenylphosphinoylmethoxy)calix[4]arene (*paco*-**1**) were synthesized according to procedures described previously [16]. The alkali picrates were obtained by neutralization of picric acid with a solution of the corresponding hydroxide. The resulting yellow precipitates were recrystallised from water, and washed with ethanol and ether, dried under vacuum, and stored in the dark. Cesium and rubidium thiocyanate were prepared by addition to a solution of ammonium thiocyanate of cesium carbonate and rubidium hydroxide, respectively. Both compounds were recrystallised from water. The other thiocyanates were from Fluka. Tetrahydrofuran (THF) was used without further purification. 1,2-Dichloroethane was washed several times with distilled water before being used for extraction and transport experiments. The UV experiments were carried out with a Perkin-Elmer 550S instrument).

2.2. COMPLEXATION STUDIES

These experiments were peformed at 20 °C using volumetric flasks of 10 mL. Variable quantities of a 0.001 M THF solution of the ligand were added to a 0.001 M solution (1 mL) of the alkali picrate in THF. The flask was then filled with the solvent. The absorbance of each solution was measured over the range 300–500 nm.

2.3. EXTRACTION PROCEDURE

As already known, extraction in the absence of calixarene was found to be zero within experimental error. Typically, 10 mL of a 2.5×10^{-4} M aqueous solution of alkali picrate and 10 mL of a 2.5×10^{-4} M solution of the ligands in 1,2-dichloroethane were transferred into a stoppered cylindrical glass tube immersed in a thermostated water bath (20 °C). The extraction equilibrium was reached after 20 minutes' stirring and the tube was subsequently allowed to stand for 10 minutes to complete the separation. The concentration of the picrate in the aqueous phase was determined spectrophotometrically at the wavelength of maximum absorption of the picrate ion ($\lambda_{max} = 355$ nm, $\epsilon_{max} = 14400$ L mol^{-1} cm^{-1}). The extraction percentage ($E\%$) was determined from the difference of picrate ion absorbances in the aqueous phase using following expression:

$$E\% = 100(A_0 - A)/A_0$$

in which A_0 is the absorbance of the aqueous phase after equilibrium with 1,2-dichloroethane, and A is the absorbance of the aqueous phase after equilibrium with a solution of ligand in 1,2-dichloroethane.

2.4. TRANSPORT EXPERIMENTS

Membrane transport experiments were carried out in a U-shaped glass tube immersed in a thermostated water bath at 25 °C. This cell was filled with 160 mL of a 7×10^{-4} M solution of ligand in 1,2-dichloroethane interfaced to 80 mL of a 0.1 M solution of alkali thiocyanate in one of the arms and 80 mL distilled water in the second arm. A uniform mixer was inserted into each arm and two synchronous motors (Heidolph RZR 2000) provided a constant rotation (100 rpm) of the mixers ensuring stirring of the phases. Transport across the organic phase was monitored by titration of thiocyanate ion appearing in the receiving phase. At a regular interval time, 2 mL of the receiving phase was sampled and diluted to 4 mL by a 0.02 M solution of $Fe(NO_3)_3$ in 0.2 M HNO_3 for spectrophotometric measurements ($\lambda = 480$ nm, $\epsilon = 4400$ L mol^{-1} cm^{-1}) [17]. In order to maintain the position of the interfaces, 2 mL of the feed phase were also removed. The variation of the volume of the receiving phase was taken into account in the calculations. Alkali metal thiocyanate concentration in the organic phase was determined by withdrawing 2 mL of the organic phase, stripping it with 5 mL of distilled water, and measuring according to the method described above.

In order to determine the equilibrium extraction concentration (C_1) 10 mL of 0.1 M aqueous solution of alkali metal thiocyanate and an equal volume of a solution of the ligand in 1,2-dichloroethane were placed in a tube immersed in the thermostated bath at 25 °C and stirred magnetically for 20 minutes. The phases were allowed to settle and 5 mL of the organic phase were removed. This solution was stripped with distilled water for spectrophotometric titration as described above.

3. Results and Discussion

3.1. COMPLEXATION AND EXTRACTION OF PICRATES

It is well known that alkali picrates form tight ion pairs (M^+Pic^-) in tetrahydrofuran (THF) solution that can be loosened (ML_n^+, Pic^-) by complexation with a calixarene ligand [18]. Complexation is shown by changes in the absorption spectrum, especially by a bathochromic shift of λ_{max}, that provide a clear isosbestic point corresponding to a single equilibrium:

$$M^+, Pic^- + nL = ML_n^+, Pic^-$$
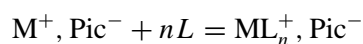
Such a behaviour was observed for *cone*-**1** and is confirmed here for *paco*-**1**, as exemplified in Figure 2 with Na^+. The bathochromic shifts for Li, Na, K, Rb, and Cs are reported in Table I.

Table I. Bathochromic shifts ($\Delta\lambda$, nm), at 20 °C in THF

Ligand	M$^+$Pic$^-$				
	Li$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
paco-**1**	37	31	24	21	10
cone-**1**	37	30	24	21	2

The stoichiometry of each complex was established by monitoring the shift in λ_{max} as a function of the ligand/cation concentration ratio (for the Na system, see Figure 3). A 1 : 1 stoichiometry ($n = 1$) was found for all complexes. Furthermore, by using the Rose-Drago method [19], stability constants (log K_f) for *paco*-**1** complexes were determined to be: 4.59, 6.50, 5.23, 4.67, 3.94, respectively for Li(pic), Na(pic), K(pic), Rb(pic), Cs(pic). Thus the selectivity sequence follows the order:

$$Na > K > Rb > Li > Cs$$

Extraction of alkali metal picrates by *paco*-**1** allowed calculation of the biphasic equilibrium constants K_{ex}:

$$M^+_{aq} + Pic^-_{aq} + L_{org} = ML^+, Pic^-_{org}$$

The corresponding values of log K_{ex} were found to be 6.9, 8.5, 8.0, 7.4, and 6.3, respectively, for Li, Na, K, Rb, Cs, leading to an extraction selectivity sequence that parallels that of the stability constants reported above for *paco*-**1** (Figure 4). Comparison between *paco*-**1** and *cone*-**1** clearly shows that there is no significant influence of the conformation on the selectivities for cations ranging from sodium to cesium, but a major disparity appears with lithium. This finding provides information on the relative involvement of PO and amide groups in the complexation of lithium, suggesting that lithium is preferentially complexed by the phosphine oxide arms rather than the amides.

3.2. EXTRACTION AND TRANSPORT OF THIOCYANATES

Extraction and transport through a bulk liquid membrane of alkali metal thiocyanates were carried out with *paco*-**1** in a similar way to those performed for *cone*-**1** [11]. The extraction by *paco*-**1** is characterised by the thiocyanate concentration C_1 in the organic phase at equilibrium determined under the following conditions: aqueous phase/0.1 M MSCN, organic phase L = 10^{-4} M in dichloroethane. The derived C_1 values (Table II) parallel the picrate extraction constants (K_{ex}). The related transport experiments (Figure 5) allowed determination of the steady-state transport rate V_s. Within the model used [11] V_s is related to C_1 via the relation:
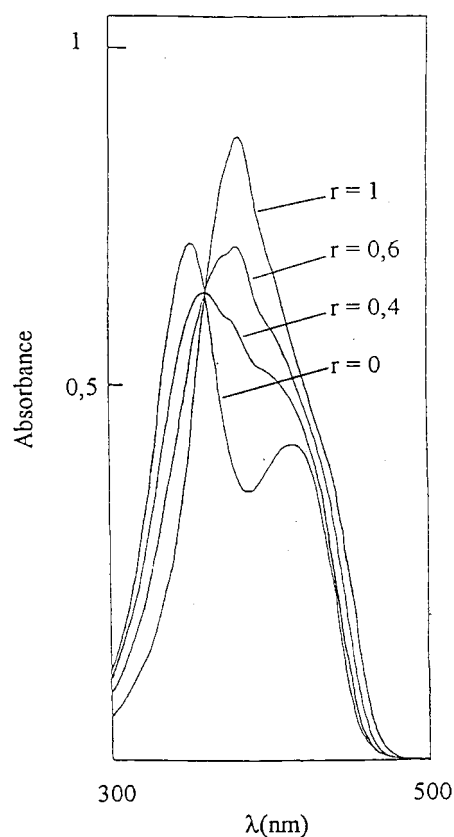
$$V_s = (1/2)k_{org}C_1S$$

Figure 2. Change of the absorption spectrum of sodium picrate in THF upon addition of various amounts of partial-cone-**1**: ligand/sodium picrate ratios (r): 0.0 (a) , 0.4 (b), 0.6 (c) and 1.0 (d).

Table II. Alkali thiocyanate extraction and transport through a solution of *cone*-**1** [10] and *paco*-**1** in 1,2-dichloroethane at 25 °C.[a]

M^+	$V_s \times 10^9$ (mol/s)		$C_1 \times 10^4$ (mol/l)		$k_{org} \times 10^5$ (dm/s)	
	cone	*paco*	*cone*	*paco*	*cone*	*paco*
Li^+	1.39	1.08	3.70	3.04	5.7	5.4
Na^+	1.40	1.42	3.71	4.01	5.7	4.8
K^+	1.34	1.35	3.66	3.94	5.6	5.1
Rb^+	0.96	1.32	2.41	3.69	6.0	5.4
Cs^+	0.16	0.68	0.40	2.14	6.1	4.8

[a]Ligand concentration: 7×10^{-4} M (160 mL); feed alkali thiocyanate concentration: 0.1 M (80 mL); receiving phase: distilled water (80 mL); stirring: 100 rpm; V_s: transport of solute at steady state; C_1: equilibrium extraction concentration of the complex in the organic phase under the conditions of transport; k_{org}: transfer coefficient.
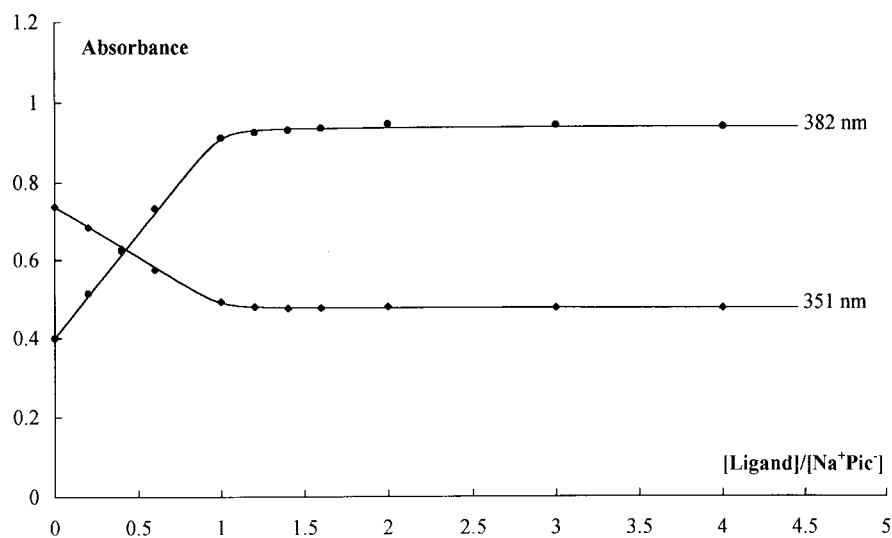
Figure 3. Plot of the absorbance vs. $[L]/[Na^+Pic^-]$ at $\lambda_{max.}$ of the tight sodium picrate (351 nm) and ligand separated sodium picrate (382 nm).
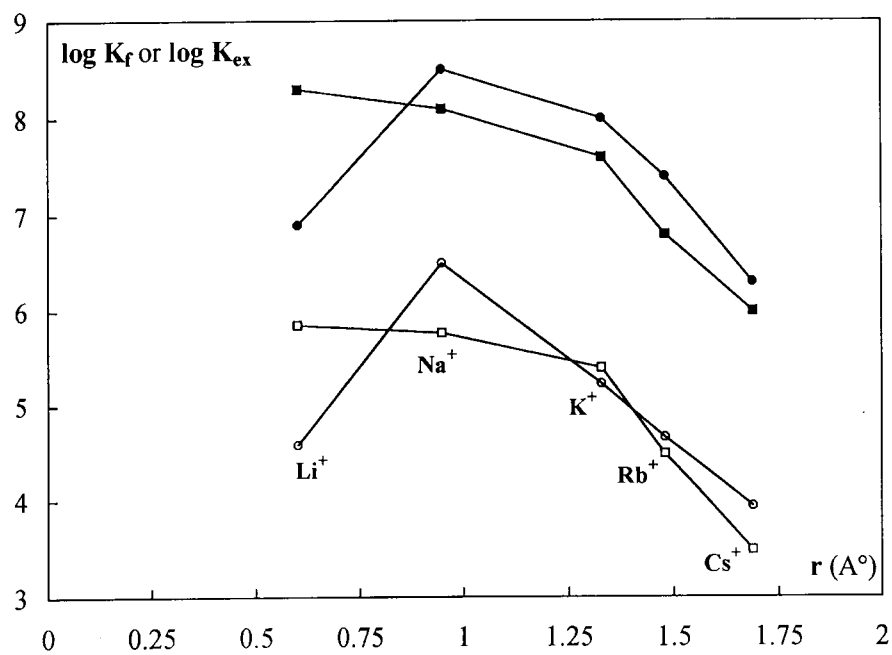

Figure 4. Plot of the alkali formation constants in THF (log K_f, empty symbols) and extraction constants (log K_{ex}, filled symbols) for the water to 1,2-dichloroethane system of alkali picrates at 20 °C vs. the ionic radius of alkali cations (*paco*-**1**: circles; *cone*-**1**: squares).
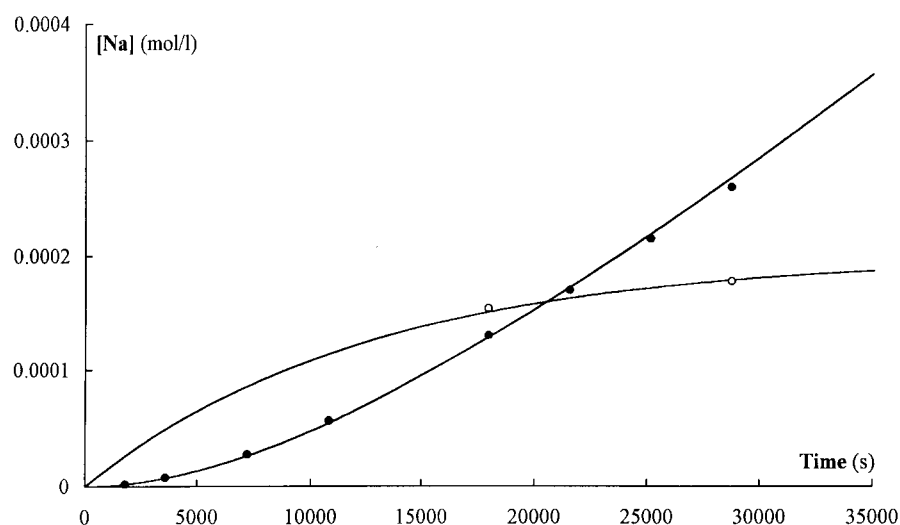
Figure 5. Evolution of the sodium thiocyanate concentration in the receiving (filled circles) and membrane (empty circles) phase as a function of time using *paco* **1** as carrier at 25 °C. Feed phase: 0.1 M sodium thiocyanate (80 mL): receiving phase: distilled water (80 mL); membrane phase: 7×10^{-4} M of carrier in 1,2-dichloroethane (160 mL); stirring: 100 rpm.

where S is the interfacial area while k_{org} is the transfer coefficient that can be evaluated from the tranport rate analysis.

Comparison of k_{org} for *cone*-**1** and *paco*-**1** (Table II) shows that the k_{org} tends to be lower for *paco*-**1**. Application of Fick's law and of the Wilke-Chang equation [20] for the diffusion coefficient leads to a relation between k_{org} and the molar volume V of the transporting complex:

$$k_{org} \propto V^{-0.6}$$

Hence a decrease of k_{org} denotes an increased size of the transporting complex on going from *cone*-**1** to *paco*-**1**.

4. Conclusion

In the present study dealing with the ion binding properties of two isomers, *paco*-**1** and *cone*-**1**, we have shown that both hybrid ligands form stable complexes with alkali metal picrates in THF having a 1 : 1 cation/ligand ratio. The study provides also a nice illustration for the preference of lithium for the phosphoryl groups: thus, while *cone*-**1** which possesses two phosphoryl groups occupying the same binding domain presents a high extractability for Li$^+$ over other cations, *paco*-**1** in which the P=O groups are anti-oriented displays poor selectivity for Li$^+$. It might be anticipated that the ligand obtained by interchanging the amides and the phosphoryl groups in *paco*-**1** should result in a new ligand displaying complexation and extraction properties close to those observed for *cone*-**1**.

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