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Calix[4]Arene Cavitands: A Solid State Study on the Interactions of their Aromatic Cavity with Neutral Organic Guests Characterised by Acid CH_3 or CH_2 Groups

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To gain information on CH-π aromatic interactions involved in the formation of host-guest adducts, the geometrical parameters which define the solid state structures of the complexes of calix[4]arenes in the *cone* conformation with guests having acid CH_3 or CH_2 groups have been studied. Most of the data have been obtained from the CH_3CN and CH_2Cl_2 calix[4]arene complexes retrieved from the literature. To understand the effect of the acidity on these parameters, *p*-cyclohexylcalix[4]arene-biscrown-3 ⊃ CH_3CN, *p-tert*-butylthiacalix[4]arene ⊃ CH_3CN, *p-tert*-butylthiacalix[4]arene ⊃ CH_3NO_2, 1,3-dipropoxy-*p-tert*-butylcalix[4]arene ⊃ $ClCH_2CN$ and 1,3-dipropoxy-*p-tert*-butylcalix[4]arene ⊃ $CH_2(CN)_2$ complexes were prepared, crystallised and investigated in the solid state. CH_3X guests are bound preferentially by hosts having a C_4 symmetry. The interaction is directional, but it is independent from the basicity of the host and acidity of the guest, indicating that classic hydrogen bond do not play a major role. On the contrary CH_2XY guests find the best matching with hosts having a C_{2v} symmetry, interacting specifically with two diametrical aromatic rings. These interactions are directional and show a correlation between the acidity of the guest and the CH-π aromatic distance, thus supporting a stronger contribution of "classic" hydrogen bond in these latter complexes. These results are in agreement with the hypothesis that CH-π aromatic interactions derive from the superimposition of different types of intermolecular forces, whose contribution depends on several factors as the nature of the interacting partners.

Keywords: Calixarenes, Molecular recognition, Host-guest chemistry, Inclusion compounds, CH-π interactions

INTRODUCTION

One of the most attractive features of calix[4]arenes is their cuplike structure, which was observed both in the solid state and in solution and from which this class of macrocycles derives the name "calixarenes".[1] The cavity defined by the *cone* conformer of this macrocycle was extensively employed as binding site for the recognition of neutral guests having complementary size.[1] Since the early studies, the selective recognition of aromatic guests (*e.g.* toluene,

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anisole) were extensively investigated in the solid state,[2] while no evidences exist of complex formation with these guests in apolar media. On the contrary, though more recently, several examples of complexes between calix[4]arene derivatives and non aromatic neutral guests (*e.g.* dichloromethane, acetonitrile) have been reported both in the solid state and in solution. In this context, from the data reported in the literature, it emerges that, in apolar media, stable *endo*-cavity complexes can be formed only when the calix[4]arene host is blocked in a rigid *cone* conformation and the guest possesses acidic CH groups.[3] In several cases specific CH-π interactions[4,5] between the CH groups of the guest and the electron-rich aromatic nuclei of the host have been hypothesised to stabilise the complexes formed.

A powerful tool to obtain new information on these interactions and in particular to understand how the co-operative action of the aromatic nuclei of the host affects the recognition process of these macrocycles toward neutral guests, is the careful examination of the structural parameters of its complexes in the solid state. Surprisingly, to the best of our knowledge, this approach has never been pursued so far.

Therefore a study to verify whether the distances correlate with the acidity of the CH donor group and to establish if these interactions are directional was undertaken.[6]

RESULTS

To compare a significant number of structures the data retrieved from the Cambridge Structural Database (CSD), from recent literature and those obtained from the X-ray crystal structure determination of specific complexes, prepared and crystallised in our laboratories, were employed.

Calix[4]arenes and resorcin[4]arenes,[1] being both similar in size and in shape were chosen as hosts. For comparison thiacalix[4]arenes,[7] with a similar shape but with a larger macrocyclic cavity, were also studied. In fact while the distance between two diametrical CH_2 bridges in calix[4]arenes is about 7.1 Å, in thiacalix[4]arenes the distance between two diametrical sulfur atoms is about 7.8 Å. Only *cone* conformers of these hosts were analysed.

The initial choice of the guests was based on the presence in the CSD of a relevant number of calixarene structures in which, due to the use of specific solvents for crystallisation, such as acetonitrile and dichloromethane, a fortuitous inclusion of one solvent molecule into the aromatic cavity of the receptor was obtained. Thus our attention was focused on these two guests which were chosen as model for organic species having acid CH_3 or CH_2 groups. A preliminary assumption of this study was that the distance of the CH groups of the guest from the aromatic nuclei of the host cannot be a cut-off value for hydrogen bond interaction. Therefore we have also studied the effects on the complex structure of the acidity of the guest. Thus, specific complexes with acetonitrile ($pKa_{DMSO} = 31.3$[8]), nitromethane ($pKa_{DMSO} = 17.2$[8]), chloroacetonitrile ($pKa_{DMSO} = 26$)[9] and malononitrile ($pKa_{DMSO} = 11.1$)[8] were prepared in our laboratories and studied in comparison with those with acetonitrile and dichloromethane ($pKa_{DMSO} = 35$[9]) found in the CSD.

Moving from our previous study on the X-ray crystal structure determination of the complex between *p*-cyclohexylcalix[4]arene-biscrown-3 and nitromethane,[3c](Figure 1b) the corresponding complex with acetonitrile was prepared and characterized in the solid state (Figure 1a). In order to study these effects with hosts having wider cavity, the complexes of *p*-*tert*-butylthiacalix[4]arene with acetonitrile and with nitromethane were prepared and characterised by X-ray diffraction (Figures 1c and 1d).

To compare the solid structures of calix[4]arene complexes with guests having methylene groups with different acidity the first choice was based on 1,3-dipropoxy-*p*-*tert*-butyl-

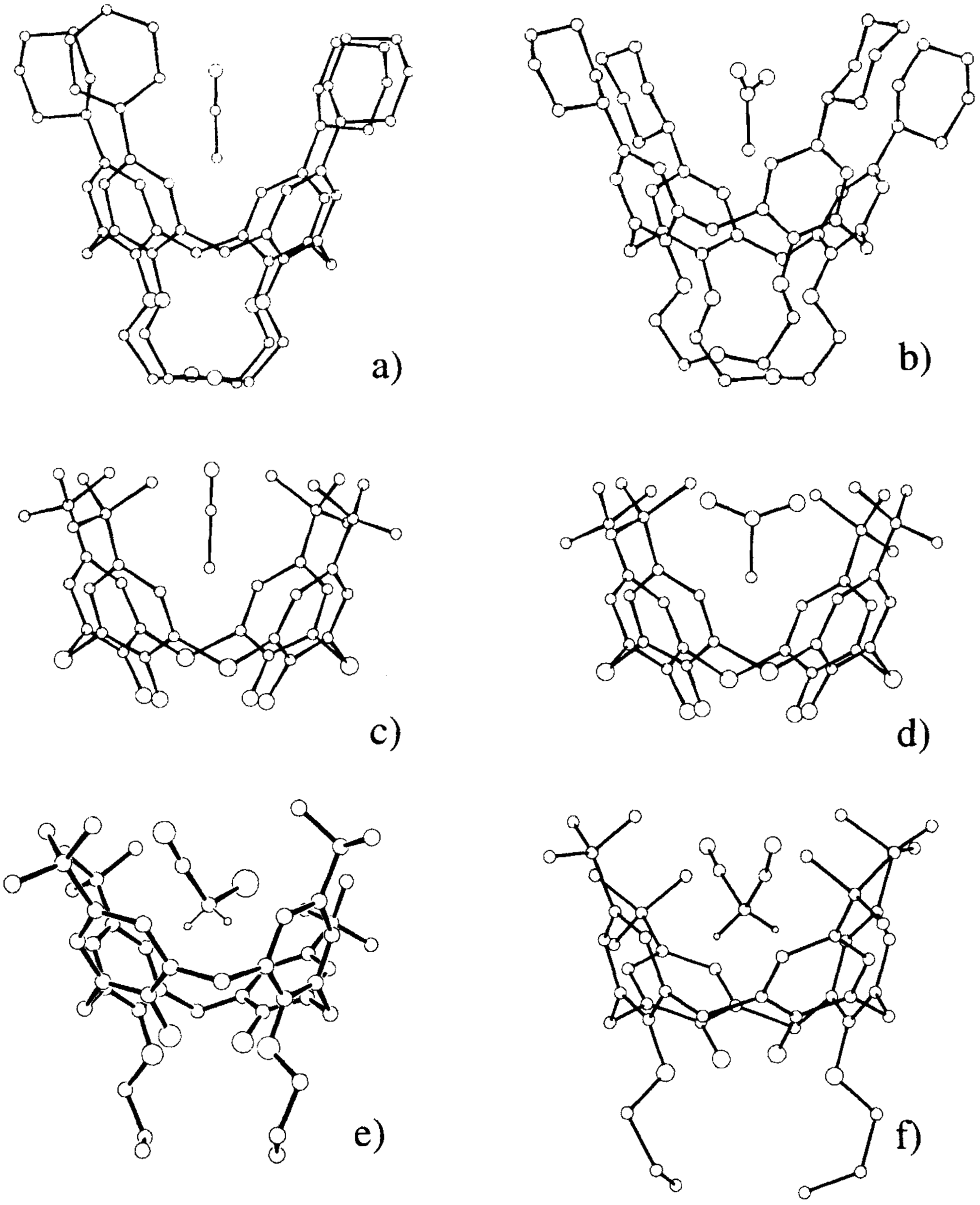


FIGURE 1 X-ray crystal structures of: a) acetonitrile $\subset$ *p*-cyclohexylcalix[4]arene-biscrown-3; b) nitromethane $\subset$ *p*-cyclohexylcalix[4]arene-biscrown-3[3c]; c) acetonitrile $\subset$ *p-tert*-butylthiacalix[4]arene; d) nitromethane $\subset$ *p-tert*-butylthiacalix[4]arene; e) chloroacetonitrile $\subset$ *p-tert*-butyl-1,3-dipropoxycalix[4]arene; f) malononitrile $\subset$ *p-tert*-butyl-1,3-dipropoxycalix[4]arene

calix[4]arene as host and dichloromethane and malononitrile as guests. The latter was prepared and its solid state structure determined (Figure 1f); on the contrary the complex with dichloromethane was prepared but it was not stable thus preventing its crystal structure analysis. Therefore the more acid chloroacetonitrile was chosen.[9] Using this guest it was possible to prepare the complex and to determine its crystal structure (Figure 1e).

Geometrical descriptors for hosts and neutral guests

In order to give an insight into these supramolecular interactions, suitable geometrical descriptors, which define the hosts geometry and the orientation of the guests in the complexes, have been selected (Figure 2).

The shape of the host cavity, and consequently its symmetry, was defined through the angle δ[1a] between each benzene ring and the **R** plane defined by the bridging methylene carbons of the calixarene or of the sulfur atoms of thiacalixarene (Figure 2a). The position of the guests, having the CH_3 group into the cavity of the host was obtained by: i) the distance **DC** between the methyl carbon and the centroids of the aromatic rings of the calixarenes, ii) the α angle defined by the line which links the carbon atom of the guest to the centroids of the aromatic rings and the normal to the plane of the aromatic rings themselves (Figure 2b), which indicates how the carbon atom is displaced from the normal to the centre of the aromatic rings of the host, and iii) the height **h** of the guest in the cavity, that is, the distance of the methyl carbon atom from the **R** plane (Figure 2a).

Beside these, other geometrical descriptors to define the orientation in the cavity of the guest were chosen. For acetonitrile and nitromethane the angle β between the normal to the **R** plane and a vector defined by the CH_3-X(C,N) moiety of the guest was considered (Figure 2a).

In addition, for CH_2XY guests, besides the previously reported geometrical parameters δ, **h** and **DC** (Figure 2c, d), being defined the position of hydrogen atoms, the trend of new parameters **DH** (distance between the hydrogen atoms and the centroid of the nearest aromatic ring), and σ (angle between CH and the line connecting hydrogen atoms to the centroid of the closest aromatic ring) was studied (Figure 2d). For CH_2XY guests three other angles are necessary: γ and η, which define the angles formed by the planes containing XCY and HCH moieties with the **R** plane respectively (Figure 2e, f), and ε which defines the angle between the plane XCY and a line joining two distal C(1) carbons of calixarene (Figure 2g). The orientation into the aromatic cavity of the NO_2 group into nitromethane complexes was defined with a similar angle ε.

In Figure 3 are reported the structures of the hosts[3c,10–25] able to bind acetonitrile and in Table I and II are presented the above mentioned geometrical data of these host-guest complexes. In these tables the data of the complexes of *p*-cyclohexylcalix[4]arene-biscrown-3 and *p*-*tert*-butylthiacalix[4]arene with nitromethane are also reported. The final crystallographic **R** factors were also reported for each complex to provide a test for the reliability of the reported geometrical parameters.

The structures of the hosts[26–39] able to include dichloromethane, chloroacetonitrile and malononitrile are presented in Figure 4. Tables III–IV report the geometrical data of these complexes

DISCUSSION

Complexes with acetonitrile and nitromethane

A critical examination of the structures of the hosts found in the CSD reveals interesting correlation with the results obtained in apolar organic solvents. In fact, the unsubstituted *p*-*tert*-butylcalix[4]arene (**9**), the metal complexes of tetrakis-N,N-diethylacetamide-*p*-*tert*-butylcalix[4]arene (**6–8**) and 1,3-dialkoxycalix[4]arenes (**4, 11, 12, 16**) which are hosts able to bind these guests in apolar solvents, do form stable complexes also in the solid state. Nevertheless, as observed *e.g.* in the solid state complexes with aromatic guests, inclusion compounds between the tetraalkoxycalix[4]arenes (hosts **1, 18** and **19**) and acetonitrile, which are not stable in apolar media, were also obtained.

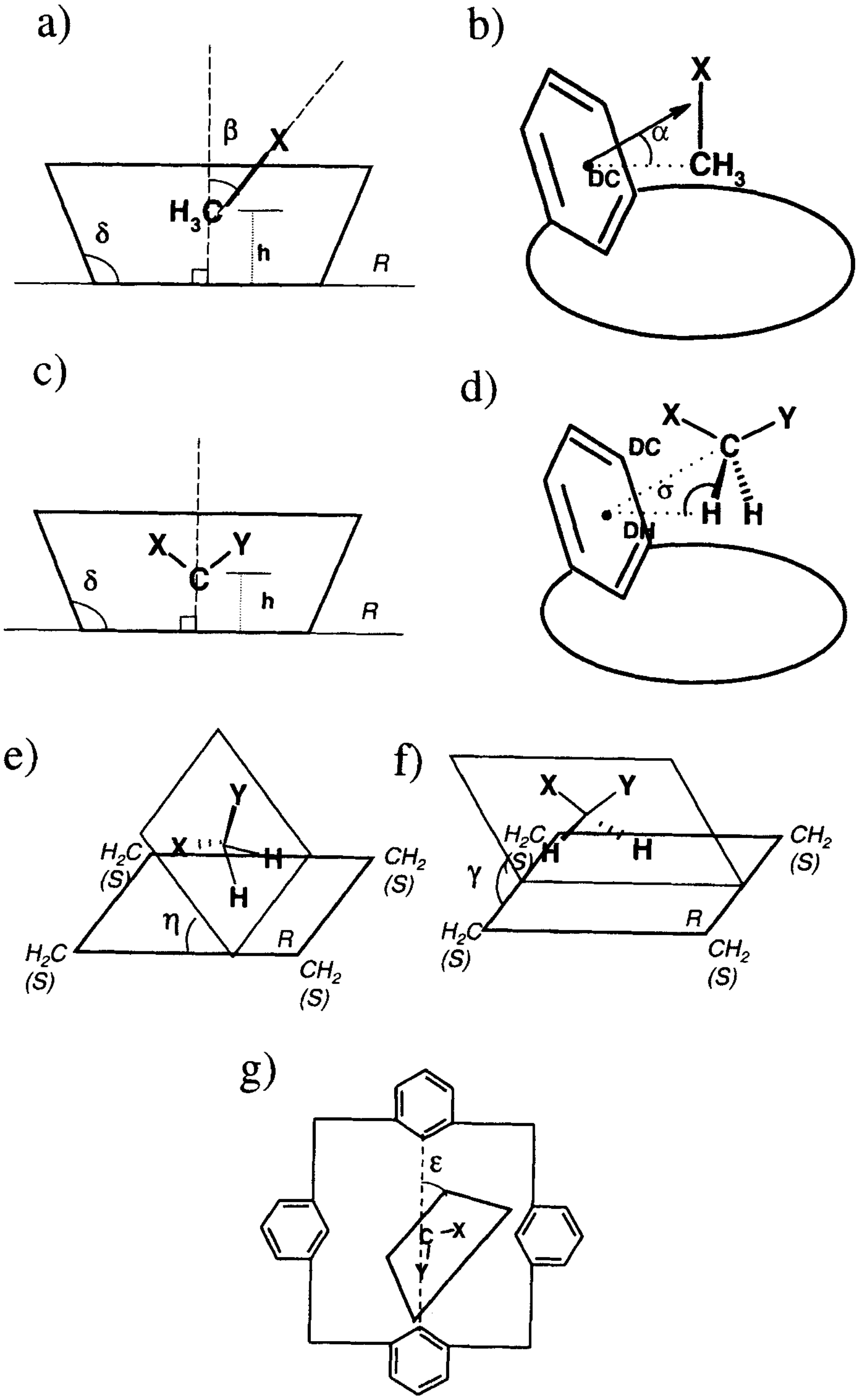


FIGURE 2 Geometrical descriptors of host-guest complexes

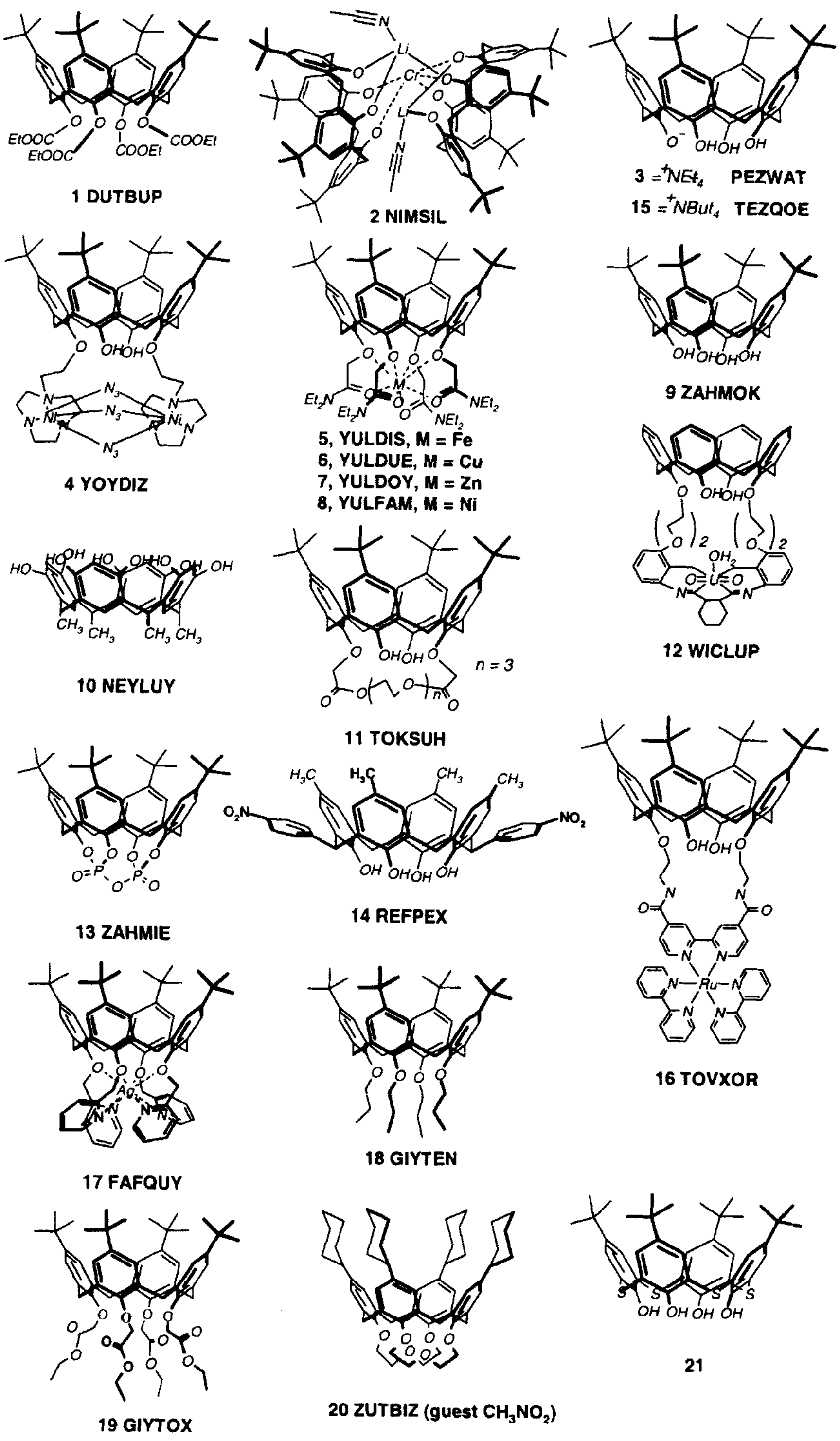
TABLE I Geometrical parameters of the acetonitrile ⊂ calix[4]arenes complexes (unless otherwise specified).[3c,10–25]

Hosts	*CSD Refcode*	*Ref.*	*R*	δ_1 (°)	δ_2 (°)	δ_3 (°)	δ_4 (°)	$\Sigma\delta_{1-4}$ (Å)	β (°)	*h* (Å)
1	DUTBUP	10	0.0560	114.581	114.581	114.581	114.581	458.324	0.000	2.603
2	NIMSIL	11	0.0873	118.687	117.752	117.475	124.933	478.847	27.882	2.585
3	PEZWAT	12	0.0640	122.376	123.093	120.282	119.599	485.350	0.374	2.531
3	PEZWAT	12	0.0640	118.062	120.647	118.062	120.647	477.418	0.000	2.689
4	YOYDIZ	13	0.0870	116.041	123.458	118.831	118.867	477.197	6.970	2.699
5	YULDIS	14	0.0810	114.695	116.386	116.714	115.081	462.876	5.995	2.756
6	YULDUE	14	0.0840	113.345	115.293	116.125	114.633	459.396	8.176	2.701
7	YULDOY	14	0.0796	113.831	116.203	115.937	116.027	461.998	6.275	2.730
8	YULFAM	14	0.0893	118.807	117.055	110.046	117.544	463.452	13.330	2.786
9	ZAHMOK	15	0.0520	123.046	123.046	123.046	123.046	492.184	0.000	2.714
10	NEYLUY	16	0.0362	137.181	111.878	137.181	115.204	501.444	25.900	2.837
11	TOKSUH	17	0.0880	112.020	125.580	112.020	125.580	475.200	0.000	2.608
12	WICLUP	18	0.0550	102.374	132.588	110.900	142.397	488.259	22.648	2.598
13	ZAHMIE	19	0.0810	140.618	113.989	150.258	110.633	515.498	49.099	2.840
14	REFPEX	20	0.0540	113.366	119.997	118.351	128.363	480.077	37.696	2.741
15	TEZQOE	21	0.1200	130.186	112.956	126.247	124.129	493.518	8.560	2.604
15	TEZQOE	21	0.1200	130.028	120.836	120.040	120.902	491.806	6.712	2.746
16	TOVXOR	22	0.1032	115.292	122.441	110.224	128.915	476.872	33.546	2.740
16	TOVXOR	22	0.1032	118.580	127.141	112.226	116.975	474.922	31.672	2.590
17	FAFQUY	23	0.0570	116.555	116.555	116.555	116.555	466.220	0.000	2.760
18	GIYTEN	24	0.0530	113.499	116.627	115.778	113.721	459.625	5.237	2.701
19	GIYTOX	25	0.1059	125.167	108.299	114.872	114.029	462.367	37.038	2.647
20			0.0594	115.150	116.911	116.446	115.760	464.267	14.371	2.747
20[a]	ZUTBIZ	3c	0.0950	118.339	115.170	118.420	117.283	469.212	2.087	2.742
21			0.1030	118.056	118.056	118.056	118.056	472.224	0.000	2.556
21[a]			0.0961	119.021	119.021	119.021	119.021	476.084	0.000	2.518

a. Nitromethane as guest.

Very interesting is the presence in three cases (hosts **3, 15** and **16**) of two different complexes in the asymmetric units. By these host-guest structures it is possible to point out that in these particular cases, the crystal packing can affect the structure of the adducts, although only a slight difference between them was observed. On these base we hypothesised that the structure of the other complexes, especially when the small size of the guest results in its deep engulfing in the host cavity, is not strongly affected by the packing of the crystal.

A simple analysis of the δ angles reveals a preferred C_4 or nearly C_4 symmetry of these hosts, whereas only few of these show a C_2 symmetry (Table I).



1 DUTBUP

2 NIMSIL

3 = $^{+}NEt_4$ PEZWAT
15 = $^{+}NBut_4$ TEZQOE

4 YOYDIZ

5, YULDIS, M = Fe
6, YULDUE, M = Cu
7, YULDOY, M = Zn
8, YULFAM, M = Ni

9 ZAHMOK

10 NEYLUY

11 TOKSUH

12 WICLUP

13 ZAHMIE

14 REFPEX

16 TOVXOR

17 FAFQUY

18 GIYTEN

19 GIYTOX

20 ZUTBIZ (guest CH_3NO_2)

21

FIGURE 3 Hosts structures of acetonitrile ⊂ calix[4]arene complexes (unless otherwise specified)

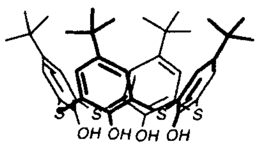
TABLE II Geometrical parameters of the guest in acetonitrile ⊂ calix[4]arenes complexes (unless otherwise specified).[3c,10–25]

Hosts	*CSD Refcode*	*DC_1 (Å)*	*DC_2 (Å)*	*DC_3 (Å)*	*DC_4 (Å)*	*ΣDC_{1-4} (Å)*	*α_1 (°)*	*α_2 (°)*	*α_3 (°)*	*α_4 (°)*	*$\Sigma\alpha_{1-4}$ (°)*
1	DUTBUP	3.570	3.570	3.570	3.570	14.280	2.147	2.147	2.147	2.147	8.588
2	NIMSIL	3.609	3.574	3.577	3.698	14.458	5.101	4.985	4.980	11.7391	26.8051
3	PEZWAT	3.567	3.567	3.567	3.567	14.268	9.521	9.70	8.654	8.469	36.344
3	PEZWAT	3.586	3.628	3.586	3.628	14.428	4.629	6.407	4.629	6.408	22.073
4	YOYDIZ	3.574	3.599	3.634	3.622	14.429	1.447	8.278	4.070	4.948	18.743
5	YULDIS	3.615	3.596	3.556	3.581	14.348	0.363	1.394	1.306	1.117	4.18
6	YULDUE	3.566	3.570	3.497	3.565	14.198	1.566	0.718	0.906	1.324	4.514
7	YULDOY	3.586	3.645	3.581	3.546	14.358	0.747	1.891	0.658	0.803	4.099
8	YULFAM	3.631	3.558	3.664	3.595	14.448	3.199	1.822	4.062	3.398	12.481
9	ZAHMOK	3.717	3.717	3.717	3.717	14.868	8.502	8.502	8.502	8.502	34.008
10	NEYLUY	4.094	3.499	4.094	3.499	15.186	20.300	3.139	20.300	0.758	44.497
11	TOKSUH	3.484	3.731	3.484	3.731	14.430	0.750	12.383	0.750	12.383	26.266
12	WICLUP	3.368	3.977	3.343	3.903	14.591	8.879	19.622	3.654	27.590	59.745
13	ZAHMIE	4.182	3.443	4.344	3.454	15.423	24.530	4.231	32.358	6.680	67.799
14	REFPEX	3.526	3.802	3.530	3.802	14.660	1.128	6.232	7.456	13.629	28.445
15	TEZQOE	3.835	3.572	3.757	3.544	14.708	16.355	2.612	13.431	10.832	43.23
15	TEZQOE	3.880	3.630	3.761	3.689	14.960	13.704	7.260	4.776	5.754	31.494
16	TOVXOR	3.524	3.738	3.607	3.781	14.650	4.850	8.400	3.422	14.132	30.804
16	TOVXOR	3.582	3.659	3.580	3.526	14.347	5.334	14.687	0.832	4.182	25.035
17	FAFQUY	3.667	3.667	3.667	3.667	14.668	1.495	1.495	1.495	1.495	5.980
18	GIYTEN	3.590	3.625	3.593	3.611	14.419	0.790	3.389	3.292	0.805	8.276
19	GIYTOX	3.465	3.684	3.593	3.716	14.458	11.581	4.567	2.235	4.130	22.513
20		3.598	3.615	3.649	3.655	14.517	2.211	1.301	1.432	4.123	9.067
20[ab]	ZUTBIZ	3.699	3.646	3.720	3.614	14.679	4.348	2.564	4.754	2.501	14.167
21		3.649	3.649	3.649	3.649	14.596	9.575	9.575	9.575	9.575	38.300
21[ac]		3.648	3.648	3.648	3.648	14.592	11.179	11.116	11.179	11.116	44.59

a. Nitromethane as guest.
b. $\varepsilon = 38.568$ (deg.).
c. $\varepsilon = 45.000$ (deg.).

To study the host-guest interactions the first parameter taken into account were the distances between the guest methyl carbon atom and the centroids of the host aromatic rings (**DC**). Only few of these distances are over the sum of the van der Waals radii (*ca.* 3.8 Å).[4]

Starting from the preferred C_4 symmetry of the hosts and moving from the hypothesis that the distances are strictly related with the intermolecular forces, to take into account the co-operative effect exerted by the four aromatic nuclei present in the receptor site, the global



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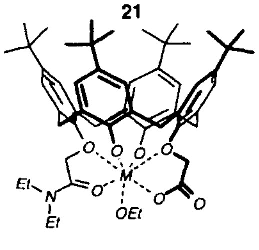
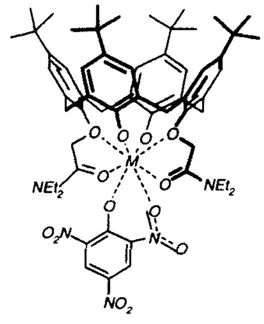
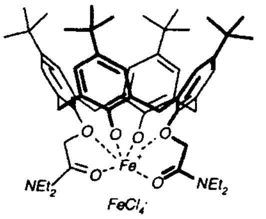


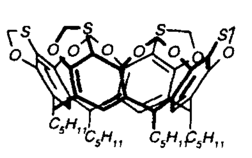
24, TARXOZ M= Eu
33, TARZUF M= Sm



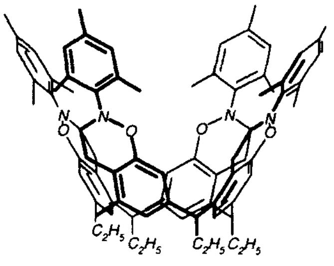
26 ZIBGUM ; M= Tm
28 ZUFNAF; M = Yb
29 ZUVNEY ; M = Lu
30 ZUVNEK10 ; M = Er



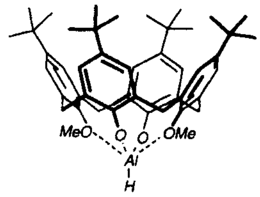
34 TOBPIJ



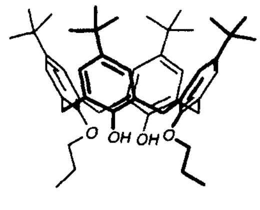
37 YOCPUB



22 NOPHEF



25 TOFYES



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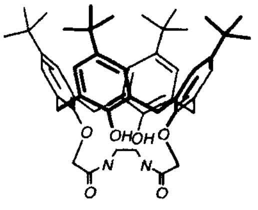

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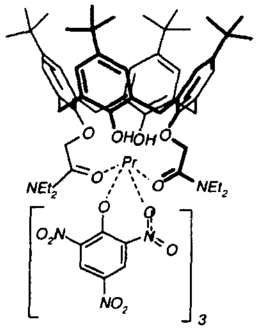
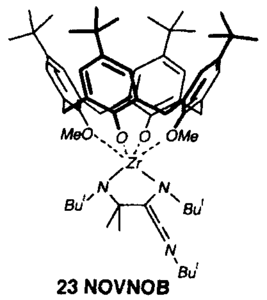
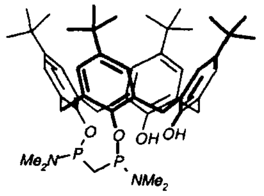


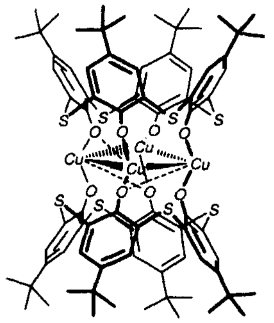
38 ZIBHEX



23 NOVNOB



27 ZIDNUV



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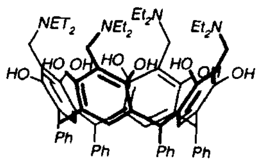

36 YEBFAM

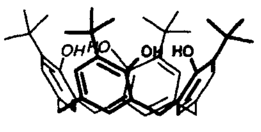

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FIGURE 4 Hosts structures of dichloromethane ⊂ calix[4]arenes complexes (unless otherwise specified) interaction of the methyl group with the aromatic cavity was evaluated by the sum of $DC_1 + DC_2 + DC_3 + DC_4$ (ΣDC_{1-4}). From these data the lowest values of ΣDC_{1-4} were observed with **6** and **1** (14.198 and 14.280 Å), both having C_4 and nearly C_4 symmetry, whereas **10** and **13**, both with a C_2 symmetry, experience the highest values (15.186 and 15.423 Å).

The presence among these hosts of calixarenes bearing on the aromatic rings groups with different electron donating ability like the monoanion **3** and **15** or the tetraethylcarbonate **1** can afford useful information on the importance of the basicity of these rings on the recognition process in the solid state. The monoanions **3** and **15**, show a lower ΣDC_{1-4} (respectively for the presence of two different complexes in the two crystal structures 14.268 or 14.428 Å and 14.708 or 14.960 Å) than the corresponding neutral guest **9** (14.868 Å) suggesting a dependence of these interactions on the aromatic ring basicity. However, by substituting the four OH groups of host **9** with four electron withdrawing ethylcarbonate groups, the host **1** which shows one of the lowest ΣDC_{1-4} values (14.280 Å) was obtained. These results indicate that the basicity of the aromatic rings whose contribution to the stability of the complexes could be intuitively predicted does not seems to play an important role.

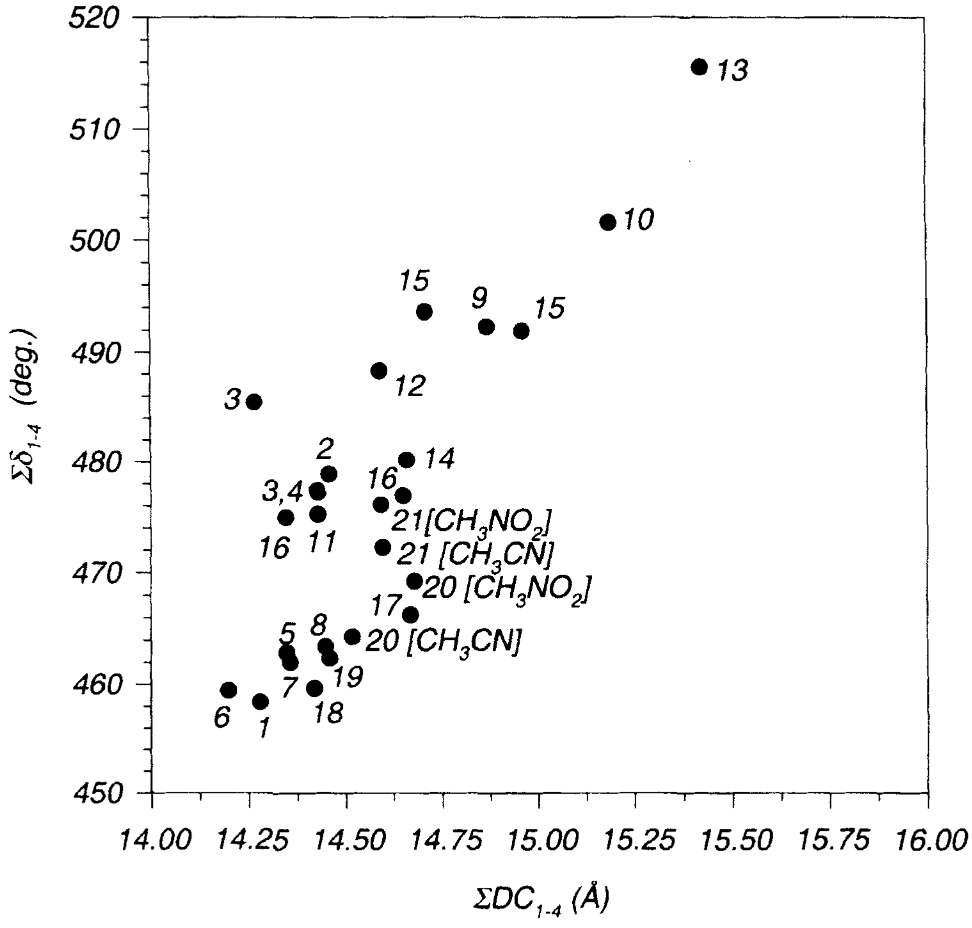

FIGURE 5 Correlation between ΣDC_{1-4} and $\Sigma\delta_{1-4}$ in acetonitrile ⊂ calix[4]arene complexes (unless otherwise specified)

TABLE III Geometrical parameters of the dichloromethane ⊂ calix[4]arenes complexes (unless otherwise specified).[26–39]

Hosts	*CSD* Refcode	*Ref*	*R*	δ_1 (°)	δ_2 (°)	δ_3 (°)	δ_4 (°)	$\delta_1+\delta_3$ (°)	ε (°)	η (°)	γ (°)	*h* (*Å*)
22	NOPHEF	26	0.1033	111.778	143.355	119.715	137.523	231.493	14.170	88.611	84.685	2.896
23	NOVNOB	27	0.0700	110.788	138.666	108.506	141.876	219.294	9.734	87.937	87.615	2.858
24	TARXOZ	28	0.0826	109.252	132.580	111.834	134.854	221.086	2.110	89.229	87.689	2.838
25	TOFYES	29	0.0770	112.765	144.189	111.778	141.524	224.543	5.325	87.456	87.334	2.968
26	ZIBGUM	30	0.0657	108.153	134.573	109.455	146.929	217.608	2.227	88.273	89.115	2.825
27	ZIDNUV	31	0.0800	116.811	134.701	109.872	125.121	226.683	7.247	84.227	85.122	2.936
28	ZUVNAF	32	0.0849	107.819	134.356	110.491	146.307	218.310	3.944	88.583	86.842	2.778
29	ZUVNEJ	32	0.0932	108.621	146.003	110.472	133.816	219.093	2.413	87.415	89.183	2.832
30	ZUVNEK10	33	0.0572	108.230	146.552	109.989	134.589	218.219	2.891	87.913	87.944	2.817
31[a]			0.1317	112.639	139.251	110.135	138.251	222.774	2.507	84.691	83.389	2.716
31[b]			0.0471	110.260	132.832	109.685	135.311	219.945	5.036	84.524	88.983	2.857
32		34	0.0460	108.900	139.080	109.820	138.880	218.720	3.962	89.64	89.18	2.960
32		34	0.0460	111.050	133.420	111.130	137.290	222.180	0.732	89.58	89.66	2.980
33	TARXUF	28	0.0764	110.786	136.307	110.262	133.527	221.048	13.406	48.472	76.867	3.199
34	TOBPIJ	33	0.0879	114.281	127.712	111.637	135.649	225.918	2.236	[c]	88.981	3.274
35	YAPTAK	35	0.0770	115.983	131.114	109.708	129.582	225.691	7.936	66.609	84.28	3.165
36	YEBFAM	36	0.0850	127.353	132.010	129.667	124.420	257.020	16.647	75.802	75.351	3.007
37	YOCPUB	37	0.0720	128.184	136.967	127.109	131.017	255.293	29.413	82.128	61.418	3.020
38	ZIBHEX	28	0.1235	112.047	125.576	118.584	122.853	230.631	0.249	46.856	77.622	3.295
39		38	0.0761	126.534	126.534	126.534	126.534	253.068	44.380	[c]	90	3.003
21[d]		39	0.1078	119.407	119.407	119.407	119.407	238.814	44.380	90	90	3.582

a. Malononitrile as guest.
b. Cloroacetonitrile as guest.
c. Hydrogen atoms not defined.
d. The data were not retrievable from CSD, therefore they were calculated on the structural data obtained in our labs.

The effect of the acidity of the guest on these intermolecular interactions was studied from the comparison of the ΣDC_{1-4} of two guests having very different acidity like acetonitrile and nitromethane,[8] in the complexes with two different hosts *i.e.* *p*-cyclohexylcalix[4]arene-bis-crown-3 derivative (**20**) and *p*-*tert*-butylthiacalix[4]arene (**21**). In all case similar distances with the two guests were observed and in particular acetonitrile gives with **20** the lowest ΣDC_{1-4} suggesting that acidity of the guest is not very important in determining the intermolecular distances.

An interesting correlation of the ΣDC_{1-4} with the $\Sigma\delta_{1-4}$ could be found. In fact (Figure 5) complexes **1** and **6** where ΣDC_{1-4} is the lowest, show also the lowest $\Sigma\delta_{1-4}$, whereas **10** and **13** where ΣDC_{1-4} is the highest, experience the highest $\Sigma\delta_{1-4}$. Moreover in the majority of the complexes a correlation between ΣDC_{1-4} and $\Sigma\delta_{1-4}$ was observed suggesting that the shape of the aromatic cavity is very important in determining

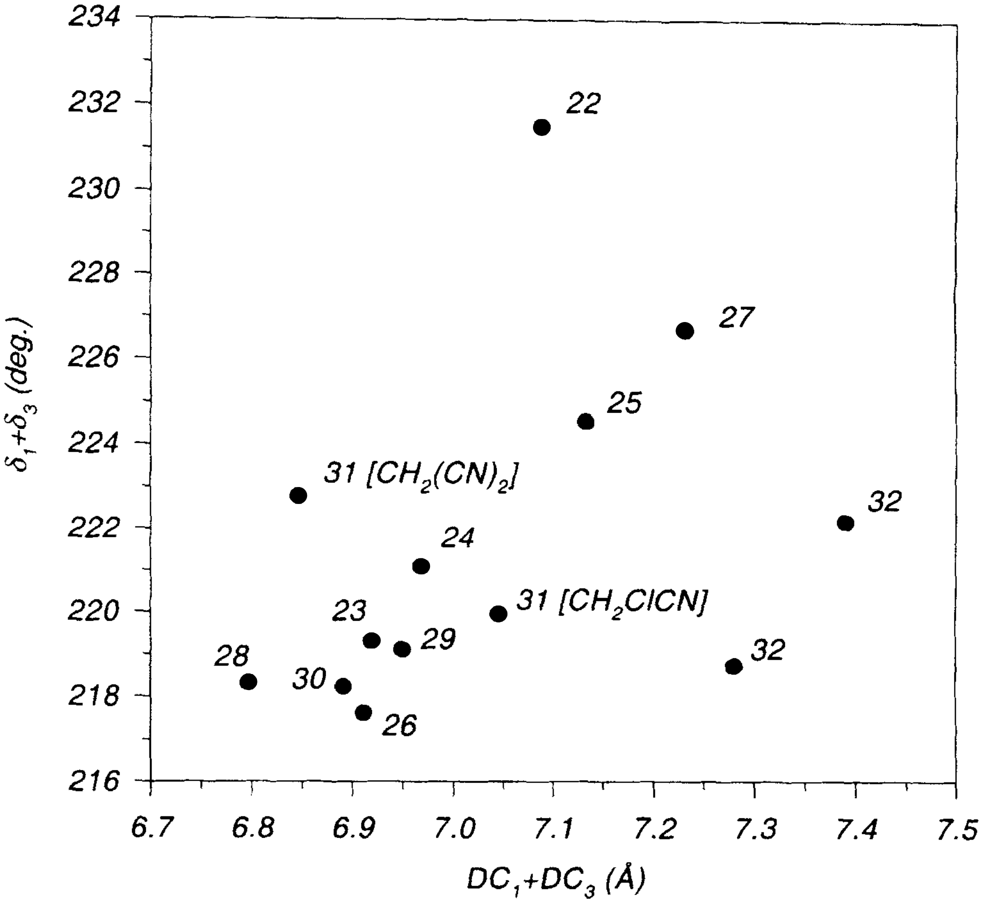

FIGURE 6 Correlation between ΣDC_{1+3} and $\Sigma\delta_{1+3}$ in dichloromethane ⊂ calix[4]arene complexes (unless otherwise specified)

the host-guest interactions. However some complexes (all the 1,3-dialkoxy calixarenes derivatives **4**, **11**, **12** and **16** and all the salified calixarenes derivatives **2**, **3** and **15**) show shorter distances in comparison with the other calixarene hosts. These data suggest that these structural parameters partially determine the complexation energy.

Since directionality can afford useful information on these intermolecular interactions, we have analysed such parameter in the host-guest interactions.[4,6] From Table II it is possible to point out that hosts having C_4 symmetry show α angles in the range 0–10° confirming a good directionality of these interactions with the methyl carbon of the guest placed over the centroids of the aromatic rings of the cavity. It thus appears that the guest methyl carbon atom finds its energy minimum when it is localised near the level of the C(4) aromatic carbon plane of the host, whereas with the thiacalix[4]arenes, which have larger cavity, at an intermediate position between the C(3) and C(4) planes (Figure 1).

As expected a good correlation between the $\Sigma\delta_{1-4}$ and $\Sigma\alpha_{1-4}$ was observed. Moreover with calix[4]arenes, the lowest distances **DC** and angles α values were found when the δ angles of the aromatic rings range between 114–115°. This suggests that the strongest interactions take place when the α angles approaches 0°, that is the CH bond of the guest is aligned along the perpendicular to the centroid of the aromatic ring of the host. When the angle β is 0°, that is the guest is perpendicular to the methylene (or sulfur) **R** plane of the calix, the CH bond of the guest can be perpendicular to the aromatic ring when δ angle of the host has the same value of sp^3 X-C-H angle, that is about 109°.

Complexes with dichloromethane, chloroacetonitrile and malononitrile

A critical examination of the data reported for these complexes (Table III and IV) and in particular of ε angles, which defines the orientation of the guest inside the cavity, reveals that only two hosts, **39** and **21**, have an ε angle near 45° whereas for all the other hosts it approaches 0°. These data suggest a strong preference of these guests for a position in the cavity in which their XCY plane is parallel to two diametrical aromatic rings and their two hydrogen atoms point toward these aromatic nuclei. On the base of the ΣDC_{1-4} these hosts can be divided in two series: the first one with values ranging from 14.884 up to 15.512 Å (hosts **22–30**), and the second from 15.812 to 16.625 Å (hosts **33–38**). In order to search for possible specific hydrogen bonding with the aromatic rings only hosts **22–30** found in the CSD, 1,3-dipropoxy-*p*-*tert*-butylcalix[4]arene (**31**), employed in our laboratory for the preparation of the complexes with chloroacetonitrile and malononitrile, and $CH_2Cl_2 \subset$ *p*-*tert*-butylthiacalix[4]arene (as copper salt, host **32**), found in the recent literature,[34] were studied in detail. Moreover in the complexes of dichloromethane with hosts **22–30** the γ and η angle values are almost 90°, that is the guest enters in the cavity with the CH_2 and no significant bending of the guest was observed, whereas, with hosts **33–38** generally a bent positions of the guest were observed.

As expected the δ angle values of these hosts reveal a preferred C_2 symmetry due to a *pinched cone* conformation of the calix which thus has an elliptical cavity, complementary to the symmetry of the guest. More interesting is the observation that the hosts found in the CSD, which show the shortest distances with dichloromethane, are generally *p*-*tert*-butylcalix[4]arenes having two anionic distal phenolic rings (**23, 24, 25, 26, 28, 30**) whereas only two hosts are unsalified (**22, 27**). It interestingly also merges that the aromatic rings which interact with the acid CH_2 group of the guest are not the anionic ones but the dialkoxy substituted aromatic rings. As verified with acetonitrile, the geometric factors seem to overcome the electronic ones, in fact the less basic alkoxy substituted aromatic rings which are almost perpendicular to the methylene plane of the calix are those which interact with the guest CH groups. In addition the other two rings interact with the chlorine atoms *via* van der Waals interactions thus further stabilising the host-guest complex. An increase of the polarizability of the anionic aromatic ring probably maximises the London dispersion forces. An interesting modification of the binding mode was observed with *p*-*tert*-butylthiacalix[4]arene (**21**). This host, which has a C_4 symmetry, includes dichloromethane through one chlorine atom which enters into the cavity. On the contrary, its copper (**II**) complex (**32**), probably as consequence of the new C_2 symmetry, and of its anionic structure binds the guest through CH_2-π aromatic interactions. On this base also this host-guest complex was studied into detail.[34] As reported for guests having acid CH_3 group the correlation between the δ angles of the host and the distances **DC** between the carbon atom of the guest and the centroids of the aromatic rings was studied. On the base of the geometry of the complexes only the two nearest diametrical aromatic rings, which interact with the hydrogen atoms of the guest, were considered. Being defined the position of the hydrogen atoms of the guest in most of the complexes, the distances **DH** between these atoms and the two nearest diametrical aromatic rings were also studied.

TABLE IV Geometrical parameters of the dichloromethane ⊂ calix[4]arenes complexes (unless otherwise specified).[26–39]

Hosts	*CSD Refcode*	DC_1 (Å)	DC_2 (Å)	DC_3 (Å)	DC_4 (Å)	DC_1+DC_3 (Å)	ΣDC_{1-4} (Å)	DH_1 (Å)	DH_3 (Å)	$DH_1+\Delta H_3$ (Å)	σ_1 (°)	σ_3 (°)
22	NOPHEF	3.583	3.975	3.505	4.293	7.088	15.356	2.548	2.705	5.253	167.358	157.116
23	NOVNOB	3.398	4.105	3.521	4.105	6.919	15.129	2.568	2.451	5.019	158.632	159.287
24	TARXOZ	3.547	3.901	3.421	4.015	6.968	14.884	2.611	2.462	5.073	160.429	167.752
25	TOFYES	3.574	4.145	3.559	4.234	7.133	15.512	2.611	2.484	5.095	159.538	169.888
26	ZIBGUM	3.459	4.136	3.452	4.075	6.911	15.122	2.507	2.508	5.015	162.110	162.792
27	ZIDNUV	3.614	3.815	3.618	4.183	7.232	15.230	2.678	2.698	5.376	166.828	166.803
28	ZUVNAF	3.375	4.085	3.422	3.995	6.797	14.877	2.419	2.486	4.905	164.778	160.995
29	ZUVNEJ	3.481	4.042	3.468	4.158	6.949	15.149	2.529	2.523	5.052	163.390	163.154
30	ZUVNEK10	3.453	4.097	3.438	4.109	6.891	15.097	2.498	2.498	4.996	161.458	164.075
31[a]		3.445	4.078	3.401	3.995	6.846	14.919	2.466	2.458	4.924	155.360	168.733
31[b]		3.530	3.929	3.515	4.104	7.045	15.078	2.585	2.591	5.176	167.916	161.795
32		3.650	4.070	3.630	4.090	7.280	15.440	2.71	2.69	5.400	129.340	131.510
32		3.690	4.110	3.700	3.980	7.390	15.480	2.77	2.73	5.500	126.350	131.090
33	TARXUF	3.668	3.649	3.787	4.708	–	15.812	2.857	2.577	5.434	162.153	139.765
34	TOBPIJ	3.927	4.895	3.942	3.357	–	16.121	[c]	[c]	[c]	[c]	[c]
35	YAPTAK	3.703	3.583	3.899	4.648	–	15.833	3.150	2.819	5.969	125.282	164.724
36	YEBFAM	4.482	3.951	3.464	3.777	–	15.674	3.216	2.934	6.150	148.749	166.070
37	YOCPUB	4.092	3.845	3.713	4.244	–	15.894	3.364	2.791	6.155	150.673	147.089
38	ZIBHEX	3.390	4.074	4.834	3.965	–	16.263	2.854	3.007	5.861	133.623	117.587
39		3.868	3.868	3.868	3.868	–	15.470	[c]	[c]	[c]	[c]	[c]
21[d]		3.754	4.558	3.754	4.558	–	16.625	3.019	3.019	6.038	133.55	133.55

a. Malononitrile as guest.
b. Cloroacetonitrile as guest.
c. Hydrogen atoms not defined.
d. The data were not retrievable from CSD, therefore they were calculated on the structural data obtained in our labs.

In Figure 6 is presented the correlation between $\delta_1+\delta_3$ and DC_1+DC_3 which shows linear trend for all the calix[4]arene hosts whereas substantial deviations were observed with copper derivative of thiacalix[4]arene (**32**) and with resorcinarene (**22**). Similar results were obtained in the correlation of $\delta_1+\delta_3$ and DH_1+DH_3.

Very interesting is the comparison of the structural parameters obtained using 1,3-dipropoxy-*p*-*tert*-butylcalix[4]arene (**31**) as host and chloroacetonitrile and malononitrile, which have similar size and shape but different acidity of the methylene group,[8,9] as guests. The more acid malononitrile shows shorter DC_1+DC_3 (respectively 6.846 vs. 7.045 Å) and DH_1+DH_3 (respectively 4.924 vs. 5.176 Å) distances in comparison with chloroacetonitrile, supporting a higher contribution of hydrogen bonding in these CH_2 aromatic interactions.

TABLE V Summary of the crystallographic data for the compounds in this study

	$\mathbf{20} \supset CH_3CN$	$\mathbf{21} \supset CH_3CN$	$\mathbf{21} \supset CH_3NO_2$	$\mathbf{31} \supset CH_2ClCN$	$\mathbf{31} \supset CH_2(CN)_2$
cryst. dim. (mm^3)	0.3×0.2×0.4	0.4×0.4×0.5	0.2×0.6×0.6	0.2×0.5×0.3	0.4×0.7×0.5
cryst. color	colorless transp.	colorless transp.	colorless transp.	colorless transp.	colorless transp.
crystal system	monoclinic	tetragonal	tetragonal	triclinic	orthorhombic
space group	$P2_1/n$	$P4/nmm$	$P4/nmm$	P-1	$Pna2_1$
a [Å]	11.080(5)	15.641(5)	15.80085)	14.166(5)	24.132(5)
b [Å]	22.733(5)	15.641(5)	15.800(5)	14.415(5)	12.438(5)
c [Å]	21.444(5)	8.575(5)	8.433(5)	12.327(5)	19.797(5)
α [°]	90	90	90	90.11(2)	90
β [°]	96.74(2)	90	90	102.33(2)	90
Y [°]	90	90	90	97.83(2)	90
V [$Å^3$]	5364(3)	2098(2)	2105(2)	2435(2)	5942(3)
Formula	$C_{62}H_{79}NO_6$	$C_{42}H_{51}NO_4S_4$	$C_{41}H_{51}NO_6S_4$	$C_{52}H_{70}ClNO_4$	$C_{53}H_{70}N_2O_6{\cdot}(C_4H_4O_2)_2$
Z	4	2	2	2	4
ρ_{calcd} [g cm^{-3}]	1.157	1.206	1.234	1.103	1.117
$2\theta_{max}$ [°]	140	140	54	140	140
λ [Å]	Cu-Kα(1.54178)	Cu-Kα(1.54178)	Mo-Kα(0.71073)	Cu-Kα(1.54178)	Cu-Kα(1.54178)
scan mode	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ
T [K]	293	293	293	293	293
$refl_{meas}$	10549	2056	5081	9687	6165
$refl_{indep}$ (R_{int}) (	9999(0.05)	1032(0.03)	1293(0.05)	9222(0.013)	5742(0.02)
$refl_{obs}$[I>4σ(I)]	2392	662	626	7303	3490
n° of parameters	614	80	75	552	518
$R1$ [I>4σ(I)]	0.059	0.104	0.096	0.047	0.131
$wR2$ [I>4σ(I)]	0.130	0.276	0.285	0.135	0.342
$R1$ (all data)	0.2	0.125	0.158	0.059	0.176
$wR2$ (all data)	0.174	0.299	0.302	0.145	0.371
larg. diff. peak/hole e/$Å^3$	0.33/-0.21	0.66/-0.44	0.65/-0.88	0.47/-0.31	0.73/-0.46

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.
$R1 = \Sigma \| Fo | - | Fc \| / \Sigma | Fo |$, $wR2 = [\Sigma w(Fo^2 - Fc^2)^2 / \Sigma wFo^4]^{1/2}$.

As the directionality of the interaction is concerned the presence of the hydrogen atom positions in the structures allows to study the σ angle between the C-H and the centroid of the closest aromatic ring. From the experimental data it was verified a deviation from the perpendicular situation (Table IV) with σ angle usually ranging between 160–170°. These results are in good agreement with those obtained by Harder who studied the C-H-(π) cyclopentadienyl anions interactions, and observed a σ value of about 165°.[6]

CONCLUSIONS

Experimental data show that the intermolecular interactions between molecules having acid CH groups and the cavity of the calix[4]arene hosts are different for CH_3X and CH_2XY guests. The former guest spreads its interactions co-operatively with all the aromatic rings of the calixarene and finds the best matching with the cavity when the host has a C_4 symmetry, the δ value is about 110°, and the methyl carbon atom is over the centroids of the four aromatic rings. No significant dependence of the interactions with the basicity of the host and acidity of the guest was observed.

On the contrary the CH of CH_2XY guests seems to interact specifically with two diametrical aromatic rings of the hosts which assume a C_{2v} symmetry. A strong dependence of the interactions from the acidity of the guest is observed. If the directionality of the CH_{guest}-$Arene_{host}$ is considered, the present study demonstrates that all these guests interact with significant directionality depending on the guest structures. CH_3 containing guests find the better interaction when the CH is perpendicular to the aromatic ring, probably as "centre of gravity" of the cooperative action of the four aromatic nuclei, whereas with CH_2 containing guests, as observed in other studies reporting specific CH-π interactions, which display hydrogen-bond-like characteristic, a preference for σ angle of 165° was observed.[6]

The INS (Inelastic Neutron Scattering) studies in the solid state of calix[4]arene guest complexes prove that their methyl groups behave as almost-free quantum rotors[40] This affords an entropic advantage to these interactions and makes difficult to recognise such interactions as a "classic" hydrogen bond. On the other hand with CH_2XY guests free rotation is partially inhibited by the complex formation. This entropic cost is partially compensated by an higher value of the interaction energy due to a larger contribution of hydrogen bonding to these interactions as evidenced by the dependence of the CH-aromatic distances on the acidity of the guest.

To verify whether these observations could be used to predict also the binding properties of these hosts with the two different guests in solution, preliminary studies were performed. It was found that while for the CH_3X[3d,41] guest type no substantial variation of the K_{ass} occur by changing the guest acidity, in the cases of CH_2XY guests when the polarizability of X and Y groups are the same, a good correlation of the K_{ass} with the guest acidity does exist.[42]

These results are in good agreement with the hypothesis that CH-π aromatic interactions derive from the superimposition of several and different types of intermolecular forces, whose percentage can depend on several factors, and further support that the relative weight of these contributions depends strongly on the nature of the interacting partners. These findings could then be exploited as a new tool to design and synthesise new receptors which, by the fine tuning of their geometrical parameters could experience enhanced efficiency and selectivity properties.

Further studies are in progress to better understand these interactions.

EXPERIMENTAL SECTION

General Remarks

Compounds 20,[3c] 21,[7] and 31[43] were synthesised according to literature procedures.

Calculations

The geometrical parameters here reported were retrieved on the CSD using the graphical search system QUEST3D and the interactive visualisation graphical software PLUTO operating on the version 5.18 (october 1999) of the CSD. *X-Ray crystallography* – Single crystal X-Ray diffraction measurements on compounds **20** ⊃ CH_3CN, **21** ⊃ CH_3CN, **31** ⊃ CH_2ClCN, **31** ⊃ $CH_2(CN)_2$ were carried out on an Enraf Nonius CAD4 diffractometer using graphite monochromated Cu-K_α radiation; the measurements on compound **21** ⊃ CH_3NO_2 were carried out on a Philips PW1100 using graphite monochromated Mo-K_α radiation. All crystals were mounted on glass fibre under a thin layer of perfluoric oil as a protection from the air.

The crystal data and the most relevant experimental parameters used in the X-ray measurements and in the crystal structure analysis are reported in Table V. The intensities were calculated from profile analysis according to the Lehmann and Larsen method.[44] For each compound during the systematic data collections two standard reflections were collected every 100 to monitor crystals decay and instrumental linearity. The intensities were corrected for Lorentz and polarization but not for absorption effects. The structures were solved by Direct Methods using SIR92.[45] The best FOM Emap showed the coordinates of almost all non-hydrogen atoms. The structures were completed by Fourier ΔF maps and then refined by blocked full-matrix least-squares methods on F^2 using SHELXL-97.[46] In the structure of compund **31** ⊃ $CH_2(CN)_2$ two dioxane guest molecules were found in the crystal lattice. Usually, the parameters refined were: the overall scale factor, the atomic coordinates and anisotropic thermal parameters for all the non-hydrogen atoms with the exception of the methyl carbon atoms of the *tert*-butyl group at the phenolic unit when they were disordered over two different orientations which were refined with isotropic thermal parameters. All the hydrogen atoms were placed at their calculated positions with the geometrical constraint C-H 0.96 Å and refined "riding" on their corresponding carbon atoms. The geometrical calculations here reported were carried out with the PLUTO program in the CCDC software.

All the calculations were carried out on the Digital Alpha 255 workstation at the Centro di Studio per la Strutturistica Diffrattometrica of C.N.R. of Parma.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication n° CCDC-139429 (**20** ⊃ CH_3CN), CCDC-139430 (**21** ⊃ CH_3CN), CCDC-139431 (**21** ⊃ CH_3NO_2), CCDC-139432 (CH_2ClCN), CCDC-139433 ($CH_2(CN)_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223–336–033: e-mail:deposit @ccdc.cam.ac.uk).

Supplementary material

List of the fractional atomic coordinates for the non-hydrogen atoms, list of the thermal parameters for the non-hydrogen atoms, list of the fractional atomic coordinates of the hydrogen atoms, complete list of bond distances and angles and list of the observed and calculated structure factors for each of the reported structures are available from F.U. (email:ugoz@unipr.it) on request.

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