

Synthesis of new artificial receptors for anion recognition: calix[4]arenes thiourea derivative

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INTRODUCTION

Calixarenes are macrocyclic compounds composed by phenolic units, connected by methylene bridges, to form a hydrophobic cavity capable of generating inclusion complexes with a variety of molecules¹. Calixarenes are particularly attractive scaffolds for receptor development, through the incorporation of numerous ligands for co-operative binding of anions. Since their discovery calixarenes have been widely used in the last two decades as building blocks for the synthesis of receptors for cations and neutral molecules. The development of synthetic anion receptors has been slow in comparison to cation receptors. Anions play a number of fundamental roles in biological and chemical processes and the development of selective synthetic anion receptors is an area of current importance.

Calixarenes bearing urea and thiourea moieties have also been prepared offering the advantages of increased proton acidity and additional proton interactions with the same directionality which can act co-operatively in binding an anion.

On the basis of the precedent information, we have synthesized and characterized new functionalized calixarenes with thiourea in the lower rim. Also, some known molecules were incorporated as fluorophores, and their binding properties with various anions, including fluoride, chloride, acetate, among others are being investigated by fluorescent titrations, Job plot experiments and ¹H NMR spectroscopy.

RESULTS AND DISCUSSION

The synthetic strategy to modify lower rim has been successfully developed before in two steps; in the first stage pattern calixarene **1** was alkylated with bromoacetonitrile followed by reduction by LiAlH₄² yielding di-amine calixarene **2**. We have previously performed the transformation of **1** into the corresponding di-iso thiocyanate derivative **3** in excellent yields, using thiophosgene³ (Scheme 1). Recently, calixarene derivative di-amine **2** and di-isothiocyanate **3** reacted with amines or isothiocyanates to give calixarenes derivative **Cth1** with thiourea bridges. The following amines, and isothiocyanates were used, some are commercially available and others have been prepared in this laboratory: 2-amino-anthracene, 2-anthraceneNCS, PhNCS, 2-amino- and 6-aminobenzothiazole.

CONCLUSION

Calix[4]arenes **4-8** containing thiourea group were synthesized and the binding properties for anions were investigated using tetrabutylammonium salts.

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