

## Anion Complexation of Three Pyridine Amide Calix[4]arenes Derivatives

Slim Manai<sup>1</sup>, Lassaad Baklouti<sup>1,2,\*</sup>, Rym Abidi<sup>1</sup> and Abdelwaheb Hamdi<sup>1,2,\*</sup>

<sup>1</sup> Laboratory of Applied Chemistry and Natural Substances Resources and Environment (LACReSNE), Faculty of Sciences at Bizerte, 7021 Zarzouna-Bizerte, TUNISIA

<sup>2</sup> Chemistry Department, Faculty of Science and Arts at El-Rass, Qassim University, Kingdom of SAUDI ARABIA

\* Correspondance: E-mail: [bakloutilassaad@yahoo.fr](mailto:bakloutilassaad@yahoo.fr) & [hamdi\\_chimie@yahoo.fr](mailto:hamdi_chimie@yahoo.fr)

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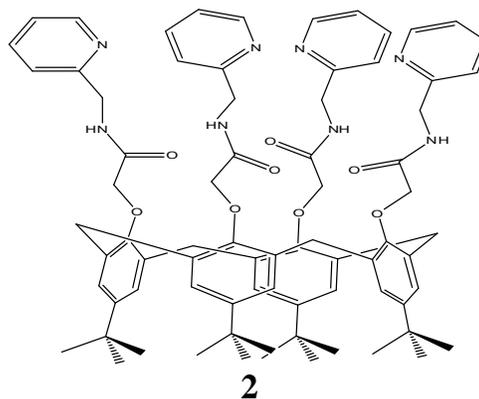
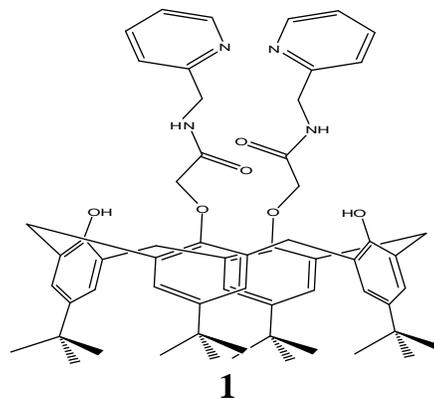
**ABSTRACT:** The binding properties of amido derivatives of p-tert-butyl calix[4]arene (1-3) towards various anions (spherical halides, planar trigonal nitrate and tetrahedral hydrogen sulphate) as their tetrabutyl ammonium (TBA) salts were studied by <sup>1</sup>H NMR technique and using EquiChem program. The stability constants, logβ<sub>ij</sub>, varying from 0.94 to 2.05 were determined for the mononuclear complexes.

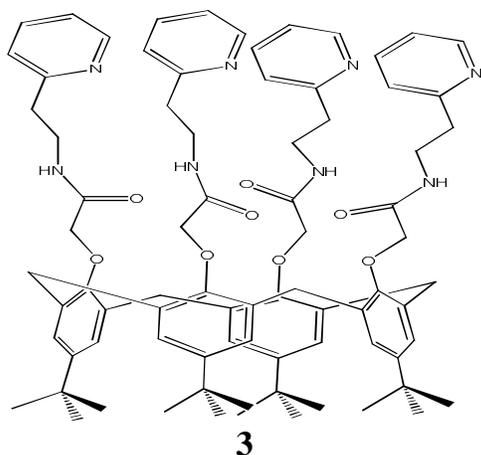
**Keywords:** Calixarenes; Anion complexation and <sup>1</sup>H NMR.

**INTRODUCTION:** The anion recognition chemistry began in 1968 with the synthesis of the first artificial anion receptor by Simmons and Park<sup>1</sup>. During the seventh decade of the last century, the metal and ammonium cations coordination chemistry generated much interest and recognition of cations became a well-developed field of supramolecular chemistry. In contrast, anion coordination chemistry has received less attention, and only after the 90s that continuous attention was paid to the problems inherent to the anionic species.<sup>2,7,9-11</sup> Notable development in this new field of coordination chemistry is due to the key role of negatively charged species in the nature. The anions are present in several biological systems.<sup>3, 8</sup> They carry the genetic information (DNA is a polyanion) and the majority of the substrates and enzymes cofactors are anionic. Types of interactions for anions binding are electrostatic interactions, hydrogen-bonding and coordination to Lewis-acidic metals.<sup>4</sup> Anion recognition is associated with the shape of the anions. Apart from spherical halides, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> are tetrahedral, NO<sub>3</sub><sup>-</sup> is trigonal planar, SCN<sup>-</sup> and N<sub>3</sub><sup>-</sup> are linear and each anion requires a receptor with specific size and shape. In this paper, we present a subsequent study on the complexation of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> by the di(2-pyridylmethyl) amide calix[4]arene **1**, tetra(2-pyridylmethyl) amide calix[4]arene **2**, tetra(2-pyridylethyl) amide calix[4]arene **3** in order to evidence the influence of the residues attached to the calix unit by amido functions.

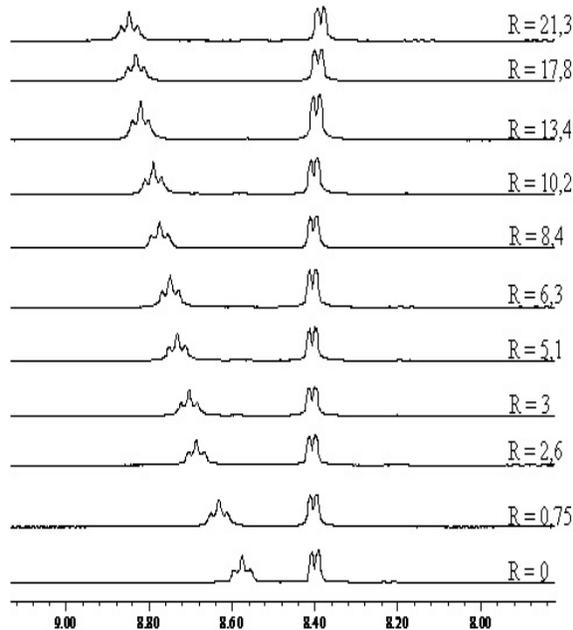
**MATERIAL AND METHODS:** The complexing power of the ligands **1-3** for the anions Cl<sup>-</sup>, Br<sup>-</sup>, F<sup>-</sup> and I<sup>-</sup> and the oxyanions NO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup> as tetrabutyl ammonium was carried out by NMR.<sup>10,11</sup> In compari-

son with the size of the calix[4]arenes cavities, the tetrabutylammonium cation is large enough to form any complex with studied calixarenes. The anions complexation is done by adding the infinitesimal solid whose ratio is calculated based on the comparison between the integration of ammonium protons and that of the calixarene protons.





**RESULTS AND DISCUSSION:** Generally, the addition of the anionic salt affects the chemical shifts of the different protons of the ligand, mainly the amide protons that are most affected, indicating the creation of hydrogen bonds with the latter. For example, the gradual addition of a  $\text{HSO}_4^-$  to ligand **2** solution causes the movement of the hydrogen amide signal downfield. However, we found that the signal of pyridine hydrogen is slightly oriented strong fields (Figure 1).



**Figure 1: Variation of chemical shifts  $\delta$  (ppm) of NH and pyridine signals on the complexation of  $\text{HSO}_4^-$  by tetra methyl pyridine amide calixarene **2**.**

Interpretation of all spectroscopic data obtained by the computer program "ChemEqui for Calculations"<sup>5</sup> led to the determination of the apparent stability constants  $\log\beta_{ij}$  of the formed complexes in  $\text{CDCl}_3$  and the type

of dissolved species as mentioned in the following table 1:

**Table 1: Stabilities of the complexes of compounds 1-3 with different anions studied in  $\text{CDCl}_3$  at 25 °C.**

Ligand	$\text{F}^-$	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$	$\text{NO}_3^-$	$\text{HSO}_4^-$
<b>1</b>	0.94	a	a	a	a	a
<b>2</b>	1.14	1.96	a	a	a	1.47
<b>3</b>	1.17	2.05	a	a	a	1.72

*a: absence of complexing*

The results of the complexing ligands by **1-3** shows the formation of 1:1 complexes with stability constants,  $\log\beta_{ij}$ , varying 0.94 (for **1** with  $\text{F}^-$ ) to 2.05 (for **3** with  $\text{Cl}^-$ ). The stability constants are in all cases less than **2**.

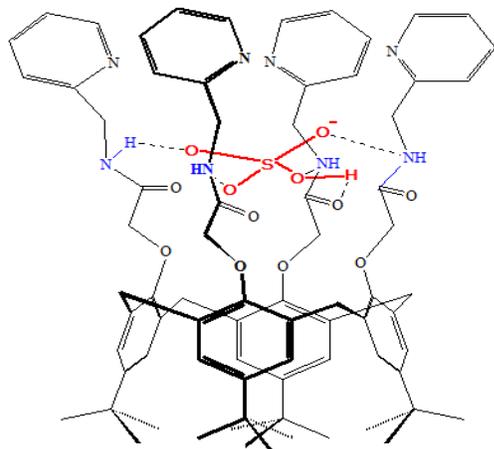
We noted that the disubstituted ligand **1** is selective for the fluoride anion. This selectivity can be attributed to the relatively high basicity of the fluoride. This disubstituted ligand didn't have an affinity for the remaining anions of the studied series.

Iodine and bromine classified by Pearson<sup>6</sup> classification as soft bases have no affinity for the three ligands. Likewise for the large monoatomic anions, they are not complexed with any of the three studied ligands; this can be explained by a size effect.

Regarding the stability of mononuclear species, we can note that the complexes with ligands **3** are more stable than those of the ligand **2**. This can be attributed to the more difficult hydrogen bond formation in the case of ligand **2** likely hampered by the closeness of the pyridine units. The determined constants show the formed mononuclear complexes by the ligand **3** are 10 times more stable than those formed with the ligand **2**. Thus the separation of the two cavities (pyridine and amide) by an ethyl group enhances the formation of mononuclear complexes with anions.

In the case of oxyanions, only  $\text{HSO}_4^-$  is complexed by the ligands **2** and **3** forming mononuclear species. This may be due to geometry complementary between the anion and the ligands. Complexes formed with the anions  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{HSO}_4^-$  are more stable with the ligand **3** with the ligand **2**, with remarkable selectivity of the ligand **3** for  $\text{Cl}^-$  anion.

We believe that the observed selectivity for  $\text{HSO}_4^-$  is probably due to the complementarity between the tetrahedral shape of the oxyanion and the complexation site of the ligand **2** with a timely three-dimensional arrangement bounded by the amide nitrogen and phenolic oxygen (Figure 2). This receiver is able to establish hydrogen 4 hydrogen bonds for each hydrogenosulfate ion  $\text{HSO}_4^-$ .



**Figure 2** Proposal for locating the hydrogen oxidation in the complex  $[2.HSO_4]^-$ .

**CONCLUSION:** This study shows the mononuclear formation of the species with ligands **1-3**, the anion being located in the calixarenic cavity near the amido functions. The logarithm of the constants of stability are weak (between 0.9 and 2), the anion being located in the calixarenic cavity near the amido functions. With remarkable selectivity of ligand **3** for the anion  $Cl^-$ . The major finding to remember is that our ditopic ligands **2** and **3** are selective to anions  $F^-$ ,  $Cl^-$  and  $HSO_4^-$  and ligand **1** is just selective for  $F^-$ .

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