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Energetics of the Inclusion of Organic Molecules by Rigidified Cone Calix[4]arenes in Carbon Tetrachloride

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The complexation of acetonitrile and nitromethane by the calix[4]biscrowns 1, 2, 3 and the upper rim pyridine brigded calix[4]arene 4, all fixed in a C_{4v} structure, was studied by ^1H NMR and calorimetry in CCl_4. The spectroscopic data show that the inclusion of the two organic guests occurs *via* their $-CH_3$ moiety in all cases. For all the investigated hosts the binding constants with both guests determined by both ^1H NMR and calorimetric titrations, show that the inclusion is favoured by the presence of functionalizing groups at the upper rim. Furthermore log K values indicate that no stability difference was found between the two guests. Calorimetric data show that the inclusion is enthalpically driven in all cases. The favourable enthalpic contribution is to be attributed mainly to the CH$-\pi$ interactions between the π-donor aromatic moieties of the hosts and the activated methyl residue of the guests. The combination of ^1H NMR and calorimetric information allows for a more detailed description of the inclusion process.

Keywords: Calixarenes; Molecular recognition; CH$-\pi$ interactions; Inclusion compounds; Host-guest chemistry; Calorimetry

INTRODUCTION

The formation of stable inclusion complexes between a receptor and a neutral guest is mainly determined by both the matching of the size and the chemical information stored in the two components. Thus a guest is efficiently bound by a receptor, provided that their sizes as well as their binding sites are complementary. Although during the last couple of decades several receptors (*e.g.*, cyclodextrin [1], cyclophanes [2] and calixarenes [3]) have been synthesised which have been shown to recognise neutral organic species, thanks also to the presence of a cavity, the study of host-guest interactions which stabilise these complexes is still a matter of extensive investigations. This is particularly true when the complexation between neutral hosts and neutral organic species takes place in solution where solvation effects may play an important role.

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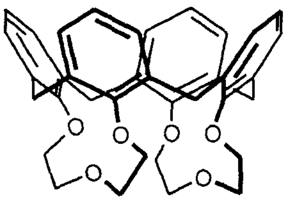
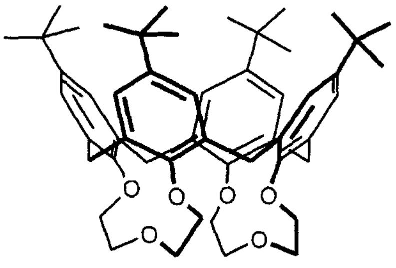
In this context, Arena and co-workers have studied the inclusion of ethanol [4] as well as valine and leucine [5] by water-soluble calix[4]-arenes having sulphonated groups at the upper rim. Aliphatic aminoacids, as well as ethanol, are included into the host cavity by their aliphatic portion, whereas the polar residues of the guest face the bulk of water molecules and interact with the charged groups present at the upper rim of the host which serve as anchoring points. In a different, though complementary approach, Aoyama and co-workers realised the complexation of monools and acetylated compounds [6] to a resorcinol cyclic tetramer in apolar media. The investigated calix[4]resorcinarene derivative binds simple monools *via* the



1



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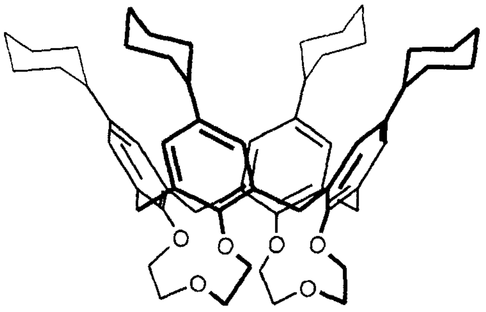

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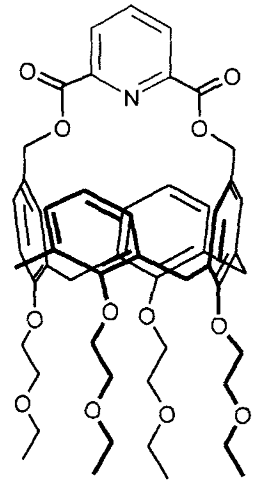

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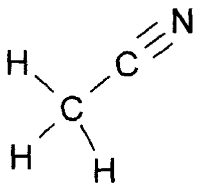

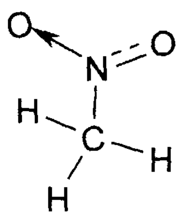

CHART 1

simultaneous action of strong and weak hydrogen bond interactions, thanks to its ability to fix the guests through multiple hydrogen bonding.

When the guest lacks classical hydrogen bond donor groups, as in the case of small neutral aliphatic molecules, only relatively weak hydrogen-bond-like interactions (*i.e.*, CH – π interactions [7]) between weak donors (as acidic CH hydrogen atoms) and weak acceptors (as the π system of aromatic rings) can be exploited, in addition to van der Waals interactions. CH – π interactions may be regarded as weak hydrogen bonds between soft acids and soft bases [7b] and are inherently directional as classical hydrogen bonds; thus they play important roles in the conformation of organic molecules, in crystal engineering [7a] and in molecular recognition processes. They involve only small energies (*ca.* 1 kcal/mol) and consequently only the multiple simultaneous interaction of CH with π groups renders the total energy sizeable [8]. In principle, receptors able to include neutral guests with high affinity in apolar media should be rigid or preorganized to a certain extent in order to exploit the cooperative and directional character of CH – π interactions.

Several inclusion complexes of calix[4]arenes and neutral molecules have been detected in the solid state [9], whereas only recently these macrocycles have been shown to form stable complexes in solution with guests having acidic CH groups. In fact Pochini and co-workers synthesised several calix[4]arenes blocked in a rigid *cone* conformation [10] by lower [11] or upper [12] rim functionalization; the calix[4]arene-biscrown-3 derivatives and the upper rim pyridine bridged calix[4]arenes thus obtained are able to form *endo* cavity inclusion complexes with neutral guests having acidic CH groups (*e.g.*, nitromethane) with a relatively high affinity. This indicates that the preoganized aromatic cavity of the host determines the stability of the complexes with neutral guests by acting as π-donor binding site, and that CH – π interactions are operating. These findings suggest that a more detailed study of the binding properties of these two type of rigid calix[4]arenes toward guests having different acidity could clarify the role of the forces that drive the recognition processes as a key step for the achievement of increasingly efficient receptors. In this paper we report a combined ^{1}H NMR and calorimetric investigation of the inclusion of nitromethane and acetonitrile by four rigid calix[4]arenes, which differ for their structural characteristics and for their cavity width (Chart 1). The study was carried out in carbon tetrachloride, to minimise the interaction of both host and guest with the solvent. The evaluation of the thermodynamic parameters ($\Delta H°$ and $\Delta S°$) is employed to clarify the nature of the interactions which drive complexation.

RESULTS AND DISCUSSION

^{1}H NMR studies of inclusion of CH_3NO_2 by compounds **1**, **2**, **3** and **4** have been previously reported [11, 12]. In all cases the upfield shifts of the CH protons of the guest indicate an interaction of the "acidic" protons of the guest with the π-donor aromatic moieties of the hosts.

Figures 1a – d show the upfield shifts ($\Delta\delta_{obs} = \delta_{obs} - \delta_{free\ guest}$) for the guest protons

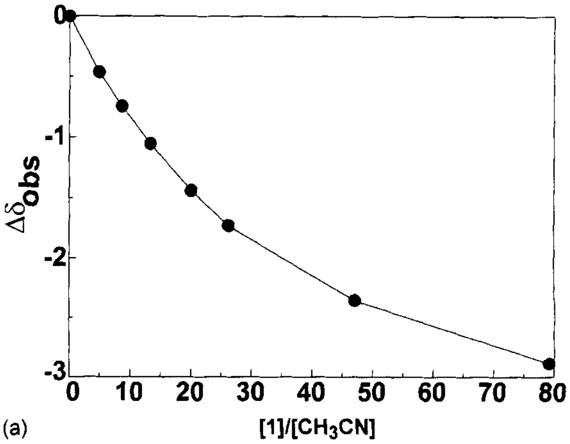

FIGURE 1

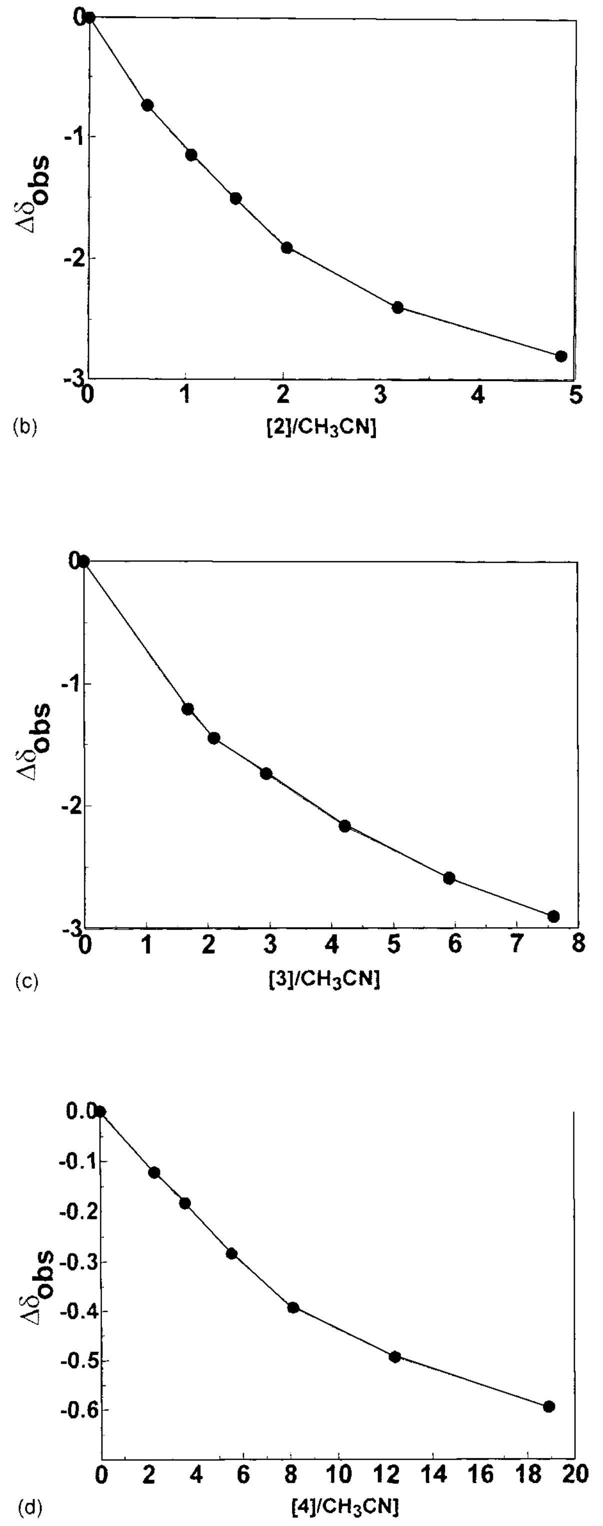

FIGURE 1 (Continued).

induced by the complexation of CH_3CN with host **1**, **2**, **3** and **4**, respectively. In every case, adding variable amounts of the hosts to a 10^{-3} mol dm^{-3} solution of CH_3CN in CCl_4 causes upfield shifts of the protons of the guest. This indicates that all inclusion processes take place in the same way: CH_3CN is included into the host cavity by means of methyl group, very likely *via* CH$-\pi$ interactions with the aromatic moieties of the four receptors.

The proton upfield shifts were treated by using non-linear least-squares fitting procedures [13], in order to obtain the binding constant values (Tab. I). log K values show that the inclusion complexes of CH_3CN and CH_3NO_2 with host **2** and **3** are the most stable ones, whereas the complexes of host **4** and much more so the complexes of host **1** are less stable than the complexes with host **2** and **3**. It is noteworthy that, although **4**-CH_3CN complex is slightly more stable than **1**-CH_3CN, a smaller $\Delta\delta$ is observed for the guest protons of the calixpyridine complex (Figs. 1a and 1d), at the same host/guest ratio. This could indicate that in the **4**-CH_3CN complex the guest is hydrogen bonded to the heteroatoms of the bridge [12] and less deeply included into the cavity of the host. Owing to the upper rim bridge functionalization, in fact, the structural characteristics of host **4** are basically different from those of the calixbiscrowns **1**, **2** and **3**. Furthermore, log K

TABLE I log K values[a] for the complex formation of CH_3CN e CH_3NO_2 with host **1**, **2**, **3** and **4**

Reaction	log K
1 + $CH_3CN \rightleftharpoons$ **1**-CH_3CN	1.2(1)
1 + $CH_3NO_2 \rightleftharpoons$ **1**-CH_3NO_2	1.4[b]
2 + $CH_3CN \rightleftharpoons$ **2**-CH_3CN	2.5(1)
2 + $CH_3NO_2 \rightleftharpoons$ **2**-CH_3NO_2	2.4[b]
3 + $CH_3CN \rightleftharpoons$ **3**-CH_3CN	2.4(1)
3 + $CH_3NO_2 \rightleftharpoons$ **3**-CH_3NO_2	2.1[b]
4 + $CH_3CN \rightleftharpoons$ **4**-CH_3CN	1.6[c]
4 + $CH_3NO_2 \rightleftharpoons$ **4**-CH_3NO_2	1.8[c]

[a] σ values are given in parentheses.
[b] Ref. [11].
[c] Ref. [12].

values indicate that no difference of complex stability was found among the two guests (*i.e.*, CH_3CN and CH_3NO_2), thus showing that the complexation efficiency is dictated by the preorganization of the hosts rather than the different "acidity" of the guests protons.

The stability constant values were also determined by direct calorimetry. The log K values determined by titration calorimetry coincide, within the experimental error, with those obtained *via* ^1H NMR titration experiments. The calorimetric experiments also allowed to obtain both the enthalpy and entropy of binding of the two guests to our hosts and this allowed a better comprehension of the forces driving the inclusion processes and to rationalize the stability differences between the four receptors. The process is enthalpically driven for all systems reported here (Tab. II), whereas the entropic contribution is always unfavourable. To explain these experimental results we have to take into account that in all inclusion processes the ΔS° results essentially from: (i) a positive contribution resulting from the release of solvent molecules from both the host and the guest and (ii) a negative term, determined by the reduction of degrees of freedom due to complex formation [14]. For the complexation between neutral partners in organic media the first term is not expected to be relevant [15]. The overall entropic changes obtained for our systems show that it is the second term that chiefly determines the order-disorder processes in these cases (Tab. II).

The ΔH° values for the interaction of **1** with both guests are less exothermic than those for the inclusion complexes of host **2** and **3**. Receptors **2** and **3**, owing to the alkyl groups present at the upper rim, have a wider and deeper cavity with respect to host **1**. These extended cavities offer the possibility of a larger number of interaction points for the guests with respect to host **1**. The guest molecules are held tightly into the cavity and the stiffening of the system is reflected in the ΔS° values, which are more unfavourable than those observed for the inclusion complexes of host **1**.

Host **4** represents a case a part. This compound, in fact, was selected *ad hoc* for his structural characteristics, basically different from those of the calixbiscrowns **1**, **2** and **3**. Whereas the calixbiscrowns were immobilized in a rigid *cone* conformation by inserting two short diethylene glicole units at the lower rim, the rigidification of host **4** was achieved by introducing a rigid bridge containing a pyridine unit at the upper rim. The upper rim pyridine bridge, whereas on one side, reduces access to the host cavity and does not implement the cavity width as do upper rim substituents in **2** and **3**, on the other side, provides an additional π-donor group, beside the several heteroatoms

TABLE II log K values[a] and thermodynamic parameters[a] of complex formation of CH_3CN e CH_3NO_2 with hosts **1**, **2**, **3** e **4**[b]

Reaction	log K	ΔG° kcal mol^{-1}	ΔH° kcal mol^{-1}	ΔS° cal mol^{-1} deg^{-1}
$\mathbf{1} + CH_3CN \rightleftarrows \mathbf{1}\text{-}CH_3CN$	1.2(1)	−1.6(1)	−6.6(1)	−16.5(4)
$\mathbf{1} + CH_3NO_2 \rightleftarrows \mathbf{1}\text{-}CH_3NO_2$	1.1(1)	−1.5(1)	−6.3(1)	−16.4(3)
$\mathbf{2} + CH_3CN \rightleftarrows \mathbf{2}\text{-}CH_3CN$	2.39(5)	−3.26(7)	−9.4(1)	−20.4(6)
$\mathbf{2} + CH_3NO_2 \rightleftarrows \mathbf{2}\text{-}CH_3NO_2$	2.18(5)	−2.97(7)	−9.0(3)	−20(1)
$\mathbf{3} + CH_3CN \rightleftarrows \mathbf{3}\text{-}CH_3CN$	2.30(5)	−3.09(7)	−9.3(2)	−20.8(8)
$\mathbf{3} + CH_3NO_2 \rightleftarrows \mathbf{3}\text{-}CH_3NO_2$	2.16(5)	−2.94(7)	−9.5(4)	−22(1)
$\mathbf{4} + CH_3CN \rightleftarrows \mathbf{4}\text{-}CH_3CN$	1.6(1)	−2.1(1)	−5.3(2)	−10.7(7)
$\mathbf{4} + CH_3NO_2 \rightleftarrows \mathbf{4}\text{-}CH_3NO_2$	1.7(1)	−2.3(1)	−5.6(3)	−11(1)

[a] σ values are given in parentheses.

[b] Non S. U. employed; 1 cal = 4.184 joules.

which are potential hydrogen bond acceptors. Solid state data [12] clearly indicate the presence of a bifurcated hydrogen bond between the acidic hydrogen atoms of CH_3NO_2 and the heteroatoms of the upper rim pyridine bridge. This peculiar nature is reflected in the thermodynamic parameters of inclusion in an unexpected mode.

It is well known that hydrogen bonding, like other non covalent interactions, is enthalpically favoured and entropically unfavoured due to the rigidifying effect [16]. Thus for the complexes of CH_3CN and CH_3NO_2 with host **4** we would expect ΔS° values more unfavourable and ΔH° values more exothermic than those reported for the complexes of host **1**, the cavity of which is similar to the cavity of host **4**, a part from the upper rim pyridine bridge. However, the experimental results go in the opposite direction (Tab. II). According to these results, we are bound to believe in one of the following hypothesis: i) host and guest are not hydrogen bonded in solution as they are in the solid state; ii) the thermodynamic data conceal subtle differences that are not revealed by other techniques. In fact, as shown by the ^1H NMR data, inclusion of CH_3CN and CH_3NO_2 into the aromatic cavity of host **4** is not as effective as in the other three hosts. This should result in less favourable ΔH° values. Although in the presence of an inclusion of lesser entity the still favourable enthalpic contributions could be the result of hydrogen bonding between the acidic hydrogen atoms of the guests and the heteroatoms of the upper rim pyridine bridge.

CONCLUSIONS

The present study shows that for the calix[4]arene-biscrown-3 (**1**, **2**, and **3**) the log K values are mainly determined by the groups present at the upper rim of the calixarene skeleton. The analysis of the thermodynamic parameters indicates that the complexation is not affected by the acidity of the CH_3 group of the guest, thus strongly suggesting that the interactions involved are mainly dispersive in nature. These data are in agreement with those obtained in a systematic study carried out by examining solid state structures of inclusion complexes between calix[4]arene derivatives and neutral organic guests having acidic CH_3 groups, which showed that the position of the CH_3 inside the cavity is independent of the acidity of the guest [9e].

The lack of correlation of the log K values and the acidity of the two guests in the complexes of receptor **4** could not be reasonably explained and needs further investigations.

EXPERIMENTAL SECTION

Materials

Nitromethane (Fluka, > 99%) and acetonitrile (LabScan, > 99.8%) were commercial products and were used without any further purification. Carbon tetrachloride (Carlo Erba, > 99.8%) was dried over $CaCl_2$ and stored over 3 Å molecular sieves before use. 18-crown6 (Aldrich, > 99.5%), NaCl (Merck, Suprapur) and methanol (Carlo Erba, > 99,8%) were used without any treatment. Calixarenes **1**, **2** and **3** were prepared as described in references 11. Calixarene **4** was synthesized following the procedure reported in reference 12.

^1H NMR Titrations

^1H NMR titrations were recorded in CCl_4 with a Varian Inova 500 MHz spectrometer and the chemical shifts (δ) are expressed in ppm using Me_4Si as internal standard. A sealed capillary tube containing deuterated benzene was coaxially inserted into each NMR sample in order to furnish the internal lock.

The titrations were carried out keeping the guest concentration constant (usually 1×10^{-3} mol dm^{-3}), while the host concentration ranged from 1×10^{-3} to 1×10^{-1} mol dm^{-3}. Each experiment consisted of about six points and was repeated at least three times.

Calorimetric Measurements

The calorimetric runs were performed at 25.000 ± 0.001°C, using a Tronac 450 (Utah, USA) isoperibol calorimeter equipped with a 25 ml dewar cell.

Several calorimetric studies have been performed in organic solvents as methanol [17], acetonitrile [17b] and benzonitrile [18], whilst few experiments have been carried out in carbon tetrachloride or chloroform [19]. The use of carbon tetrachloride was dictated by the need to have a solvent capable to form hydrogen bonds neither with the guest nor with the host. Several blank-tests were performed in order to determine the best experimental conditions for our measurements. Fast evaporation phenomena were observed when the calorimeter was equipped with a 4 ml dewar. These problems were minimized by using a much larger dewar (25 ml). The baselines of the thermograms thus obtained were very regular and had a positive slope and, in addition, the thermograms were highly reproducible. Based on these experimental findings the 25 ml cell was used throughout, although this remarkably increased the amount of calix[4]arene needed for each titration.

Usually a 0.5–1.0 mol dm^{-3} solution of the guest (CH_3CN or CH_3NO_2) was added to a 1.0–2.0 × 10^{-3} mol dm^{-3} solution of host **1** to **4**, recording 20–30 points for each of the 4–6 independent titrations. Blank experiments were carried out in all cases to account for heat of dilution and heat of friction effects resulting from the addition of the titrant to the solution contained in the calorimetric vessel. The calorimeter was calibrated both chemically (from time to time) and electrically (twice for each single run) to check for accuracy and reproducibilty. The chemical calibration was performed by titrating a solution of 18-crown6 in methanol with a methanolic solution of NaCl. The ΔH° and log K values obtained were in good agreement with the literature data [20].

Calculations

In order to obtain log K values the ^{1}H NMR data were treated by using non-linear least squares curve fitting procedures [13]. The data were satisfactorily fitted by assuming the formation of a 1:1 species only. K and ΔH° values were obtained by using a modified version of the computer program EQDH [21].

Acknowledgements

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