

# Synthesis and alkali-complexation behaviour of 1,3-di-diethyl-acetamide *p*-*tert*-butyl calix[4]crowns

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## ABSTRACT

It is reported the synthesis of 1,3-di-diethyl-acetamide *p*-*tert*-butyl calix[4]crowns-*n* (*n* = 4-6), 4-6, combining amido functions and crown ether unit attached to a calixarene in [2+2'] fashion. Complexation of alkali picrates in CDC13 by 1H-NMR spectrometry showed that the cations are located in the crown loop. Separated ion pairs have been observed in THF leading to conclude an encapsulation of the metal in the calixcrown cavity.

## Introduction

Calixcrowns, and more particularly calix[4]-mono-crowns, are one of the most widely investigated class of cation ligands based on calixarenes.<sup>1</sup> They are hybrid macrocycles constructed from a calix[4]arene unit and a crown ether element to lead to 1,3-dihydroxy-calix[4]arene-mono-crowns.<sup>1</sup> Due to the presence of the crown loop, they show complexing properties towards alkali metals, alkaline earth metals and ammonium cations which can be tuned by subtle conformational and chemical changes around the crown ether binding region.<sup>1</sup> In addition, metal-ion complexation feature at the narrow rim in [2+2'] mixed O-tetra-substituted calix[4]arene derivatives has been shown to depend on the combined functionalities attached onto the calixarene.<sup>2,3</sup> Therefore it seemed interesting to us that by introducing ligating functions on the remaining hydroxy groups of the calix-mono-crown we will take advantage of both the complexation-tuning with various crown ether loops and the complexing behaviour of the added ligating functions.

In the present paper we report the synthesis of 1,3-di-diethyl-acetamide *p*-*tert*-butyl calix[4]crowns-*n*, (**4-6**), combining two amido functions and one crown ether unit.<sup>4</sup> The complexation behaviour of **4-6** has been studied by <sup>1</sup>H-NMR technique and UV-Vis spectrometry was used to show evidence of ion-pairing formation. Luminescence of Eu<sup>3+</sup> and Tb<sup>3+</sup> complexes with calixarene **5** has already been subject to publication.<sup>5</sup> And recently, Parma's group reported the synthesis and complexing properties toward alkali cations of related 1,2-di-diethyldiacetamido *p*-*tert*-butyl calix[4]crown-5 (the crown-5 polyether chain is linked on two proximal phenolic oxygen atoms instead of on two opposite ones) in cone and 1,2-alternate conformations.<sup>6</sup>

## Experimental section

**General :** Melting points (Mps) were taken on Büchi 500 apparatus in sealed tubes under nitrogen. <sup>1</sup>H-NMR were recorded on Bruker SY 200 ( $\delta$  are in ppm from tms, *J* are given Hz). Elemental analyses were done at the Service de Microanalyse of the Institut de Chimie de Strasbourg. All reactions were run under nitrogen. SiO<sub>2</sub> (Geduran 1.11567) was used for column chromatography. TLC plates were from Merck (Silica 60, F<sub>254</sub>-0.5 mm, Art 5744). All reagents

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and solvents were commercial and used without further purification. Dihydroxy *p*-*tert*-butyl calix[4]crown-4, -crown-5 and -crown-6 were prepared as described in the literature.

**UV-Vis studies.** For each ligand, variable quantities of a  $10^{-3}$  M THF solution of the ligand were added to a  $10^{-3}$  M solution (1 mL) of the alkali picrate in THF. THF was then added and made up to a volume of 10 mL. The absorbance of the solutions were measured in the range 300 - 500 nm (Perkin-Elmer model 2010PC).

**Preparation of 1,3-di-diethyl-acetamide *p*-*tert*-butyl calix[4]crown-4 (4).** Dihydroxy *p*-*tert*-butyl calix[4]crown-4 (**1**) (2.02 g, 2.62 mmol) and  $K_2CO_3$  (3.62 g, 26.2 mmol) were stirred in  $CH_3CN$  (250 ml) for 30 min at rt. Then, NaI (3.93 g, 26.2 mmol) and  $\alpha$ -chlorodiethylacetamide (3.93 g, 26.2 mmol) were added. Reflux was maintained for three days. Then, the solvents were evaporated to dryness. The residue was dissolved in the  $CH_2Cl_2$  and water (HCl 1N). The organic layer was dried over  $NaSO_4$ . After filtration and evaporation, the crude mixture was separated using a chromatography  $SiO_2$ -column (300 g). The eluent was a mixture of  $CH_2Cl_2$ /acetone with a gradient varying from 95/5 to 80/20. **4** (2.20 g, 2.22 mmol, 86 % yield) was obtained pure as a white solid. M. p. 162-163° C.  $^1H$ -NMR ( $CDCl_3$ )  $\delta$  : 7.15 (s, 4H, Ar-H), 6.48 (s, 4H, Ar-H), 4.50 (s, 4H,  $-OCH_2CO-$ ), 4.42 (d,  $J = 13.43$  Hz, 4H, Ar- $CH_2$ -Ar), 4.38 (t, 4H,  $-CH_2CH_2O-$ ), 4.11 (t, 4H,  $-CH_2CH_2O-$ ), 3.88 (s, 4H,  $-CH_2CH_2O-$ ), 3.46 (q,  $J = 6.33$  Hz, 4H,  $-NCH_2CH_3-$ ), 3.41 (q,  $J = 6.33$  Hz, 4H,  $-NCH_2CH_3-$ ), 3.23 (d,  $J = 13.43$  Hz, 4H, Ar- $CH_2$ -Ar), 1.42 (s, 18H,  $C(CH_3)_3$ ), 1.13 (t,  $J = 6.52$  Hz, 12H,  $NCH_2CH_3$ ), 0.81 (s, 18H,  $-C(CH_3)_3$ ). FAB-MS (positive)  $m/z = 989,8$  (97%); 1012,39 (95%) (ligand +  $Na^+$ ).

**Preparation of 1,3-di-diethyl-acetamide *p*-*tert*-butyl calix[4]crown-5 (5).** Same procedure as for **4** : dihydroxy *p*-*tert*-butyl calix[4]crown-5 (**2**) (2.51 g, 3.09 mmol),  $K_2CO_3$  (3.62 g, 26.2 mmol),  $CH_3CN$  (275 ml), NaI (4.63 g, 30.9 mmol),  $\alpha$ -chloro-diethylacetamide (4.63 g, 30.9 mmol). **5** (2.99 g, 2.9 mmol, 94 % yield) was purified by precipitation with acetone. M.p. 252-253° C.  $^1H$ -NMR ( $CDCl_3$ ) : 7.12 (s, 4H, Ar-H), 6.48 (s, 4H, Ar-H), 4.5 (s, 4H,  $-OCH_2CO-$ ), 4.42 (d,  $J = 13.43$  Hz, 4H, Ar- $CH_2$ -Ar), 4.25 (s, 4H,  $-CH_2CH_2O-$ ), 3.71-4.1

(m, 12H,  $-CH_2CH_2O-$ ), 3.28-3.5 (m, 8H,  $-NCH_2CH_3$ ), 3.18 (d,  $J = 13.04$  Hz, 4H, Ar- $CH_2$ -Ar), 1.32 (s, 18H,  $-C(CH_3)_3$ ), 1.15 (t,  $J = 6.52$  Hz, 12H,  $-NCH_2CH_3$ ), 0.81 (s, 18H,  $C(CH_3)_3$ ). FAB MS (positive)  $m/z = 1033,8$ ; 1071,8 (ligand +  $K^+$ ).

**Preparation of 1,3-di-diethyl-acetamide *p*-*tert*-butyl calix[4]crown-6 (6).** Same procedure as for **4** : dihydroxy *p*-*tert*-butyl calix[4]crown-6 (**3**) (3.11 g, 3.52 mmol),  $K_2CO_3$  (4.83 g, 35 mmol),  $CH_3CN$  (300 ml), NaI (5.25 g, 35 mmol),  $\alpha$ -chloro-diethylacetamide (5.25 g, 35 mmol), column chromatography  $CH_2Cl_2$ /acetone (gradient of eluent from 95/5 to 80/20). **6** (3.47 g, 3.24 mmol, 92% yield). M.p. 137-138° C.  $^1H$ -NMR ( $CDCl_3$ ) : cone conformation : 7.12 (s, 4H, Ar-H), 6.71 (s, 2H, Ar-H), 6.57 (s, 2H, Ar-H), 4.42 (d,  $J = 13.18$  Hz, 4H, Ar- $CH_2$ -Ar), 3.22-4.2 (m, 36H,  $-CH_2-$ ), 1.32 (s, 18H,  $C(CH_3)_3$ ), 1.20 (t,  $J = 6.7$  Hz, 12H,  $NCH_2CH_3$ ), 0.81 (s, 18H,  $C(CH_3)_3$ ). FAB MS (positive)  $m/z = 1077,8$ ; 1099,8 (ligand +  $Na^+$ ).

#### $^1H$ -NMR of the complexes with alkali metal picrates.

The suitability of **4-6** as potential ligands able to form complexes with alkali cations was demonstrated by the use of  $^1H$ -NMR spectroscopy. For this purpose  $CDCl_3$  solutions of **4-6** ( $10^{-2}$  M) were reacted with alkali metal picrates,  $M^+Pic^-$  with  $M = Li^+, Na^+, K^+, Rb^+$  and  $Cs^+$ . The ratio of the extracted cation to ligand in solution was estimated by integration of the picrate protons resonance *vs* those of the aromatic protons of the calix unit.

**4.2Li<sup>+</sup>Pic<sup>-</sup>** :  $\delta = 8.95$  (s, 4H, Picrate), 7.2 (s, 4H, Ar-H), 6.68 (s, 4H, Ar-H), 4.52 (s, 4H,  $-OCH_2CO-$ ), 4.35 (t, 4H,  $-CH_2CH_2O-$ ), 4.31 (d,  $J = 13.43$  Hz, 4H, Ar- $CH_2$ -Ar), 4.12 (s, 8H,  $-CH_2CH_2O-$ ), 3.49 (q,  $J = 6.32$  Hz, 4H,  $-NCH_2CH_3$ ), 3.32 (d,  $J = 13.43$  Hz, 4H, Ar- $CH_2$ -Ar), 3.15 (q,  $J = 6.32$  Hz, 4H,  $-NCH_2CH_3$ ), 1.42 (s, 18H,  $C(CH_3)_3$ ), 1.20 (t,  $J = 6.51$  Hz, 6H,  $NCH_2CH_3$ ), 1.10 (t,  $J = 6.51$  Hz, 6H,  $NCH_2CH_3$ ), 0.85 (s, 18H,  $C(CH_3)_3$ ). **4.Na<sup>+</sup>Pic<sup>-</sup>** :  $\delta = 8.8$  (s, 2H, Picrate), 7.2 (s, 4H, Ar-H), 6.8 (s, 4H, Ar-H), 4.7 (s, 4H,  $-OCH_2CO-$ ), 4.5 (d,  $J = 13.43$  Hz, 4H, Ar- $CH_2$ -Ar), 4.35 (s, 4H,  $-CH_2CH_2O-$ ), 4.19 (s, 8H,  $-CH_2CH_2O-$ ), 3.42 (q,  $J = 6.50$  Hz, 4H,  $-NCH_2CH_3$ ), 4.34 (d,  $J = 13.43$  Hz, 4H, Ar- $CH_2$ -Ar), 3.10 (q, 4H,  $J = 6.50$  Hz,  $-NCH_2CH_3$ ), 1.28 (s, 18H,  $C(CH_3)_3$ ), 1.16 (t,  $J = 6.50$  Hz, 6H,  $NCH_2CH_3$ ), 1.04

(t,  $J = 6.50$  Hz, 6H,  $\text{NCH}_2\text{CH}_3$ ), 0.90 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).

**5.Li<sup>+</sup>Pic<sup>-</sup>**:  $\delta = 9$  (s, 4H, Picrate), 7.1 (s, 4H, Ar-H), 6.6 (s, 4H, Ar-H), 4.55 (s, 4H,  $-\text{OCH}_2\text{CO}-$ ), 4.4 (d,  $J = 13.04$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 4.3 (s, 4H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.9 (s, 8H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.42 (q, 8H,  $-\text{NCH}_2\text{CH}_3$ ), 3.2 (d,  $J = 13.04$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 3.15 (t, 4H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 1.3 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.2-1.05 (m, 12H,  $\text{NCH}_2\text{CH}_3$ ), 0.9 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).

**5.Na<sup>+</sup>Pic<sup>-</sup>**:  $\delta = 8.8$  (s, 2H, Picrate), 7.04 (s, 4H, Ar-H), 7.02 (s, 4H, Ar-H), 4.8 (s, 4H,  $-\text{OCH}_2\text{CO}-$ ), 4.51 (d,  $J = 13.04$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 4.15-3.8 (m, 16H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.45 (q, 4H,  $-\text{NCH}_2\text{CH}_3$ ), 3.32 (d,  $J = 13.04$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 3.1 (q, 4H,  $-\text{NCH}_2\text{CH}_3$ ), 1.13 (t, 12H,  $\text{NCH}_2\text{CH}_3$ ), 1.11 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.09 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).

**5.K<sup>+</sup>Pic<sup>-</sup>**:  $\delta = 8.81$  (s, 2H, Picrate), 7.06 (s, 8H, Ar-H), 4.59 (s, 4H,  $-\text{OCH}_2\text{CO}-$ ), 4.48 (d,  $J = 13.04$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 4 (s, 8H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.88 (t, 8H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.46 (q, 4H,  $-\text{NCH}_2\text{CH}_3$ ), 3.31 (d,  $J = 13.04$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 3.1 (q, 4H,  $-\text{NCH}_2\text{CH}_3$ ), 1.18 (t, 12H,  $\text{NCH}_2\text{CH}_3$ ), 1.1 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.09 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ). **5.Rb<sup>+</sup>Pic<sup>-</sup>**:  $\delta = 8.81$  (s, 2H, Picrate), 7.15 (s, 4H, Ar-H), 7.05 (s, 4H, Ar-H), 4.49 (s, 4H,  $-\text{OCH}_2\text{CO}-$ ), 4.43 (d,  $J = 13.04$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 4.03-3.9 (m, 8H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.34 (s, 8H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.48 (q, 4H,  $-\text{NCH}_2\text{CH}_3$ ), 3.32 (d,  $J = 13.04$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 3.11 (q, 4H,  $-\text{NCH}_2\text{CH}_3$ ), 1.21 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.15-1.05 (m, 12H,  $\text{NCH}_2\text{CH}_3$ ), 1 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).

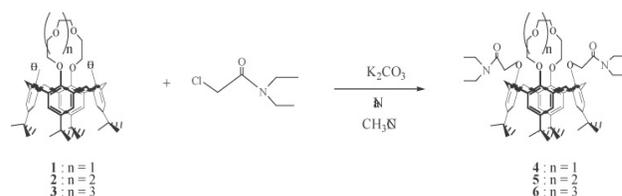
**6.Cs<sup>+</sup>Pic<sup>-</sup>**:  $\delta = 8.75$  (s, 2H, Picrate), 7.01 (s, 4H, Ar-H), 6.41 (s, 4H, Ar-H), 4.37 (s, 4H,  $-\text{OCH}_2\text{CO}-$ ), 4.36 (d,  $J = 12.74$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 4.19-4.12 (m, 8H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.75-3.69 (m, 8H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.67 (s, 8H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ), 3.33 (q, 4H,  $-\text{NCH}_2\text{CH}_3$ ), 3.08 (d,  $J = 12.74$  Hz 4H, Ar- $\text{CH}_2$ -Ar), 3.22-3.17 (q, 4H,  $-\text{NCH}_2\text{CH}_3$ ), 1.22 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ), 1.09-1.03 (m, 12H,  $\text{NCH}_2\text{CH}_3$ ), 0.75 (s, 18H,  $\text{C}(\text{CH}_3)_3$ ).

## Results and discussion

### Synthesis of ligands 4-6.

The synthesis of ligands **4-6** is shown in Fig. 1. 1,3-Dihydroxy *p*-*tert*-butyl calix[4]arene crowns-n (**1-3**) (with  $n = 4-6$  respectively) were reacted with 10 equivs of  $\alpha$ -chloro-diethyl-acetamide in the presence of 10 equivs of  $\text{K}_2\text{CO}_3$  and

10 equivs of NaI in refluxing acetonitrile for 3 days under  $\text{N}_2$ .<sup>5</sup> **4** and **6** were purified by chromatography on  $\text{SiO}_2$  using a mixture of  $\text{CH}_2\text{Cl}_2$ /acetone with a gradient of eluent from 95/5 to 80/20. **5** was precipitated with acetone from the crude mixture. That di-O-alkylation of **1-3** occurred and the conformations of calixarenes **4-6** were deduced from the analytical data.<sup>5</sup> For example, singlets were observed at 4.50 ppm for the  $-\text{OCH}_2\text{CO}-$  protons in the  $^1\text{H-NMR}$  of **4** and **5**. Calixarenes **4** and **5** were deduced to be in the cone conformation because of the observation of AB systems for the Ar $\text{CH}_2$ Ar at 4.40 ppm and 3.18 ppm ( $J = 12.5$  Hz) for **4** and 4.48 ppm and 3.18



**Fig. 1.** Synthesis of di-diethyl-acetamide *p*-*tert*-butyl calix[4]arene crown- $n$  (**4-6**)

ppm ( $J = 12.7$  Hz) for **5**. Ligand **6** was observed to be a mixture of cone and flat partial cone conformations in 8/2 equilibrium. The cone conformation presented an AB system at 4.38 ppm and 3.07 ppm with  $J = 13.0$  Hz. The flat partial cone conformation was deduced from the presence of three singlets at 0.79 ppm, 1.16 ppm and 1.20 ppm in a 1 : 2 : 1 ratio for the *tert*-butyl groups and of three singlets at 6.50 ppm, 6.90 ppm and 6.93 ppm in a same ratio for the ArH.

### Alkali-complexation studies.

The suitability of **4-6** as potential ligands able to form complexes with alkali cations was demonstrated by the use of  $^1\text{H-NMR}$  spectroscopy. For this purpose  $\text{CDCl}_3$  solutions of **4-6** ( $10^{-2}$  M) were reacted with alkali metal picrates,  $\text{M}^+\text{Pic}^-$  with  $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$  and  $\text{Cs}^+$ . The ratio of the extracted cation to ligand in solution was estimated by integration of the picrate protons resonance *vs* those of the aromatic protons of the calix unit (see Table 1).

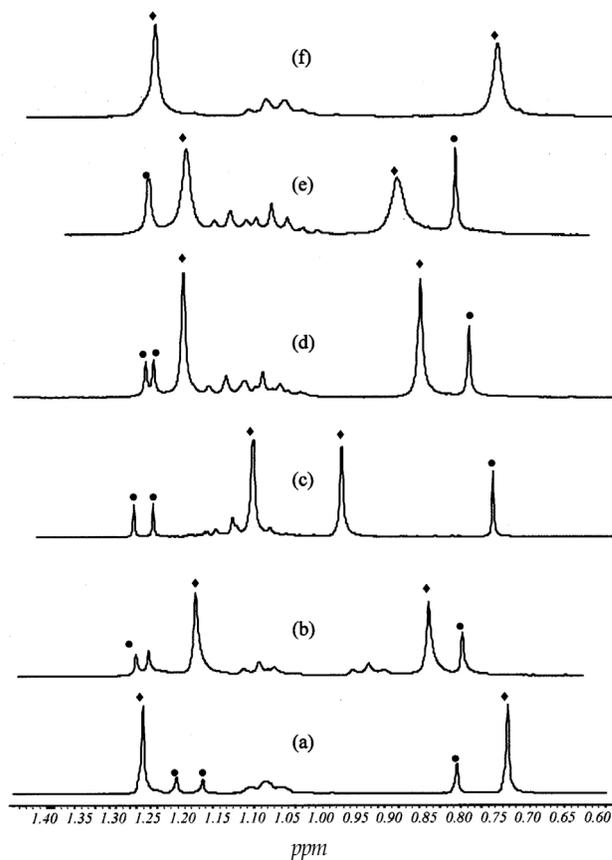
1:1 Complexes **4.Na<sup>+</sup>Pic<sup>-</sup>**, **5.Na<sup>+</sup>Pic<sup>-</sup>**, **5.K<sup>+</sup>Pic<sup>-</sup>**, **5.Rb<sup>+</sup>Pic<sup>-</sup>**,

**Table 1.** Stoichiometries of complexes of 4-6 with alkali metal picrates as detected by  $^1\text{H-NMR}$ .

Ligand	metal				
	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$
4	2 : 1	1 : 1	i	i	i
5	2 : 1	1 : 1	1 : 1	1 : 1	i
6	2 : 1	1 : 1	1 : 1	1 : 1	1 : 1

<sup>i</sup>No evidence of complexation.

**6.Na<sup>+</sup>Pic<sup>-</sup>**, **6.K<sup>+</sup>Pic<sup>-</sup>** and **6.Rb<sup>+</sup>Pic<sup>-</sup>** were observed showing that an increase of the length of the crown loop allows a complexation of larger cations. This was a preliminary indication of a complexation of the metal at the level of the crown ether. The detection of 2:1 complexes with  $\text{Li}^+$  is probably due to its smaller radius. All the complexes spectra had signals patterns similar to that of the free ligands suggesting that the molecular symmetry is not altered by the presence of the metal in the receptor. The induced shifts of the  $-\text{OCH}_2\text{CH}_2\text{O}-$  by the presence of the cations also confirmed that the cations are located in the crown unit. Large shifts were observed for the  $-\text{NCH}_2\text{CH}_3$  and  $-\text{NCH}_2\text{CH}_3$  signals. For example, the triplet at 1.13 ppm ( $J = 6.52$  Hz) for the  $-\text{NCH}_2\text{CH}_3$  of **4** splitted into two triplets at 1.16 ppm and 1.04 ppm ( $J = 6.50$  Hz) of **4.Na<sup>+</sup>Pic<sup>-</sup>**, while the two quartets at 3.41 ppm and 3.46 ppm ( $J = 6.52$  Hz) shifted to 3.10 ppm and 3.42 ppm ( $J = 6.50$  Hz) respectively. This was attributed to a change from disordered diethyl amido arms in the free ligand into convergent ones in the complex as previously described elsewhere.<sup>7</sup> The coordination of the cation in the crown ether with the amido function pointing toward the cations has been evidenced by X-ray feature by the Parm's group in related 1,2-calix[4]crowns in cone conformation.<sup>6</sup> At the same time, the singlets at 0.81 ppm and 1.42 ppm of the  $-\text{C}(\text{CH}_3)_3$  shifted to 0.90 ppm and 1.28 ppm showing that the calix[4]arene moiety tends towards a more symmetrical cone conformation. Similar observations were made with ligand **5**. More particularly, for ligand **6** (fig. 2) both cone/flat partial cone conformations were observed with all metals except for cesium which draw the equilibrium between the two conformations to the cone conformation. This induced change of conformation by the presence of a metal in the binding crown cavity of calix[4]arenes has already been described by other authors.<sup>8</sup>



**Fig 2.**  $^1\text{H-NMR}$  spectra in the *tert*-butyl region of (a) free ligand **6**, (b) **6.Li<sup>+</sup>Pic<sup>-</sup>**, (c) **6.Na<sup>+</sup>Pic<sup>-</sup>**, (d) **6.K<sup>+</sup>Pic<sup>-</sup>** (e) **6.Rb<sup>+</sup>Pic<sup>-</sup>** and (f) **6.Cs<sup>+</sup>Pic<sup>-</sup>**.

(♦) denotes the signals of cone conformation  
(●) denotes the signals of flat partial cone conformation).

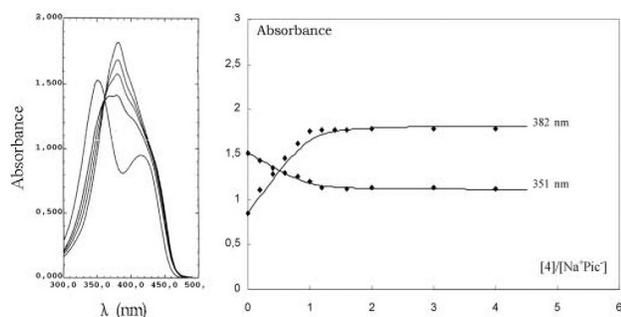
### Ion pairing study.

Complexation in THF of an alkali picrate salt can lead to the transformation of a tight alkali picrate ion pair ( $\text{M}^+\text{Pic}^-$ ) into a separated one characterized by a bathochromic shift in UV-Vis spectrum of the alkali picrate. The shifts observed are reported in table 2. The  $\lambda_{\text{max}}$  values of Li, Na, K, Rb and Cs picrates ( $\text{M}^+\text{Pic}^-$ ) are 344, 351, 357, 360 and 362 nm respectively. The complexation accompanied by full separation of the cation and picrate is characterized by the occurrence of an absorption at 382 nm. It is seen that separated ion pairs are present in all the ligand-sodium systems and in the  $\text{K}^+.\mathbf{5}$ ,  $\text{K}^+.\mathbf{6}$  in  $\text{Rb}^+.\mathbf{5}$  suggesting ion encapsulated in the corresponding calixcrown cavity.

**Table 2.**  $\lambda_{\max}$  (nm) values of the complexes of **4-6** with metal picrates and bathochromic shifts  $\Delta\lambda$  (nm) given in brackets.

Ligand	$M^+Pic^-$				
	$Li^+$	$Na^+$	$K^+$	$Rb^+$	$Cs^+$
4	344 (0)	382 (31)	357 (0)	360 (0)	362 (0)
5	344 (0)	382 (31)	380 (23)	380 (20)	362 (0)
6	344 (0)	382 (31)	380 (23)	370 (10)	362 (6)

The absorbance at  $\lambda_{\max}$  of the metal picrates before and after complexation was studied as a function of the ligand/ $M^+Pic^-$  concentration ratios. Only for sodium systems the formation of a 1: 1 complex could unambiguously be assessed by the occurrence of an isosbestic point (Fig. 3). The logarithm of the stability constants were determined by means of the Rose Drago method<sup>9</sup>: 5,33, 5,40 and 5,03 for the **4-6** respectively. These values are in the same order of magnitude than that found for other calix[4]arenes in cone conformation having two amide pendent groups in the 1,3 postions showing that cation is predominantly maintained in the calixcrown cavity by the amido functions.<sup>10</sup>



**Fig 3.** left : change of the absorption spectrum of  $Na^+Pic^-$  upon addition of various amounts of **4** : right : plots of absorbance vs  $[4]/[Na^+Pic^-]$  at  $\lambda_{\max}$  of tight (351nm) and separated ion pairs (382 nm) in THF.

Further studies of the role played by amido groups in the vicinity of a calixcrown on the selectivity of complexation

are in progress.<sup>11</sup>

## References

- (1) Casnati, A.; Ungaro, R.; Asfari, Z.; Vicens, J. *Calixarenes 2001*, Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J. Eds; Kluwer Academic Publishers, Dordrecht, Holland, **2001**, chapter 20.
- (2) Arnaud-Neu, F.; McKervey M. A.; Schwing-Weill, M.-J. *Calixarenes 2001*, Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J. Eds; Kluwer Academic Publishers, Dordrecht, Holland, 2001, chapter 21
- (3) Abidi, R.; Baklouti, L.; Harrowfield, J.; Sobolev, A.; Vicens, J.; White, A. H. *Org. Biomol. Chem.* **2003**, *1*, 3144.
- (4) While preparing this manuscript a publication has appeared reporting the complexation behaviour of a related pyrenyl methyl diamino calix[4]crowns : Lee S. H.; Kim, J. Y.; Kim, S. K.; Lee, J. H.; Kim, J. S. *Tetrahedron* **2004**, *60*, 5171.
- (5) Sabbatini, N., Casnati, A., Fischer, C., Girardini, R., Guardini, R., Manet, I., Sarti, G., Ungaro, R. *Inorg. Chim. Acta* **1996**, *252*, 19.
- (6) Arduini, A.; Bozzoli, M.; Massera, C.; Pochini, A. ; Secchi, A. ; Ugozzoli, F. *Collect. Czech. Chem. Commun.* **2004**, *69*, 1309.
- (7) Guibaud, P.; Varnek, A.; Wipff, G. *J. Amer. Chem. Soc.* **1993**, *115*, 8298.
- (8) Yamamoto, H.; Sakaki, T.; Shinkai, S. *Chem. Lett.*, **1994**, 469 and Ungaro, R.; Pochini, A.; Andreetti, G. D. *J. Incl. Phenom.*, **1984**, *2*, 199.
- (9) Rose, N. J.; Drago, R. S. *J. Am. Chem. Soc.*, **1959**, *81*, 6138.
- (10) Yaftian, M. R.; Burgard, M.; Matt, D.; Wiesser, C.; Dieleman, C. J. *J. Incl. Phenom.*, **1997**, *27*, 127.
- (11) Haddaoui, J.; Burgard, M.; Asfari, Z.; Vicens, J. (to be published)

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