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ORIGINAL ARTICLE

Study by fluorescence of calix[4]arenes bearing heterocycles with anions: highly selective detection of iodide

Horacio Gómez-Machuca · Cinthia Quiroga-Campano · Carolina Jullian · Julio De la Fuente · Hernán Pessoa-Mahana · Carlos A. Escobar · José A. Dobado · Claudio Saitz

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Abstract The present work describes a study of complexation efficiency of calix[4]arenes bearing benzoimidazolyl, benzothiazolyl, and benzoxazolyl heterocycles (**5–7**) towards several anions. The binding ability of calixarene derivatives **5–7** towards selected anions of different molecular geometries such as: F^-, HSO_4^-, I^-, N_3^-, NO_3^-, NO_2^-, SCN^-, ClO_4^-, Br^-, CN^-, Cl^-, CH_3COO^- $CF_3SO_3^-$ in methanol, has been investigated by fluorescence spectroscopic techniques, all anions were used as tetrabutylammonium salts to avoid possible complexation of cationic species by the derivative calix[4]arenes. Fluorescent chemosensor ability of these three calixarene derivatives was highly selective for iodide in contrast with other anions studied. The best chemosensor found, corresponds to compound 7, with an association constant of $2.01 \times 10^4\ mol^{-1}\ L$ and a detection limits of 0.22 ppm for iodide.

Keywords Fluorescence · Calix[4]arene · Anions · Complexation · Heterocycles · Iodide

Introduction

The development of design and synthesis of new artificial receptors for selective anion recognition is increasingly a topic field in supramolecular chemistry [1–6], due to important roles of anions in biomedicinal and chemical process. Anionic receptors can be used as sensors, selective extractants, and phase-transfer agents.

The problem of anion recognition still remains poorly solved despite its exceptional importance, and the development of synthetic anion receptors has been slow in comparison to cation receptors. The reason is due to a number of unique properties of anions that need to be addressed in the design of receptors which are usually larger than cations and are characterized by a variety of structures (spherical for halide ions, linear for azide ions, planar for nitrate ions, tetrahedral for perchlorate, etc.) [1, 4, 6]. These include the negative charge, which is often delocalized over a number of atoms, greater solvation energy, and more diffuse nature [1, 4, 6]. Binding of anions is also affected by their pH dependence (anions can also form acids, for example, the oxo acids) and solvation: for a given anion and cation of comparable size, the anion is more strongly hydrated and thus more difficult to desolvate, a pre-requisite for binding [1, 4, 6].

Calixarenes has been widespread used as receptors for cations, anions and neutral molecules [7]. Incorporation of thoughtfully designed binding motifs and chemical groups that respond to analyte complexation has given these macrocycles further applications as highly selective chemical sensors. A recent review paper has focused on

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H. Gómez-Machuca · C. Quiroga-Campano · C. Jullian · J. De la Fuente · H. Pessoa-Mahana · C. Saitz (✉)
Departamento de Química Orgánica y Físicoquimica, Facultad de Ciencias Químicas y Farmaceúticas, Universidad de Chile, Sergio Livingstone 1007 (Ex Olivos) Independencia, Casilla 233, Santiago 1, Chile
e-mail: clsaitz@ciq.uchile.cl

C. A. Escobar
Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, República 275, Santiago, Chile

J. A. Dobado
Departamento de Química Orgánica, Facultad de Ciencias, calle Severo Ochoa s/n, Universidad de Granada, 18071 Granada, Spain

different analytical applications of calixarenes [8] in the main fields of separation, electroanalysis, spectroscopy and chemometrics. Fluorescence is by far the most sensitive method of analysis used to monitor calixarene–analyte complexation. Optical fluorescence-based sensors seem especially attractive because they provide a more efficient and less expensive alternative to standard practices. A typical optical chemosensor for recognition of metal ions and/or anions consists of a selective ligand (ionophore) with a covalently attached fluorophore which responds to the complexation induced changes in the electron environment by spectral variation, these molecules are called fluoroionophores. Fluoroionophores built on the calixarene scaffolds are a promising and quickly developed group [7, 9, 10]. Calixarenes are macrocyclic compounds composed of phenolic units, connected by methylene bridges, to form a hydrophobic cavity that is capable of generating inclusion complexes [11]. An important reason for the current widespread interest in calixarenes is the remarkably simple route used for the synthesis of the parent compound, *p-tert* -butyl calix[4]arene, made up by base-induced condensation of *p*-substituted phenols and formaldehyde [12]. Calix[4]arenes provide optimal scaffolds for the preparation of anion receptors because of its tunable and unique tridimensional structure. In addition, they are readily accessible for chemical modification on both narrower and wider rims by attachment of a wide range of potential ligating groups that create additional recognition sites. The expanded or extended cavity could be of benefice to the encapsulation and recognition properties. Furthermore, the extended calixarene skeleton with π-conjugated units could act as a chromophore or fluorophore. Upon binding with a guest, the change of the spectral properties would give rise to a sensing mechanism.

Since their discovery, the calixarenes have gained much attention and they have been widely used as building blocks focused to the synthesis of ion receptors and neutral molecules in the last two decades [13–16].

The calix[4]arene-based anion receptors [17–20] are synthesized by introducing functionalities such as amide, urea, or thiourea, which can interact with anions through hydrogen bonding. Incorporation of fluorophores into such bonding cores would be of great use in monitoring the binding aspects. Fluorescent moieties available are typically aromatics such as substituted benzenes, anthracenes, heterocycles, naphthalenes and pyrenes. Nevertheless, even less examples of calix[4]arenes bearing heterocycles are found.

Iodide is recognized as an ion of significant physiological importance due to its essential role in several biological activities such as neurological activity and thyroid function, development and functioning of the brain and body. Any deficiency of iodide can give rise to serious diseases such as enlarged goiters or mental retardment. Iodine is a biologically essential element in seawater, where it exists predominantly as the iodide species and some organic iodine compounds. Moreover, elemental iodine has been frequently used in many areas of chemistry for synthesizing valuable molecules such as drugs and dyes. Therefore, developing receptors that can bind iodide selectivity is strongly desired [21–23]. Several different hydrogens bonding groups as amide [24], sulfonamide [25], urea [26] and thiourea [24, 27], have been used in the design of neutral anion receptors, there being a few reports on the recognition of iodide, and in-depth research has not been done on the estimation of iodide in the presence of other anions, i.e., selective estimation of iodide. With regard to the iodide ion only a few report dealing with fluorescent sensors can be found in the literature [28–35] and only three with calixarene as receptor [36–38].

Recently, we report in this journal [39], the fluorescence chemosensor ability of a new series of calix[4]arenes bearing benzothiazole, benzoxazole, and benzoimidazole groups. They were highly selective for Pb(II) in contrast with other eight divalent metals studied. Herein, we report a study of complexation efficiency and selectivity of these calixarenes towards selected anions using fluorescence spectroscopy.

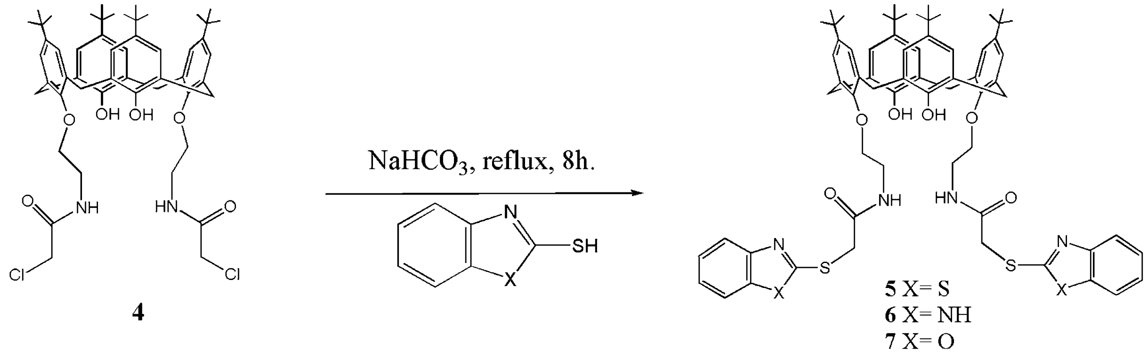
Synthesis of calixarene derivatives

For the synthesis of fluorescent chemosensor, 5,11,17,23-tetra-tert-butyl-25,27-bis[2-(chloroacetamido) ethoxy]-26, 28-di-hydroxycalix[4]arene (**4**) was chosen as starting material, obtainable by modification of the compound: 5,11,17,23-tetra-tert-butyl-25,27-bis[2-aminoethoxy]-26,28-di-hydroxycalix[4]arene (**3**), Scheme 1. Precursor compounds **1–3** were prepared by previously published procedures [11, 40–42]. The two arms of compound **4** were efficiently linked by treatment with the corresponding 2-mercapto-heterocycle and sodium bicarbonate in refluxing acetonitrile, yielding the calixarene derivatives **5–7** in good yields [42]. Spectroscopic data (^{1}H- and ^{13}C-NMR) indicates that these compounds are consistent with the *cone* conformation.

Experimental

General experimental information

The Fluorescence measurements of complexes of calixarene-anion were carried out on a LS 55 Perkin-Elmer spectrofluorometer equipped with a xenon lamp source using standard 1.00 cm quartz cells. Spectra ^{1}H and ^{13}C NMR were recorded using a Bruker DRX-300 using a



Scheme 1 Synthesis of calixarene derivatives **5**–**7**

5 mm diameter sample tube. All the reagents and solvents were of analytical grade and used without further purification.

Analytical procedure

General procedure of fluorescence studies

In order to evaluate binding affinities of synthesized calix[4]arene **5**–**7** with anions, 1.5 mM stock solutions of **5**–**7** in chloroform and 15 mM for anions (F^-, HSO_4^-, I^-, N_3^-, NO_3^-, NO_2^-, SCN^-, ClO_4^-, Br^-, CN^-, Cl^-, CH_3COO^-, $CF_3SO_3^-$) in methanol were used. The counter ion for all anions used were tetrabutylammonium salts to avoid possible complexation of cationic species by the calix[4]arene.

Test solutions for screening and selectivity studies were prepared by placing 15 μL of **5**–**7** into a quartz cell, adding adequate aliquot of each anion to give a final concentration of 30 equivalents, and diluting the solution up to 2.6 mL with methanol. Tests solution for titration and sensibility studies were prepared by placing 15 μL of **5**–**7** into a cuvette, adding appropriate aliquots from 0 to 60 eq of anion, and diluting with methanol to final volume of 2.6 mL. The stoichiometry of inclusion complexes was determined by continuous variation method, Job's Plot [43]. Equimolar solutions of calixarene **5**–**7** and anion were mixed to a standard volume varying the molar ratio but keeping the total concentration of the species constant. All these studies were performed by fluorescence spectroscopy exciting at 225 nm with bandwidths of 9 and 20 nm for excitation and emission, respectively.

Results and discussion

The characteristics of the calixarene **5**–**7** in emission and excitation spectra are almost the same, with a strong band at 210 nm for absorbance which is attributed to π–π* transition and at 280 nm a band due to n–π* transition. Hence the band at 210 nm should be the superposition of two bands as reported by Gupta et al. [38].

The fluorescence response of calixarenes towards different anions was investigated by fluorescence spectroscopy. Emissions of derivatives **5**, **6** and **7** were recorded in methanol, exciting at 225 nm and reading the intensity at its maximum 313, 330 and 313 nm respectively. The exciting wavelength was selected because scanning excitation spectra show the maxima at 225 nm [39]. With the addition of the different anions F^-, HSO_4^-, I^-, N_3^-, NO_3^-, NO_2^-, SCN^-, ClO_4^-, Br^-, CN^-, Cl^-, CH_3COO^- $CF_3SO_3^-$ to the solutions of **5**–**7** in methanol, no changes in the maximum was observed and the emission fluorescence was slightly influenced by the presence of each anion, except for iodide, nitrite, azide, nitrate and thiocyanate. Interestingly, no interaction is observed in the case of fluoride, which usually is able to deprotonate thiourea and amide groups in the selective binding anion receptors [24, 44, 45]. The reason is that fluoride is too small to have cooperative binding of the appended side-arms of calixarene. Instead iodide is big enough to close up the appended side-arms and stiffened the system. Figure 1 shows the intensity ratio of calixarene **5**–**7** with and without the different anions. It is evident that for the three calixarene the behavior is practically the same. No change for almost all anion studied is detected, except for nitrate where a decrease in the emission intensity is observed only for receptor **6** and **7**. For the other anions the behavior is similar for the three receptors, for azide its initial signal decrease about a 15 %, for nitrite and thiocyanate the signal decrease around a 50 %, but where a noticeable quenching is observed, is for iodide, where the intensity practically disappears (90 %). To get insight into the binding properties of calixarene **5**–**7** with these anions, we determine the association constant and stoichiometry of the inclusion complexes.

The association constants were calculated from the gradual changes in fluorescence intensity at any wavelength of calixarene upon stepwise addition of each anion

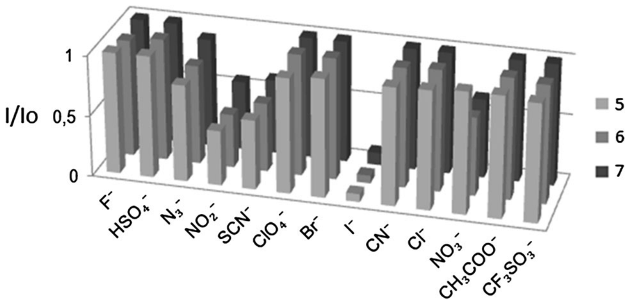


Fig. 1 Fluorimetric ratiometric behavior (I/I$_0$) of the host **5–7** (8.6 μmol L^{-1}) upon addition of 30 equivalents of F$^-$, HSO$_4^-$, I$^-$, N$_3^-$, NO$_3^-$, NO$_2^-$, SCN$^-$, ClO$_4^-$, Br$^-$, CN$^-$, Cl$^-$, CH$_3$COO$^-$, CF$_3$SO$_3^-$ as tetrabutylammonium salts in methanol

to the solution by a non-linear regression (NLR) [46] described by the following equation:

$$F = F_0 + \frac{(F_\infty - F_0)K_a[\mathrm{A}^-]_t}{1 + K_a[\mathrm{A}^-]_t} \quad (1)$$

Where F$_\infty$ is the fluorescence intensity when the total calixarene has been complexed with the anion, F$_0$ is the fluorescence of calixarene in the absence of anion, F is the observed fluorescence at each anion concentration tested and [A$^-$] is the anion concentration.

The association constant, K$_a$, of calixarene **5–7** with azide, nitrite, nitrate, thiocyanate and iodide were determined and the results are summarized in Table 1. For azide anion the fluorescence intensities are slight changed upon addition of azide implying the difficulty to determine the association constant for the three receptor. From Table 1, we can observe that the association constants of all anion studied are in the same range, except for iodide, where the K$_a$ values is five times higher than the other anions, indicating a preference of this anion by three receptors.

In Fig. 2, gradual addition of a standard solution of iodide in a fluorescence titration of **5–7**, exhibited a progressive decrease in the intensity of the peak at 313, 330 and 313 nm respectively and saturation in its quenching is observed at 40 equivalents. Experimental data of the intensity F as a function of iodide concentration is fitted to Eq. 1, (Figure S1 – S3). The NLR program estimates K by fitting the data through iteration and these representations

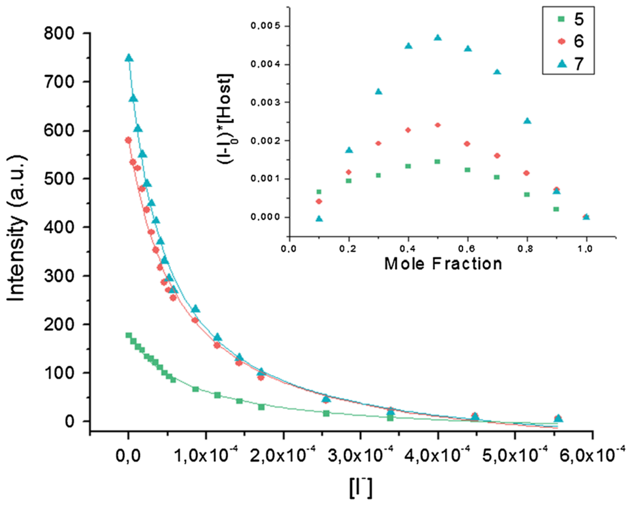


Fig. 2 Nonlinear curve fitting of **5–7** (8.6 μmol L^{-1}) of the emission intensity upon addition of various equivalents of tetrabutylammonium iodide in methanol ($\lambda_{ex} = 225$ nm). Inset: Job plot of a calixarene **5–7** with I$^-$ ion. The total concentration of **5–7** and I$^-$ is 5×10^{-5} mol L^{-1}

showed a good correlation with the experimental comportment observed when the different anion concentration was increased. (Figure S4 – S6).

For fitting the experimental data we have considered the presence of 1:1 calixarene-anion complex which was calculated by the continuous variation method (Figure S7). The job plots were constructed from the fluorescence experiment using the continuous variation method. The total concentration of calixarene and anions was kept constant while the molar fraction of anion was continuously varied. The result obtained indicates a maximum when the molar fraction is 0.5 for the three calixarenes, demonstrating that the formation of the iodide complex have a stoichiometry of 1:1 for each one. (Inset Fig. 2).

Once the stoichiometry of the inclusion complex and association constants was determined, the inclusion complex can be considered to use as chemosensor for iodide, therefore determining the sensitivity for this anion is important.

To study the influence of the other anions on I$^-$ binding with derivatives **5–7**, we performed competitive experiments. As shown in Fig. 3a for compound **7**, it can be seen

Table 1 Association constants of different ions with receptors **5–7**

	Calix[4]arene	5	Calix[4]arene	6	Calix[4]arene	7
Anion	K$_a$ ($\times 10^{-4}$ mol^{-1} L)	R	K$_a$ ($\times 10^{-4}$ mol^{-1} L)	R	K$_a$ ($\times 10^{-4}$ mol^{-1} L)	R
NO$_2^-$	0.32 ± 0.03	0.975	0.34 ± 0.02	0.982	0.32 ± 0.02	0.974
NO$_3^-$	nd	nd	0.22 ± 0.02	0.978	0.23 ± 0.03	0.977
SCN$^-$	0.35 ± 0.06	0.979	0.30 ± 0.05	0.980	0.35 ± 0.01	0.975
I$^-$	1.49 ± 0.10	0.989	1.79 ± 0.08	0.995	2.01 ± 0.08	0.996

K$_a$ association constant, *nd* not change detected

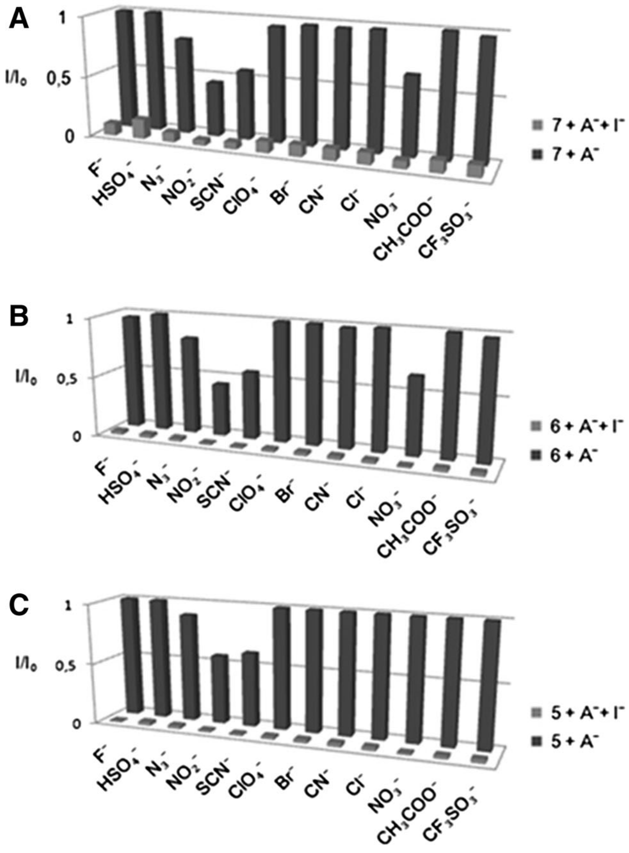


Fig. 3 Fluorimetric ratiometric behavior (I/I_0) of **7** (3A) **6** (3B) and **5** (3C) in the presence of 30 equivalents of different anions upon addition of 30 equivalents of iodide in methanol solution

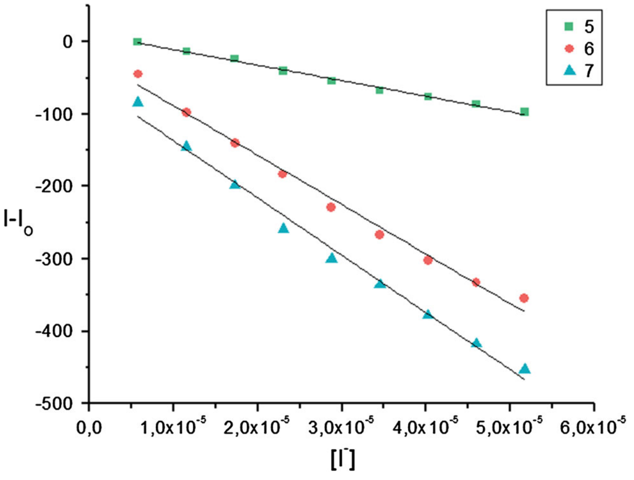


Fig. 4 Calibration curve of **5**–**7** with I^- ion in methanol for determination limit of detection in the lineal range from 5×10^{-6} to 5×10^{-5} mol L^{-1}

Table 2 Limit of detection of the different calixarene with Iodide

Calix[4]arene	LOD (mg L^{-1})	m ($\times 10^6$)	Sb	R
5	1.81 ± 0.05	2.15 ± 0.06	10.25	0.994
6	0.23 ± 0.01	6.83 ± 0.26	4.04	0.988
7	0.22 ± 0.01	7.90 ± 0.29	4.64	0.989

LOD limit of detection, *m* calibration sensitivity, *Sb* standard deviation of the blank solution

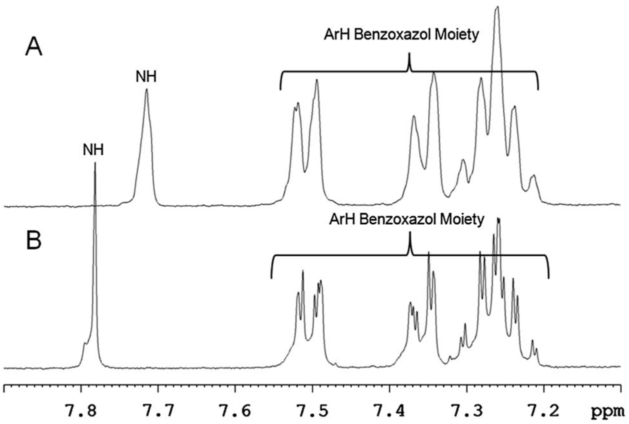


Fig. 5 Selected portion of the ^{1}H-NMR spectral change of calixarene **7** (7.2 mM) upon addition of five equivalent of tetrabutylammonium iodide in MeOD-d_4

that F^-, HSO_4^-, N_3^-, NO_3^-, NO_2^-, SCN^-, ClO_4^-, Br^-, CN^-, Cl^-, CH_3COO^- and $CF_3SO_3^-$ anions have small or no obvious interference with the addition of iodide ion, this behavior is analogous to the other derivatives **6** and **5,** Fig. 3b, c. These results suggest that calixarene **5**–**7** can be used as a potential selective fluorescent chemosensor for I^-.

The Limits of Detection (LOD) for the analysis for iodide are determined from the plot of fluorescence intensity [39] as a function of the concentration of anion in the lineal range from 5×10^{-6} to 5×10^{-5} mol L^{-1} in methanol (Fig. 4). The results are presented in Table 2, which indicates that host **6** and **7** practically has the same detection limits for iodide, 0.23 and 0.22 ppm, respectively. Therefore, calixarene **7** would be the best chemosensor, which present the highest association constants and recognizes iodide anion in a micromolar concentration scale. Moreover, as described in a previous report, this calixarene also detected lead in methanol solutions, which correspond to a new bifunctional chemosensor, due to the presence of the amide group, which provides simultaneous detection selectivity for both cations, through carbonyl oxygen atoms, and anions, through the hydrogen bonding with acidic hydrogen atoms on nitrogen atoms [47–49].

In order to gain insight into the structures of the complex formation of receptor **7**, we have carried out ^{1}H-NMR studies with iodide anion. Figure 5A shows the proton spectra of compound **7** in a methanol-d_4 solution. Upon addition of 5 equiv of iodide salt, the signal of N–H from

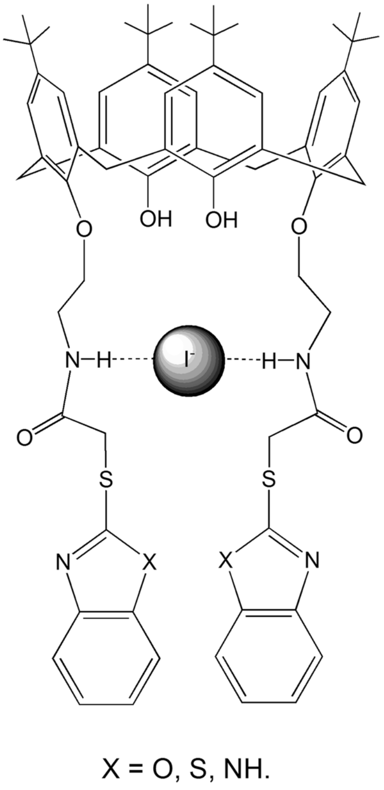


Fig. 6 Proposed molecular structure receptors of calixarenes **5–7** with iodide

the amide function and the signals for Ar–H of benzoxazole moiety exhibit evident changes, Fig. 5B. We can see that the signal from N–H amide function is deshielded owing to the proximity of the anion. Also the gain in resolution of the Ar–H of benzoxazole signals can be explained due to the rigidity of the system when the iodide anion form the complex [24]. These observations clearly suggest that the amide protons are involved in the H-bonding interaction. The possible binding mode is shown in Fig. 6, where the –S–CH_2–(C=O)–NH– feature plays a vital role in the binding with iodide because this behavior is observed for the three calixarene.

Conclusion

In summary, effective receptors calixarenes bearing heterocycles **5–7** for the selective recognition of iodide anion were investigated by fluorescence spectroscopy. Fluorescent chemosensor ability of the calixarene derivatives have high association constants and sensibility for iodide in contrast with the other twelve anions studied. All the inclusion complexes studied have a 1:1 stoichiometry. The best chemosensor found, corresponds to compound **7,** with an association constant of 2.01×10^4 mol^{-1} L and a detection limits of 0.22 ppm for iodide.

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