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Interactions of the aromatic cavity of rigid calix[4]arene cone conformers with acid CH_3 and CH_2 containing guests in apolar solvents

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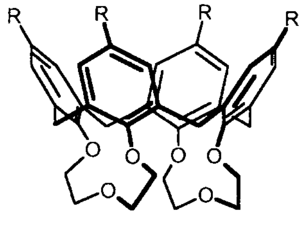
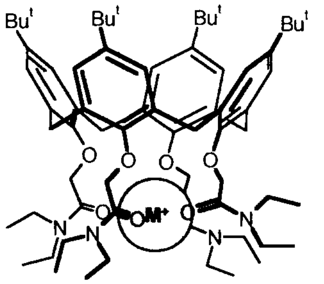
Abstract—The effect of the acidity of CH groups within the guests on the binding ability of the aromatic cavity of rigid *cone* conformers of *p-tert*-butylcalix[4]arene toward guests containing acid CH_3 and CH_2 groups have been investigated in apolar media by ^1H NMR spectroscopy. In $CDCl_3$ and/or CCl_4, CH_3Y and CH_2XY guests show different binding modes. In particular the acidity of the CH_2XY guests strongly affects the binding efficiency whereas the guest acidity does not seem the sole parameter in determining the stability of the complexes with CH_3Y guests. With methylene containing guests, the polarizability of the X and Y groups strongly affect the binding process and the ΔG^0 of complexation is linearly correlated with both pK_a and polarizability of the guests. Solid state structures of sodium and potassium complexes of tetrakisdiethylamide of *p-tert*-butylcalix[4]arene$\supset CH_3CN$ complexes are discussed. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

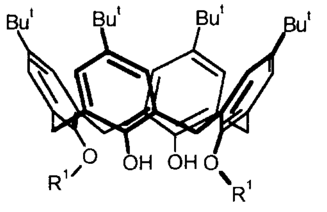
The *cone* conformers of calix[4]arenes posses a π-rich cavity defined by its four aromatic rings, which is suitable for the inclusion of neutral guests of complementary size. In apolar media[1] the ability of these hosts to form *endo*-cavity inclusion complexes was evidenced only when the guests molecule possesses acidic CH_3 or CH_2 groups.[2,3] The additional prerequisite is that the conformational flexibility of the receptor is reduced by the introduction of short ethereal chains (**1**),[2] by cation complex formation (**2**)[2,3] or by hydrogen bonding at the lower rim of partially alkylated derivatives (**3a–e**)[3] (see Formulas).



1a R = H
1b R = Bu^t
1c R = cyclohexyl



2a M⁺ = Na
2b M⁺ = K



3a R^1 = Pr
3b R^1 = Me
3c R^1 = $CH_2CH_2OCH_2CH_3$
3d R^1 = $CH_2C_6H_5$
3e R^1 = CH_2COOEt

Specific CH–π (aromatic) interactions,[4] which are electrostatic in nature and considered as weak hydrogen-bonds, have been hypothesized to drive the formation of these complexes. In an attempt to understand how these interactions drive the recognition of CH_3Y and CH_2XY guests by *cone* conformers of calix[4]arene derivatives, we have recently carried out a study on the structure of these complexes in the solid state (see Fig. 1).[5] We found that CH_3Y guests are preferentially included by receptors having C_4 symmetry and no significant effect of the acidity of the guest on the binding mode was observed. On the contrary, strong differences were observed for CH_2XY guests with different acidities. In particular, the latter guests are included by hosts having a C_{2v} symmetry, and the CH_2 groups interact specifically with the two 'pinched' diametrical aromatic rings. These interactions are directional and the increase of the CH acidity results in a decrease of the distances between the CH protons and the *centroid* of the interacting aromatic ring. These results suggest a different binding mode for the two classes of guests and support the hypothesis that 'classic' hydrogen bonding strongly

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Keywords: calix[4]arenes; molecular recognition; neutral molecules; host–guest chemistry; inclusion compounds; CH–π interactions.

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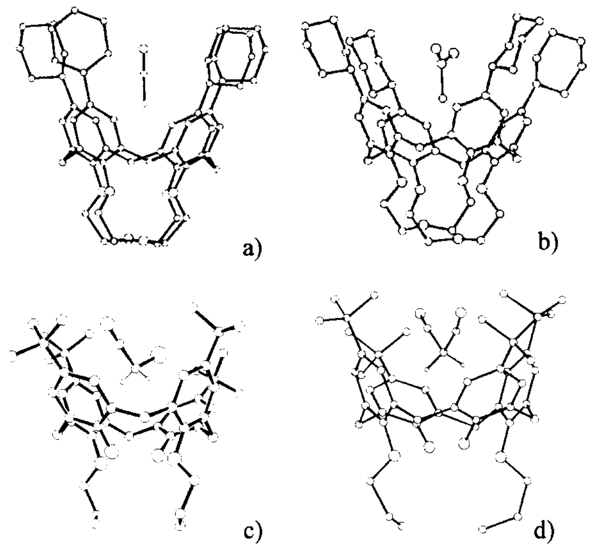

Figure 1. X-Ray crystal structures of: (a) acetonitrile$\subset$*p*-cyclohexylcalix[4]arene-biscrown-3 (**1c**);[5] (b) nitromethane$\subset$*p*-cyclohexylcalix[4]arene-biscrown-3 (**1c**);[2] (c) chloroacetonitrile$\subset$*p*-*tert*-butyl-1,3-dipropoxycalix[4]arene (**3a**);[5] (d) malononitrile$\subset$*p*-*tert*-butyl-1,3-dipropoxycalix[4]arene (**3a**).[5]

contributes to the overall CH–π interactions only with CH_2XY guests.

In apolar media the data collected so far on the binding of CH_3Y and CH_2XY guests using rigidified calix[4]arenes, seems to indicate that, as also observed in the solid state, the CH–π interactions, which stabilize the complexes formed, result from the combination of several forces with different relative magnitudes for these two types of guest. In fact, careful analysis of the results obtained by Stibor and co-workers[3] provided evidence that, in spite of the different association constant experienced by a series of dialkoxycalix[4]arenes, the same host shows comparable efficiency toward acetonitrile ($pK_{a\text{-DMSO}}=31.3$)[6] and nitromethane ($pK_{a\text{-DMSO}}=17.2$)[6] suggesting that for these guests the acidity does not affect the extent of binding. On the other hand Fukazawa and co-workers,[7] by studying the binding ability, in carbon tetrachloride, of monomethoxy monodeoxy derivative of *p*-*tert*-butylcalix[4]arene toward small neutral guests with acid methylene groups, found a linear correlation of the binding enthalpy with the acidity of the guests.

In this paper we present the results of a systematic study aimed at quantitatively establishing the role of the structure of these guests, in particular of the acidity of their CH groups, on the recognition processes involving rigid *cone* conformers of calixarene hosts in apolar solvents.

Table 1. Association constants (K_{as}, M^{-1}) for hosts **2a–b** with nitromethane and acetonitrile guests

Host	CH_3NO_2	CH_3CN
2a	28(3)	35(3)
2b	17(1)	17(1)

Determined by ^1H NMR in $CDCl_3$, $T=300$ K; all values result from at least duplicate experiments, standard deviations are in brackets.

For this purpose the magnitude of complexation was evaluated by ^1H NMR using $CDCl_3$ or CCl_4 as solvents, a series of CH_3Y and CH_2XY guests having different structural features as guests and metal complexes of tetraamide (**2a–b**) or 1,3-dipropoxy calix[4]arene (**3a**) as hosts.

2. Results and discussion

With the aim of verifying whether the lack of dependence of the acidity of CH_3Y guests on the extent of complexation was restricted to hosts rigidified by intramolecular hydrogen bonding as in 1,3-dialkoxycalix[4]arenes (**3**)[3] or through the insertion of crown of the phenolic oxygens as in biscrown-3-calix[4]arenes (**1**),[8] we initially studied the complexing ability of calix[4]arenes rigidified through alkali metal cation complexation at the lower rim of tetrakisdiethylamide-*p*-*tert*-butylcalix[4]arenes (**2**).[2] In addition, solid state studies[5] suggest the possibility of modulating the δ angle between the aromatic nuclei and the r plane (see Fig. 3) containing the CH_2 bridging units of the host by changing the cation bound through the amide groups of the lower rim. Therefore two metal complexes of **2** with cations having different radii were obtained using sodium and potassium picrates (**2a** and **2b** respectively). The results obtained with the sodium (**2a**) and potassium (**2b**) complexes as hosts and nitromethane and acetonitrile as guests in $CDCl_3$ are reported in Table 1.

These data confirmed that also with this type of rigidified calixarenes the acidity of the CH_3Y guests does not affect the stability of these complexes. In addition, the effect of the cation size is small and does not seem to be a control element in this recognition process.

In order to verify whether this behavior could also be reflected in the solid state structural parameters of these metal complexes, the X-ray structural determination of **2a**$\supset CH_3CN$ and **2b**$\supset CH_3CN$ complexes was carried out (see Fig. 2).

In both the two host–guest supermolecules, the cationic complex lies around a crystallographic fourfold axis of symmetry which contains the metal cation and the CH_3CN guest molecule. Moreover, the metal cation is co-ordinated by the four phenol and by the four carbonyl oxygen atoms disposed in the form of a regular antiprism and thus it is shielded from strong interactions with the picrate counteranion. Relevant bond distances and angles in the two complexes are reported in Table 2. No significant differences have been observed for the bond distances in the KPic cationic complex with respect to the analogous ones in the KSCN and KI complexes previously characterized by us.[9]

Some geometrical parameters[5] are required to describe the host–guest structure: the δ angle(s) formed between each benzene ring and the r plane containing the four bridging methylene carbons of the calixarene, defines the shape of the host cavity, and consequently its symmetry (see Fig. 3a), whereas the position of the guests into the host cavity is described through two other parameters: the DC distance that occurs between the methyl carbon and the centroids

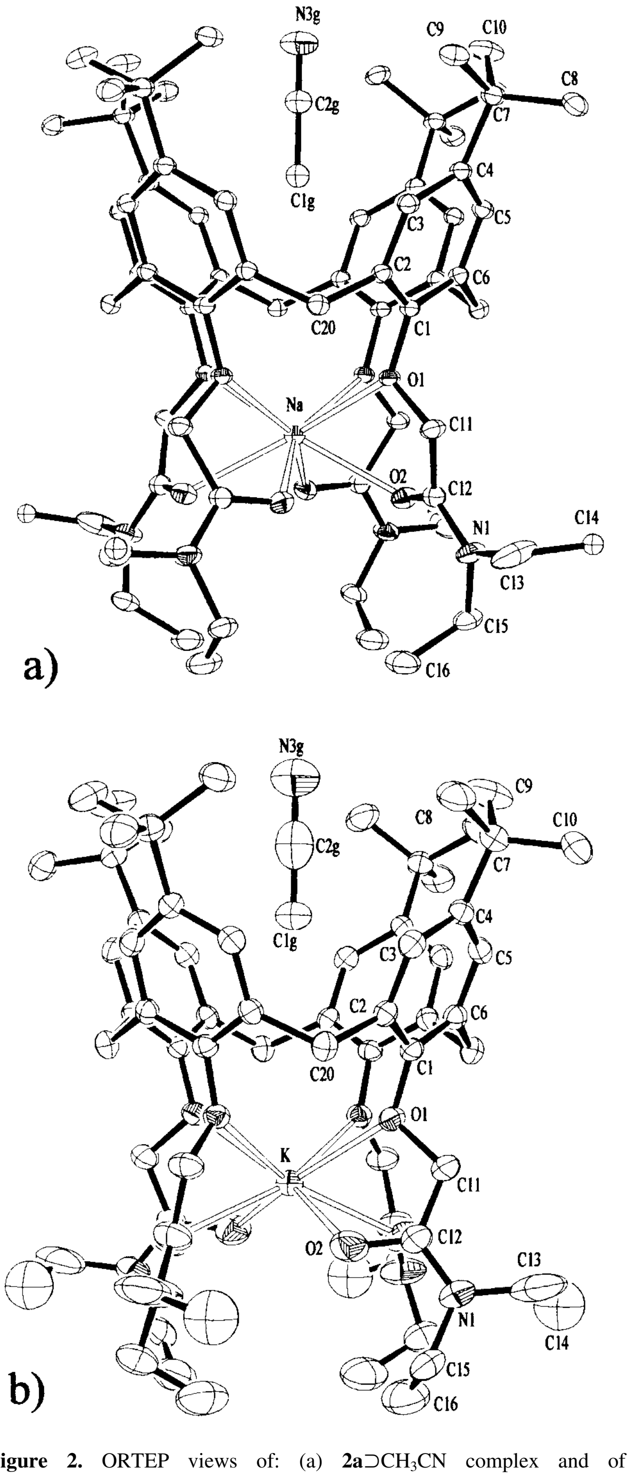

Figure 2. ORTEP views of: (a) **2a**$\supset$CH$_3$CN complex and of (b) **2b**$\supset$CH$_3$CN complex with the atoms numbering schemes.

Table 2. Selected bond distances (Å) and angles (°) in the two cationic complexes with acetonitrile

2a$\supset$CH$_3$CN		**2b**$\supset$CH$_3$CN	
Na–O1	2.536(2)	K–O1	2.704(3)
Na–O2	2.455(3)	K–O2	2.744(5)
O1–C1	1.401(3)	O1–C1	1.386(6)
O1–C11	1.428(4)	O1–C11	1.441(6)
O2–C12	1.226(4)	O2–C12	1.267(10)
N1–C12	1.347(5)	N1–C12	1.282(10)
N1–C13	1.442(7)	N1–C13	1.506(17)
N1–C15	1.468(5)	N1–C15	1.455(13)
C1–C2	1.383(4)	C1–C2	1.403(7)
C1–C6	1.372(7)	C1–C6	1.397(4)
C2–C3	1.403(4)	C2–C3	1.383(7)
C2–C20	1.526(4)	C2–C20	1.532(6)
C3–C4	1.390(4)	C3–C4	1.371(7)
C4–C5	1.391(4)	C4–C5	1.373(7)
C4–C7	1.543(4)	C4–C7	1.525(7)
C5–C6	1.393(4)	C5–C6	1.397(7)
C7–C8	1.540(5)	C7–C8	1.550(9)
C7–C9	1.524(6)	C7–C9	1.536(9)
C7–C10	1.526(5)	C7–C10	1.554(8)
C11–C12	1.510(5)	C11–C12	1.455(9)
C13–C14	1.469(10)	C13–C14	1.40(2)
C15–C16	1.510(7)	C15–C16	1.46(2)
C1G–C2G	1.440(10)	C1G–C2G	1.38(4)
C2G–N3G	1.132(11)	C2G–N3G	1.31(4)
O1–Na–O2	63.61(8)	O1–K–O2	58.28(13)
Na–O1–C1	137.39(16)	K–O1–C1	136.0(3)
C1–O1–C11	110.9(2)	C1–O1–C11	111.6(3)

of the aromatic rings of the calixarenes, and the α angle which is defined by the line that links the carbon atom of the guest to the centroids of the aromatic rings and by the *normal* to the plane of the aromatic rings themselves (see Fig. 3b). Moreover the distance (h) of the methyl carbon atom from the r plane, the angle β formed by the *normal* to the r plane and by a vector containing the CH$_3$–X (C,N) moiety of the guest were considered (see Fig. 3a).

The comparison of the geometrical parameters of the two complexes (see Table 3) confirms the hypothesis that the cation modifies the host–guest structure. In fact the increase of the cation radius decreases the δ angle between the four aromatic rings and the r plane, which is 114.2(1)° and 112.7(1)° in the sodium and potassium complex, respectively. These values are the smallest among those observed in the crystal structures of cone conformers of calix[4]arenes$\supset$CH$_3$CN complexes.[5]

The guest enters into the aromatic cavity through its CH$_3$ group. The guest axis is perpendicular to the r plane ($\beta=0°$) with the methyl carbon that lies on the normal from the *centroid* of the aromatic rings ($\alpha \cong 0°$). It is interesting to note that the DC distances are practically identical in the limit of the e.s.d.: 3.530(4) and 3.526(7) Å in the sodium and potassium complexes (see Table 3).

This means that the variation of the cation radius in the complex results in a significant modifications of the geometry of the cavity, but no significant modifications in the DC values. This is in agreement with the comparable efficiency observed in CDCl$_3$ for these sodium and potassium complexes in the binding of the two CH$_3$Y guests, thus suggesting that the acidity of the guests and the size of the

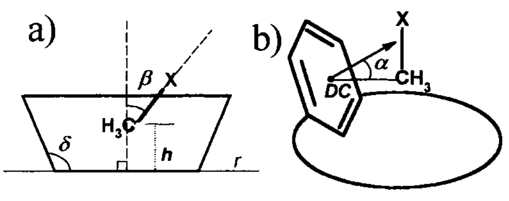

Figure 3. Geometrical descriptors for solid state host–guest complexes (see text).

Table 3. Geometrical descriptors for the solid state host–guest complexes

Complex	*R*	*δ* (°)	*β* (°)	*h* (Å)	DC (Å)	*α* (°)
2a	0.094	114.2(1)	0.000	2.551(7)	3.530(4)	2.58(1)
2b	0.089	112.7(1)	0.000	2.58(2)	3.526(7)	1.0(2)

cation do not seem to be control elements in determining the complexation efficiency.

Based on the results obtained in the solid state,[5] which indicate that CH_2XY guests are bound in a complementary manner by 1,3-dialkoxycalix[4]arene derivatives, 1,3-dipropoxy-*p*-*tert*-butylcalix[4]arene (**3a**) was chosen as host for the studies in apolar solvents. Malononitrile ($pK_{a\text{-DMSO}}=11.1$)[6] was studied only in $CDCl_3$ for solubility reasons and its association constant was compared, in this solvent, with those of $ClCH_2CN$ ($pK_{a\text{-DMSO}}=26$),[7] CH_3CH_2CN ($pK_{a\text{-DMSO}}=31$)[7] and CH_2Cl_2 ($pK_{a\text{-DMSO}}=35$).[7] All the other guests were studied in CCl_4 and in Table 4 are reported the two series of measurements in the two solvents.

Analysis of the data obtained in $CDCl_3$ showed a logarithmic dependence of the stability constants with the acidity of the guest, therefore a linear correlation $\Delta G^0 = m\mathrm{p}K_a + C$ was devised and although determined considering few experimental points, gave a satisfactory result: $m=0.39\pm0.03$, $C=-15.9\pm0.7$, $r^2=0.989$ (see Fig. 4).

More interesting insights into the role played by intermolecular forces in the recognition phenomena[10] can be obtained taking into account a wider number of acidic guests; therefore we considered the results obtained in the less polar CCl_4, where also the less acidic guests are bound. The negligible complexing ability experienced by **3a** with $C_6H_5CH_2CN$ ($pK_{a\text{-DMSO}}=21.9$) and $C_2H_5OCOCH_2CN$ ($pK_{a\text{-DMSO}}=13.1$)[6] as guests, reveals a strong effect of the phenyl and ester group on the extent of binding, which is probably due to the steric requirement of these substituents, which affords, in spite of the high acidity of their CH_2 groups, a very low binding interaction.

Table 4. Free energy of binding (ΔG^0, kJ/mol) for hosts **3a** with various CH_2XY guests

Guest	pK_a[6]	ΔG^0 (kJ/mol)		MR_x[a]
		$CDCl_3$	CCl_4	
$CH_2(CN)_2$	11.1	−11.4(0.2)		
$ClCH_2CN$	26	−6.5(0.3)	−11.34(0.05)	13.376
CH_3CH_2CN	31	−3.5(0.3)	−8.2(0.3)	14.827
$ClCH_2Cl$	35	−1.7(0.3)	−5.2(0.3)	12.605
$EtOCOCH_2CN$	13.1		[b]	–
$PhCH_2CN$	21.9		[b]	–
FCH_2CN	25[11]		−8.9(0.5)	8.67
$BrCH_2CN$	29		−10.9(0.4)	16.449
$BrCH_2Cl$	38		−5.0(0.3)	15.587
$BrCH_2Br$	41		−6.4(0.3)	18.824

Determined by ^1H NMR in CCl_4, D_2O as external standard, and $CDCl_3$ ($T=295$ K); all values result from at least duplicate experiments, standard deviations are in brackets.

[a] Solute molar refraction index.[12]

[b] Negligible complexation.

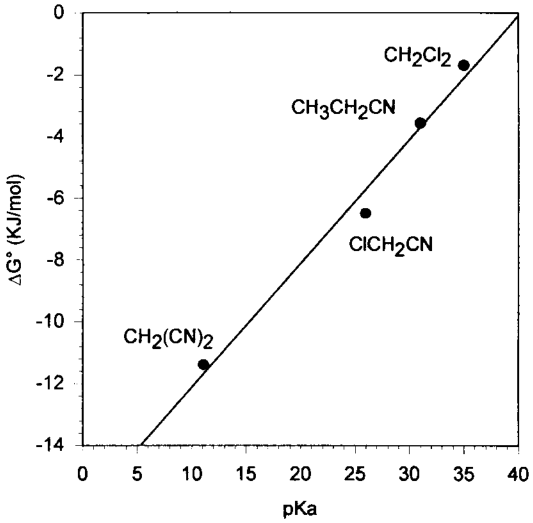

Figure 4. Correlation between ΔG^0 and pK_a of CH_2XY guests with host **3a** in $CDCl_3$.

Despite this steric effect, a good linear correlation between ΔG^0 and pK_a was observed considering all complexed guests except CH_2Br_2 and FCH_2CN ($m=0.58\pm0.06$, $C=-26\pm2$, $r^2=0.973$, see Fig. 5—continuous line). The deviation from linearity shown by these guests suggests that guest acidity cannot be considered as the sole factor responsible for the formation of the host–guest adducts. In fact, careful examination of the plotted data shows that only guests having very similar polarizability such as $ClCH_2CN$, CH_3CH_2CN and CH_2Cl_2 afford linear correlation ($m=0.67\pm0.02$, $C=-28.8\pm0.6$, $r^2=0.999$, see Fig. 5—dashed line), that, although not statistically significant, since determined considering only three experiments, strongly suggest that dispersive interactions can strongly affect the recognition phenomena. In fact, with guests having the more polarizable Br atom ($BrCH_2CN$, $BrCH_2Cl$ and CH_2Br_2), a stronger contribution of the dispersive interactions with the winged diametrical aromatic rings results in an higher association constant. On the contrary the lower polarizability of the fluorine atom of FCH_2CN consequently determines a lower value of the binding free energy (see Fig. 5).[11]

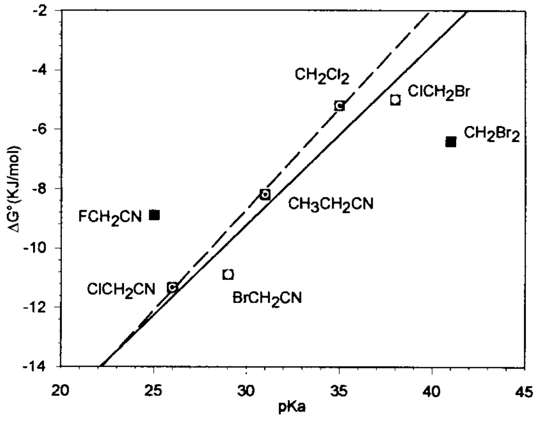

Figure 5. Plot of ΔG^0 vs. pK_a of CH_2XY guests with host **3a** in CCl_4.

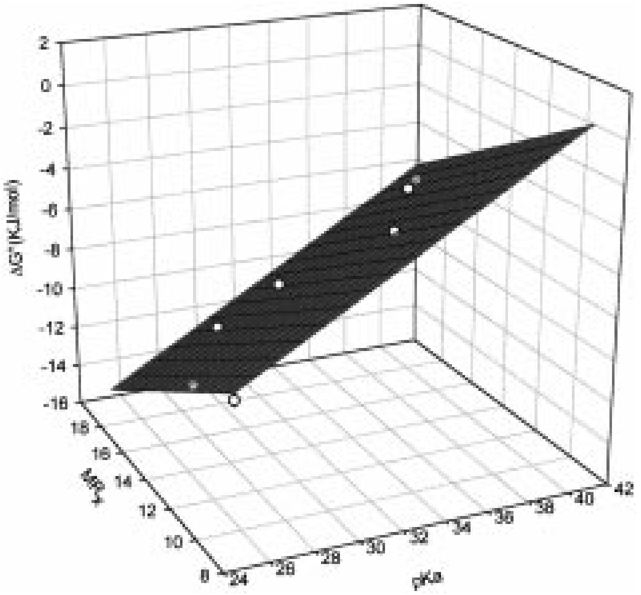

Figure 6. 3D Graphical representation of the multilinear correlation $\Delta G^0 = a \cdot pK_a + b \cdot MR_x + C$

These findings point out that the binding of this class of guests with host **3a** derive mainly from hydrogen bonding interactions of the acidic CH_2 groups with the diametrical 'pinched' aromatic rings, with a not negligible contribution of London forces of the X and Y groups with the diametrical *winged* aromatic rings. This was confirmed by applying a multilinear correlation: $\Delta G^0 = a pK_a + b MR_x + C$ (a=0.57±0.06, b=−0.6±0.1, and C=−18±1); which also takes into account the guest polarizability (Fig. 6). This data treatment shows a good correlation (r^2=0.961), of the ΔG^0 of binding with the pK_a and the solute molar refraction MR_x which is related to the guest polarizability.[12]

In conclusion, these results strongly support that in apolar solvents guests with acid methylene groups bound to substituents with low steric hindrance interact with the aromatic cavity via specific CH–π aromatic interactions but strong contributions of the London forces are present.

Unfortunately, as most of the CH_3Y guests are gases at room temperature, a similar approach to evaluate the parameters affecting the binding with these guests has strong drawbacks. However, it was verified that CH_3I, more polarizable than CH_3CN, is not complexed by **3a** in CCl_4. This result suggests that with these guests polarizability is not the main parameter which determines these host–guest interactions. Furthermore, entropy loss could strongly determine the binding process. In particular with CH_3CN the minor loss of mobility[13] in comparison with that verified with CH_2XY guests could explain the observed higher binding constants observed with CH_3Y guests.

Studies are in progress to obtain further information on the parameters affecting the stability of these complexes.

Table 5. Crystal data and experimental details for the inclusion compounds

	2a$\supset CH_3CN$	**2b**$\supset CH_3CN$
Formula	$C_{74}H_{102}N_7O_{15}Na \cdot CH_3CN$	$C_{74}H_{102}N_7O_{15}K \cdot CH_3CN$
Crystal system	Tetragonal	Tetragonal
Space group	*P*4/*ncc*	*P*4/*ncc*
T (K)	173	298
Cell parameters[a]		
a (Å)	16.722(5)	16.852(5)
c (Å)	28.837(5)	29.006(5)
V (Å^3)	8064(4)	8237(4)
Z	4	4
D_{calcd} (g cm^{-3})	1.148	1.137
F(000)	2992	3024
Molecular weight	1393.7	1409.81
Linear absorption coefficient (mm^{-1})	0.69	0.128
Diffractometer	Enraf Nonius CAD4	Bruker SMART
Radiation	CuK$_\alpha$(λ=1.54178 Å)	MoK$_\alpha$(λ=0.71073 Å)
Reflection measured	8027	43113
Index range	$-17 \leq h \leq 20$	$-19 \leq h \leq 20$
	$-11 \leq k \leq 20$	$-20 \leq k \leq 19$
	$-31 \leq l \leq 35$	$-25 \leq l \leq 34$
Unique data	3796 ($R_{int.}$=0.04)	3628 ($R_{int.}$=0.14)
Parameters, restraints	243,0	237,0
Observed reflection	2496 $F_o \geq 4\sigma(F_o)$	1224 $F_o \geq 4\sigma(F_o)$
Final R indices[b]	R_1=0.094	R_1=0.089
Goodness-of-fit	1.075	0.8
	wR_2=0.291	wR_2=0.277
Highest peak, deepest hole in final difference map (eÅ^{-3})	68, −0.30	0.42, −21

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 reflections found in a random search on the reciprocal space.

[b] $R_1 = \sum |F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}$; goodness-of-fit=$[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

3. Conclusions

This study confirms that in apolar solvents CH_3Y and CH_2XY guests show different binding modes, as previously observed in the solid state. In particular the acidity of the CH_2XY guests strongly affects the binding efficiency whereas modification of this parameter with the former guests gives the same association constants. With methylene containing guests, the polarizability of the X and Y groups strongly determines the binding process.

4. Experimental

4.1. NMR binding studies

Binding studies were carried out in $CDCl_3$ and/or CCl_4 solution using ^1H NMR spectroscopy (T=300 K; $[H_0]$=0.01 M and $[G_0]$=0.1 M). In all titration experiments an upfield Complexation Induced Shift (CIS) was observed for the guests signal and the ^1H NMR spectra showed time-averaged signals for the free and complexed species, therefore the binding constants (K_{as}) were calculated using methods already described,[14] having verified a 1:1 complex stochiometry, monitoring the CH_3 or CH_2 signal of the guests. 5,11,17,23-Tetrakis(1,1-dimethylethyl)-25,27-dihydroxy-26,28-di-*n*-propoxycalix[4]arene (**3a**) was synthesized according to literature procedures.[15]

4.2. Crystallography

The crystal data and the experimental details of the data collections and structures refinement for both the complexes are summarized in Table 5.

A single crystal of **2a**$\supset CH_3CN$ complex of c.a. 0.2×0.3×0.4 mm suitable for the X-ray analysis was mounted on a glass rod and protected from air contamination by a film of perfluoric oil and maintained at 173 K. The intensities were calculated from the analysis of the $\omega/2\theta$ diffraction profiles according to the Lehmann and Larsen method.[16] The unit cell parameters were obtained by least-squares fit of 30 $I(\theta\chi\phi)_{hkl}$ reflections in the range: $23° \leq \theta \leq 26°$. During the systematic data collection one standard reflection was monitored every 100, showed a intensity decay of 30%. The intensities were corrected for Lorentz and polarization effects but not for absorption. Data of **2b**$\supset CH_3CN$ complex were collected at room temperature on a Bruker SMART diffractometer equipped with graphite monochromated MoKα radiation source (λ=0.71073 Å) and a CCD detector.

The two structures were solved by direct methods using SIR92[17] the E-map of which revealed almost all the non-hydrogen atoms of the cationic complex including the guest CH_3CN molecule inside the cavity of the calix[4]arene basket. The rest of the structures were located by successive cycles of Fourier ΔF maps revealing, in both complexes, the picrate anion affected by a severe static disorder which was impossible to rationalize with different orintations with different occupancy factors. The structure refinements were carried out by full matrix least-squares on F^2 with SHELXL-97[18] using anisotropic atomic displacements for all non-hydrogen atoms. The hydrogen atoms were set in their calculated positions and refined riding on their corresponding parent atoms. Geometrical parameters were calculated by PARST97.[19] The plots of the molecules were obtained by ORTEP3 included in the WINGX suite.[20] All the calculations were carried out on the DEC Alpha 250 workstation at the Centro di Studio per la Strutturistica Diffrattometrica of C.N.R., Parma. CCDC reference numbers: 150943 (**2a**$\supset CH_3CN$) and 150944 (**2b**$\supset CH_3CN$).

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References

1. (a) Böhmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *32*, 713–745. (b) Pochini, A.; Ungaro, R. In *Comprehensive Supramolecular Chemistry*, Atwood, J. L., Davies, J. E. D., McNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 103–142. (c) Gutsche, C. D. In *Calixarenes Revisited—Monographs in Supramolecular Chemistry*, Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1998; Vol. 6.
2. Arduini, A.; McGregor, W. M.; Paganuzzi, D.; Pochini, A.; Secchi, A.; Ugozzoli, F.; Ungaro, R. *J. Chem. Soc. Perkin Trans. 2* **1996**, 839–846.
3. Smirnov, S.; Sidorov, V.; Pinkhassik, E.; Havlicek, J.; Stibor, I. *Supramol. Chem.* **1997**, *8*, 187–196.
4. (a) Nishio, M.; Umezawa, Y.; Hirota, M.; Takeuchi, Y. *Tetrahedron* **1995**, *51*, 8665–8701. (b) Umezawa, Y.; Tsuboyama, S.; Honda, K.; Uzawa, J.; Nishio, M. *Bull. Chem. Soc. Jpn* **1998**, *71*, 1207–1213. (c) Braga, D.; Grepioni, F.; Tedesco, E. *Organometallics* **1998**, *17*, 2669–2672. (d) Desiraju, R. G.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*, *IUCr Monographs on Crystallography*, Vol. 9; Oxford Science: New York, 1999. (e) Further information about CH–π interactions is available in the following web site: http://www.tim.hi-ho.ne.jp/dionisio/
5. Arduini, A.; Nachtigall, F. F.; Pochini, A.; Secchi, A.; Ugozzoli, F. *Supramol. Chem.* **2001** (in press).
6. Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.
7. Yoshimura, K.; Fukazawa, Y. *Tetrahedron Lett.* **1996**, *37*, 1435–1438.
8. Arena, G.; Contino, A.; Magrì, A.; Sciotto, D.; Arduini, A.; Pochini, A.; Secchi, A. *Supramol. Chem.* **2001** (in press).
9. Arduini, A.; Ghidini, E.; Pochini, A.; Ungaro, R.; Andreetti, G. D.; Calestani, G.; Ugozzoli, F. *J. Inclusion Phenom.* **1988**, *6*, 119–134.
10. Schneider, H.-J.; Mohammad-Ali, A. K. In *Comprehensive Supramolecular Chemistry*, Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 69–101 and references therein.
11. The pK_a value of FCH_2CN was estimated following the procedure reported in Gushurst, A. J.; Jorgensen, W. L. *J. Org. Chem.* **1986**, *51*, 3513–3522.

12. Abraham, M. H.; Whiting, G. S.; Doherty, R. M.; Shuely, W. J. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1451–1460.
13. Arduini, A.; Caciuffo, R.; Geremia, S.; Ferrero, C.; Ugozzoli, F.; Zontone, F. *Supramol. Chem.* **1998**, *10*, 125–132.
14. Fielding, L. *Tetrahedron* **2000**, *56*, 6156–6170.
15. Cobben, P. L. H. M.; Egberink, R. J. M.; Bomer, J. G.; Bergveld, P.; Verboom, W.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1992**, *114*, 10573–10582.
16. Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A* **1974**, *30*, 580–584.
17. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. SIR92. *J. Appl. Crystallogr.* **1994**, *27*, 435.
18. Sheldrick, G. M., *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, 1997; http://shelx.uni-ac.gwdg.de/shelx/index.html
19. Nardelli, M. PARST 97, Updated version of PARST 95. *J. Appl. Crystallogr.* **1995**, *28*, 659.
20. Farrugia, L. J. WinGx. *J. Appl. Crystallogr.* **1999**, *39*, 837–838.