Inclusion of Organic Cations by Calix[4]arenes Bearing Cyclohepta-2,4,6-trienyl Substituents

Marzena Orda-Zgadzaj,[a] Volker Wendel,[a] Matthias Fehlinger,[a] Burkhard Ziemer,[a] and Werner Abraham*[a]

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Only very weak complexation of organic cations such as ammonium and iminium ions by simple calix[4]arenes has been reported to date. Newly designed calix[4]arenes, substituted with a different number of 1,3,5-cycloheptatrien-7-yl functions at the upper rim, can engender an improvement in the inclusion capability, due to an enlargement of the π-basic wall of the host cavity. The complexation capability of these calix[4]arenes for organic cations is studied in this paper. For the first time, aryl tropylium salts have been used as cationic guests in addition to ammonium and iminium salts. Three structural types of hosts can be distinguished, all of which exhibit remarkably different inclusion abilities towards the organic cations. Flexible hosts with an OH-unmodified lower rim undergoing ring inversion form complexes of modest stability, provided that the host lacks bulky *tert*-butyl substituents at the upper rim. Tetra-*O*-alkylated derivatives, which are assumed to exhibit a flexible cone conformation, do not bind organic cations. Among the calix[4]arenes bearing cycloheptatrienyl groups, the complexation requirements are best matched by hosts with four cycloheptatrienyl groups on the upper rim and two alkyl groups on the lower rim; these compounds are assumed to possess a more rigid cone conformation, due to intramolecular hydrogen bonds. The tropylium component of phenyl tropylium ions penetrates inside the π-basic cavity of the host. The absorption coefficient of the longest wavelength absorption band of these guests in the visible region is drastically lessened upon inclusion.

Introduction

Calixarenes are an interesting class of macrocycles, thanks to their molecular recognition properties.[1]

Solids containing deprotonated calixarenes have been isolated both as rare earth ion complexes [2] and as transition metal[3] ion complexes, as well as weakly coordinating cations.[4] Alkali metal ions are complexed in solution at the lower rim made up by substituents such as ester groups which are attached through the oxygen atoms.[5] Solid salts are formed with quaternary ammonium hydroxides, because the phenols of the calixarenes are stronger acids than phenol itself.[6]

Organic cations should interact with the aromatic clouds in the calixarene cavity in the absence of contributions such as ion pairing or classical hydrogen bonding with the host. The cation−π interaction has come to the forefront of interest relatively recently.[7] However, only a few reports on the binding of quaternary ammonium salts by calix[4]arene-based host molecules in nonpolar solvents have appeared.[8−11] Association constants reported so far suggest that the cavity of the calix[4]arene is too small to be able to bind ammonium and iminium ions effectively.[9,11]

For example, the tetrapropylammonium cation was not included either by calix[4]arene or by *tert*-butylcalix[4]arene. On the other hand, choline and acetylcholine form inclusion complexes with calix[4]arene, but complexation by a calix[4]arene is hindered by *tert*-butyl substituents on the upper rim.[6] Phenyl and cyclohexyl groups on the upper rim of rigid cone calix[4]arenes have been reported to reduce the complexation ability.[8] It has also been shown that the encapsulation of ammonium ions is strongly improved by interconnecting two calix[4]arenes at the upper rims with two spacers, but that larger iminium ions such as **34** (see Scheme 3) were not bound.[11] Calixarenes with a wider cavity, such as calix[5]arenes[12] and homooxacalix[4]arenes,[13] are fairly efficient receptors for ammonium and iminium salts.

Therefore, the question arises of whether the cavity of calix[4]arenes is generally unsuitable for the binding of organic cations. In particular, it should be noted that substituents at the lower and at the upper rim of calix[4]arenes may control the complexation behaviour of these cyclophanes in the same way that alkylated phenol functions control the conformational flexibility of cyclophanes.[1a] The preorganisation of the macrocycle may be a prerequisite for the complexation of organic cations.[14,15] Substituents at the *para* position of the phenol units influence the diameter of the cavity that is intended to include organic cations.

Recently, we synthesised calix[4]arenes and calix[6]arenes containing cycloheptatrienyl or tropylium groups at the upper rim,[16] the intended purpose of the cycloheptatrienyl groups being to enlarge the hydrophobic cavity of the newly designed hosts. Furthermore, the introduction of the cycloheptatriene substituent into the calixarenes offers the possibility of creating a switchable host. The seven-membered olefinic ring can be transformed into the positively charged

[a] Institut für Chemie der Humboldt-Universität zu Berlin
Hessische Strasse 1−2, 10115 Berlin, Germany

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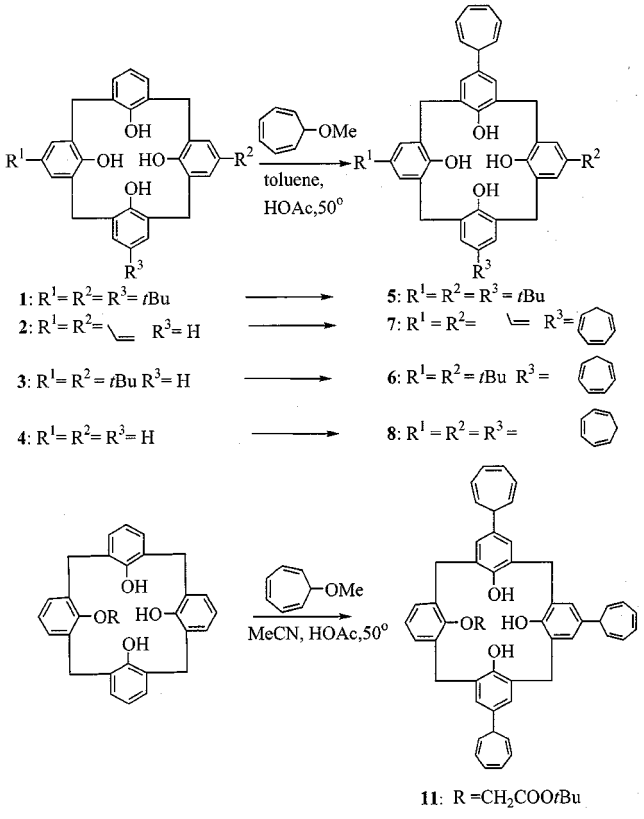
tropylium ion by the use of electrochemical[17] or photochemical[18] methods.

In this paper we are concerned with the synthesis of several calix[4]arenes **5**−**17**, all possessing different substitution patterns at the upper and lower rim, as illustrated in Scheme 2. Also, a number of cationic guests **26**−**37**, shown in Scheme 3, were tested with selected hosts in lipophilic solution. Ammonium, iminium and tropylium salts were chosen as representatives of three quite different families in their shape and charge distribution. To date, no report has offered details on the binding properties of the calixarenes towards aryltropylium ions while recently the unsubstituted tropylium ion has been used to build up a resorcinarene dimer.[19]

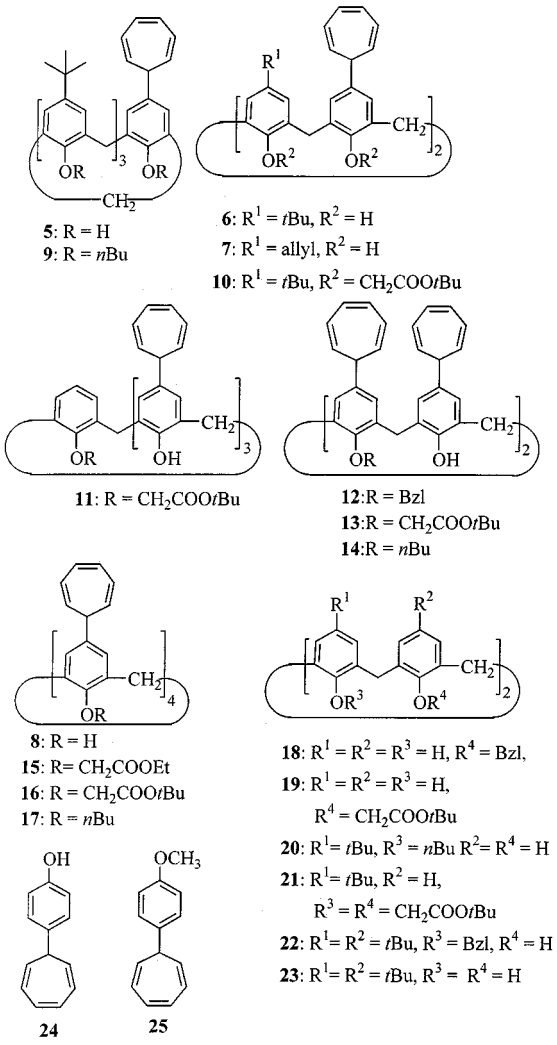
Results and Discussion

Synthesis

Compounds **5**−**8** were obtained by means of the reaction between 7-methoxy-1,3,5-cycloheptatriene and the partially dealkylated phenolic unit of the corresponding calix[4]arenes (Scheme 1). The cycloheptatrienyl substituents can also be introduced by means of the selective reaction between 7-methoxy-1,3,5-cycloheptatriene and the phenolic unit of the completely dealkylated upper rim of calix[4]arenes partially alkylated on the lower rim (Scheme 1). Alkylation of the lower rim was carried out according to known procedures. Two, three or four alkyl groups were introduced, depending upon the reaction conditions (see Scheme 2). Compounds **18**−**23** were included in order to compare their properties with those of the calixarenes bearing cycloheptatrienyl substituents on the upper rim.



Scheme 1. Syntheses of calix[4]arene compounds



Scheme 2

Conformation

Conformationally Mobile Calix[4]arenes

Calix[4]arenes **5**−**8** exhibit slow (on the NMR timescale at room temperature) interconversion between two cone conformations. The existence of the cone conformation in solution is indicated by (i) the remarkable difference between the chemical shifts of the equatorial and axial methylene protons (see Table 1) and (ii) the methylene carbon resonance at $\delta = 32$ in the ^{13}C NMR spectrum.[20]

The cycloheptatrienyl substituents have no appreciable effect on the barrier to inversion. For example, the activation energy of the interconversion of **8** (15 kcal mol^{-1} in toluene), estimated from the coalescence temperature (323 K) of the two singlets of the methylene bridges, corresponds to that observed with other calix[4]arenes.[21]

Table 1. Selected ^{1}H NMR proton resonances ($CDCl_3$; ppm) of calixarene hosts bearing cycloheptatrienyl groups; CHT = 2,4,6-cycloheptatriene

Compound	Ar−CH_2−Ar (eq)	Ar−CH_2−Ar (ax)	Δδ	C^1−H of CHT	Ar	OH
5	3.50 (d)	4.26 (br. m)	0.76	2.50 (t)	7.05 (m)	10.33
6	3.51 (d)	4.28 (d)	0.77	2.49 (t)	7.06 (s), 7.04 (s)	10.31
7	3.50 (br. d)	4.26 (br. d)	0.76	2.53 (t)	6.85 (s), 7.04 (s)	10.24
8	3.54 (br. d)	4.32 (br. d)	0.78	2.53 (t)	7.05 (s)	10.35
9	3.13, 3.11 (dd)	4.45, 4.42 (dd)	1.31, 1.31	2.18 (t)	6.46 (s), 6.58 (s), 6.95 (m)	
10	3.21 (d)	4.89 (d)	1.65	2.25 (t)	6.91	
11	3.46 (d)	4.35 (d), 4.55 (d)	0.89, 1.09	2.49 (br. t)	6.89 (t), 7.05 (m)	9.28, 10.06
12	3.34 (d)	4.34 (d)	1.0	2.43 (t), 2.58 (t)	7.02 (s), 6.92 (s)	7.92
13	3.38 (d)	4.54 (d)	1.16	2.43 (t), 2.56 (t)	6.92 (s), 7.02 (s)	7.81
14	3.32 (d)	4.30 (d)	1.0	2.36 (t), 2.49 (t)	6.90 (s), 6.96 (s)	8.40
15	3.25 (d)	4.92 (d)	1.68	2.45 (t)	6.75 (s)	
16	3.17 (d)	4.87 (d)	1.70	2.38 (t)	6.66 (s)	
17[a]	3.20 (d)	4.61 (d)	1.41	2.78 (t)	6.89 (s)	
21	3.18 (d)	4.85 (d)	1.68		6.12 (d), 6.28 (t), 7.02 (s)	

[a] In [D_8]toluene.

In every case, only one set of resonances arising from the protons of the seven-membered rings was observed. According to the chemical shift, the proton bound to the sp^3-C atom (C-1) is axial (such a proton resonates at δ = 2.7 in 1-phenylcyclohepta-2,4,6-triene whereas an equatorial proton would resonate at δ = 3.5)[22] and the bond to the calixarene is equatorial.

Calix[4]arenes Alkylated at the Lower Rim

Because of the presence of four alkyl groups on the lower rims of **9**, **10**, **15**−**17** and **21**, the cone conformation is immobilised, as is generally observed in other compounds.[23] The ^{1}H NMR spectrum of **9** in $CDCl_3$ clearly shows a cone conformation and a pattern typical for two different substituents in the ratio 3:1 on the upper rim (two AX systems for the methylene protons, three triplets 2:1:1 for the OCH_2 groups).

It has been shown that, in solution, cone tetraalkoxycalix[4]arenes experience residual conformational mobility by means of transitions between two C_{2v} (pinched cone) structures.[24,25] Usually, the rate of C_{2v}−C_{2v} interconversion at room temperature is fast on the NMR timescale.[26] Indeed, in the ^{1}H NMR spectra of **15**−**17**, the four (alkoxyphenyl)-cycloheptatriene units appear equivalent.

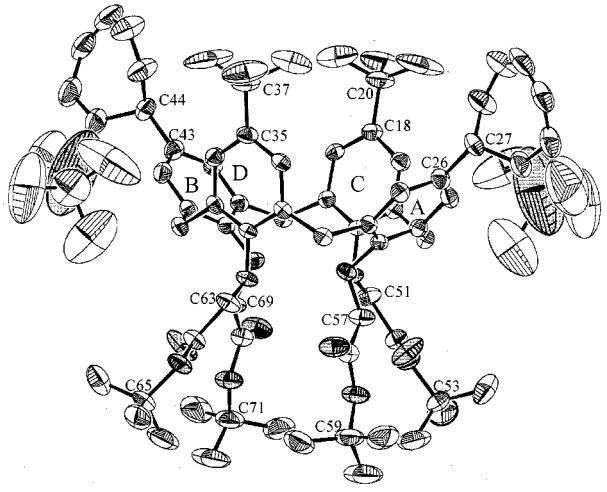
In the ^{1}H NMR spectrum, the splitting of the aromatic hydrogen signals of the calix[4]arene skeleton has recently[27] been used to distinguish between C_{2v} structures in solution, upfield shifts of up to 1 ppm having been observed for hydrogen signals of parallel oriented aromatic rings. Two sets of signals arising from the alkoxy groups also point to a flattened cone conformation.[28,29] According to the upfield shift of the aromatic hydrogen signals (**9** and **21**) and the two sets of resonances of the alkoxy groups, the calixarenes **9**, **10** and **21** adopt a pinched cone conformation in solution (see Table 1).

The calixarenes possessing four cycloheptatrienyl substituents at the upper rim but only two alkyl groups in the distal position of the lower rim (**12**−**14**) also exhibit slightly different aromatic proton resonances, indicating a cone distortion.[15] Furthermore, these derivatives are assumed to adopt a pinched cone structure with a *syn* configuration of the alkyl groups, as on one hand the axial and the equatorial protons of methylene bridges resonate with a difference of about 1 ppm, and on the other hand two sets of resonances arising from the protons of the cycloheptatrienyl rings are observed (see Table 1); in other words, (hydroxyphenyl)-cycloheptatriene subunits can be distinguished from (alkoxyphenyl)cycloheptatriene subunits of the calixarene skeleton. This finding contrasts with the comparison of the entities **24** and **25**, which exhibit only slightly differing signals arising from the seven-membered ring hydrogen atoms (for example: δ = 2.66 vs. δ = 2.61 for H-1). Therefore, in this case, the signal splitting must also be assigned to conformational effects leading to different environments for each of the distal pairs of cycloheptatriene rings.

If chemical shift changes of the phenylcycloheptatriene moieties bearing the free hydroxy group can be ignored by going from derivatives **5**−**8** to derivatives **12**−**14**, the upfield-shifted set of proton resonances of the cycloheptatriene rings can be assigned to those cycloheptatrienyl substituents which are connected with the alkylated phenol units (Table 1). The protons of the two cycloheptatriene rings which are tilted away from the calixarene cavity in **10** also resonate at a higher field than those in the cycloheptatriene rings of **5**−**8**. Thus, this upfield shift indicates a flattened cone conformation of **12,** with (alkoxyphenyl)cycloheptatrienyl subunits tilted away from the cavity. According to the CH_2-bridge protons (see Table 1) host **11**, bearing three cycloheptatrienyl substituents on the upper rim and only one alkyl group on the lower rim, also displays a cone conformation. The substitution pattern gives rise to three signals from the bridging protons, two signals from the OH protons and only one set of proton signals from the three cycloheptatrienyl groups. Strong hydrogen bonds on the lower rim are indicated by the strong downfield shift of one proton signal compared to the others of protons adjacent to the alkoxy group.

It should be noted that differences between the signals of equatorial and axial protons in the $ArCH_2Ar$ groups also strongly depend upon the substitution pattern on the lower

rim (see Table 1). On going from unsubstituted entities to derivatives with two and four alkyl groups at the lower rim, the difference is increased; this is due to the doublet of the four axial protons resonating further downfield as the number of alkyl groups increases. This indicates an increasing angle of inclination between the two distal phenyl groups.[26]



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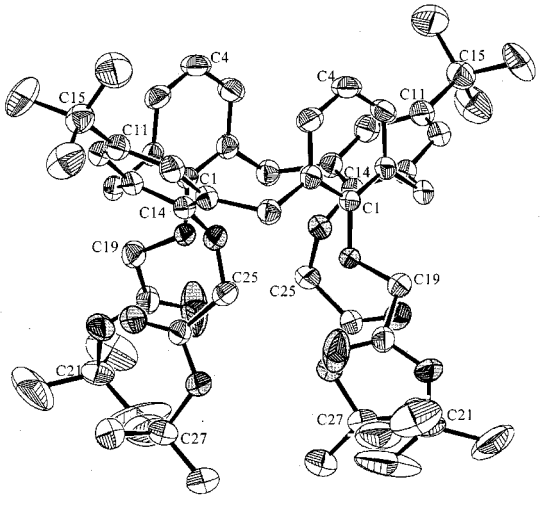


21

Figure 1. Molecular structures of **10** and **21**

X-ray Structure Determination

Single crystals suitable for X-ray structure determination could only be obtained from compounds **10** and **21**. The molecular structure of **10**, which is depicted in Figure 1, revealed a pinched cone conformation.

Two solvent molecules (*tert*-butyl methyl ether) are situated outside the cavity, between the host molecules in the crystal lattice. Deformation of the cone is associated with the tilting of the phenyl rings towards the main molecular plane. The phenyl rings bearing the cycloheptatrienyl substituents are tilted away from the cavity. The angle between these two phenyl rings (A and C in Figure 1) is 84.6°. The other two phenyl rings bearing the *tert*-butyl groups are almost parallel (angle 10.8°). The distances between the two cycloheptatrienyl rings ($C^{27}-C^{44}$) and the *tert*-butyl groups ($C^{18}-C^{35}$) amount to 11.4 and 6.3 Å, respectively. The main plane of the cycloheptatrienyl substituent is twisted with respect to the plane of the aromatic ring in the calixarene moiety bearing the substituent, thus forming torsion angles of 67° (dihedral angle along $C^{25}-C^{26}-C^{27}-C^{28}$) and 57° [along $C^{25}-C^{26}-C^{27}-C^{33}$ (see Figure 1)], respectively.

The calixarene **21** also adopts a pinched cone conformation, in which the two unsubstituted aromatic units are oriented face-to-face, whereas the phenyl groups bearing the *tert*-butyl substituents are tilted away from the cavity. Comparing calixarenes **10** and **21**, it may be concluded that the steric interference between two distal cycloheptatrienyl groups is larger than that of two *tert*-butyl substituents.

Complexation Studies

Firstly, we qualitatively estimated the inclusion capability of each calix[4]arene **5**−**23** in $CDCl_3$, using the ^1H NMR chemical shift change when organic cations were applied as guests. If significant complexation occurs, the proton resonance of the guest is shifted to a higher magnetic field, due to the shielding effect of the aryl rings of the host. No complexation was observed with host **9**, in contrast to the hosts listed in Table 2.

The dynamic process occurring during complexation and decomplexation is fast on the NMR timescale (300 MHz). The addition of increasing amounts of host-to-guest solutions resulted in upfield shifting of the guest proton signals; the resonances of the different guest protons were monitored whenever possible. In general, signals of guest protons close to the positive charge of the ions are shifted upfield more strongly than others (see Figure 2); evidently, complexation involves a close contact between the charged part of the guest and the aromatic faces of the host.

The existence of 1:1 complexes in solution and the gas phase was proven for complexes of tropylium ions (as guests) and using **12** as the ligand; this was achieved using both Job plots[30] and mass spectrometry (FAB and ESI). For example, the ESI mass spectrum recorded with CH_2Cl_2 solutions of the calixarene **12** with **37** as the guest displays a base peak corresponding to the *m*/*z* value expected for the ionic guest. The only significant signal besides that of the tropylium ion **37** corresponds to the complex **12**/**37**. A closer examination of the results summarised in Table 2 identifies three discussion points related to the binding strength: (i) the influence of the host, (ii) the influence of the nature of the guest, and (iii) the influence of solvent polarity.

Table 2. Association constants and the free enthalpy of host-guest complexes and calculated chemical shifts of guest protons in the complexes

Entry	Host	Guest	Solvent	K [M^{-1}]	$-\Delta G°$ [kcal mol^{-1}]	$-\delta_{\infty}$ [Hz]
1	**5**	**34**, **37**	$CDCl_3$	–	–	–[a]
2	**6**	**37**	$CDCl_3$	–	–	–
3	**7**	**37**	$CDCl_3$	16	1.6	83 (Tr[b])
4	**8**	**31**	$CDCl_3$	33	2.1	420 (NCH_3)
5	**8**	**36**	$CDCl_3$	45	2.3	359 (Tr)
6	**10**	**26**	$CDCl_3$	–	–	–
7	**10**	**37**	$CDCl_3/CD_3CN$ (3:2)	–	–	–
8	**11**	**37**	$CDCl_3$	26	1.9	219 (Tr)
9	**12**	**26**	$CDCl_3$	52	2.3	321 (NCH_3)
				52	2.3	155 (CH_3CO)
10	**12**	**27**	$CDCl_3$	3	0.7	231 (NCH_3)
11	**12**	**28**	$CDCl_3$	27	2.0	513 (NCH_3)
12	**12**	**29**	$CDCl_3$	28	2.0	517 (NCH_3)
13	**12**	**30**	$CDCl_3$	20	2.2	386 (NCH_3)
14	**12**	**31**	$CDCl_3$	82	2.6	420 (NCH_3)
15	**12**	**32**	$CDCl_3$	95	2.7	368 (NCH_2)
16	**12**	**33**	$CDCl_3$	93	2.7	505 (NCH_3)
17	**12**	**34**	$CDCl_3$	189	3.2	456 (NCH_3)
18	**12**	**35**	$CDCl_3$	121	2.8	495 (Tr)
19	**12**	**36**	$CDCl_3$	213	3.2	358 (Tr)
20	**12**	**36**	$[D_6]$acetone	35	2.1	543 (Tr)
21	**12**	**37**	$CDCl_3$	190	3.1	350 (Tr)
22	**12**	**37**	$CDCl_3/CD_3CN$ (3:2)	29	1.8	319 (Tr)
23	**13**	**34**	$CDCl_3$	214	3.2	442 (NCH_3)
24	**13**	**37**	$CDCl_3$	185	3.1	248 (Tr)
25	**13**	**37**	$CDCl_3/CD_3CN$ (3:2)	17	1.7	394 (Tr)
26	**14**	**37**	$CDCl_3$	130	2.9	334 (Tr)
27	**15**	**37**	$CDCl_3$	–	–	–
28	**16**	**37**	$CDCl_3$	–	–	–
29	**17**	**37**	$CDCl_3$	–	–	–
30	**18**	**37**	$CDCl_3$	92	2.7	246 (Tr)
31	**18**	**34**	$CDCl_3$	277	3.3	392 (NCH_3)
32	**18**	**36**	$CDCl_3$	360	3.5	324 (Tr)
33	**19**	**37**	$CDCl_3$	79	2.6	291 Tr)
34	**20**	**37**	$CDCl_3$	95	2.7	335 Tr)
35	**21**	**26**, **37**	$CDCl_3$	–	–	–
36	**22**	**34**	$CDCl_3$	18	1.7	551 (NCH_3)
37	**22**	**36**	$CDCl_3$	33	2.1	198 (Tr)
38	**23**	**34**, **36**, **37**	$CDCl_3$	–	–	–

[a] No significant chemical shift was observed.– [b] Tropylium ring protons.

(i) Host Variation

The calix[4]arenes investigated can be divided into three structural types:

(a) OH-unmodified calixarenes containing cycloheptatrienylphenyl units, which are oriented toward each other due to the array of hydrogen bonds on the lower rim. This class of macrocycles displays cone-to-cone interconversion (hosts **5**–**8**, **23**).

(b) Calixarenes partially alkylated at the lower rim, displaying a more rigidly fixed pinched cone conformation in solution (hosts **11**–**14**, **18**–**20**, **22**).

(c) Tetraalkylated calixarenes undergoing a fast interconversion between two pinched cone conformations (hosts **9**, **10**, **15**–**17**, **21**).

The three types of calixarene hosts exhibit remarkably different inclusion capabilities with cationic guests:

(a) The most flexible hosts, as might be expected, display rather weak complexation; if complexation is observed, the association constants are low (Table 2, Entries 3–5). Hosts **5** and **6** do not bind organic cations such as **34** and **37**, due to the bulky *tert*-butyl groups on the upper rim. Such steric interference with guest inclusion by *tert*-butyl groups has often been noticed.[8,9,28] Replacement of *tert*-butyl groups by allyl substituents (**6** vs. **7**) improves the binding capability of the host (Entries 2, 3). Comparison of hosts **8** and **23** (Entries 4, 5, 38) makes the role of cycloheptatrienyl substituents obvious; the seven-membered ring on the upper rim supports complexation.

(b) The best conditions for the binding of organic cations were found in calix[4]arenes bearing two distal alkyl groups on the lower rim. The immobilised pinched cone conformation of these host molecules facilitates the complexation, and the binding ability is governed by substituents on the upper rim (H, *tert*-butyl, cycloheptatriene); *tert*-butyl substituents reduce the binding ability through steric interference. Cycloheptatrienyl groups on the upper rim improve the binding properties (compared to the unsubstituted counterpart) when guest **37** is used (Entries 24, 33). In contrast, the binding of guests **34** and **36** is not significantly enhanced by the presence of a cycloheptatrienyl group on the upper rim (Entries 17, 31; 19, 32). Replacement of the *tert*-butyl groups by hydrogen atoms has been found to improve the ability of 1,3-bridged calix[5]crowns to bind iminium ions such as **34**.[12] The reported association constants

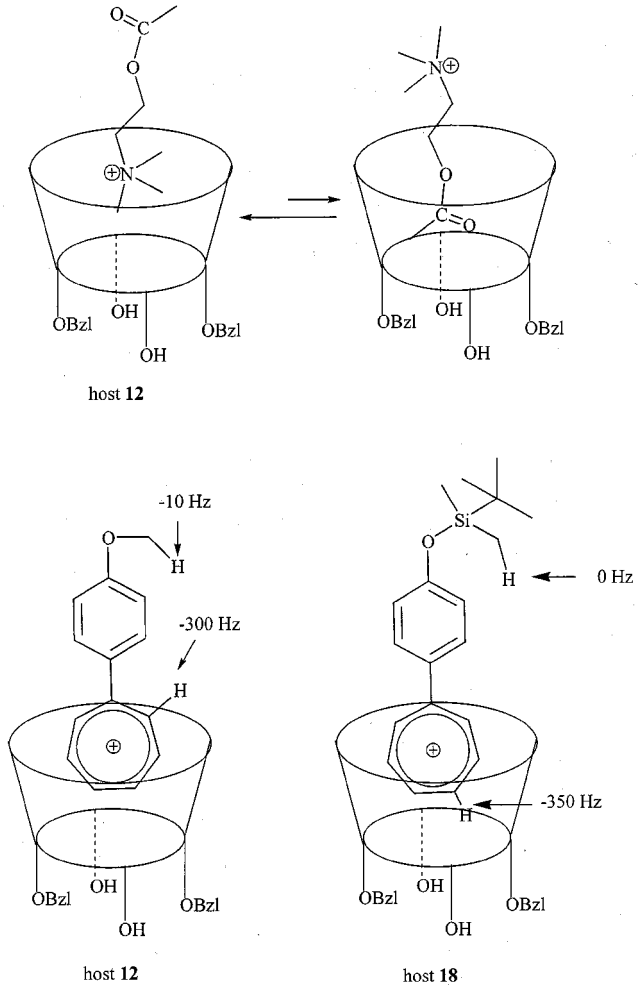


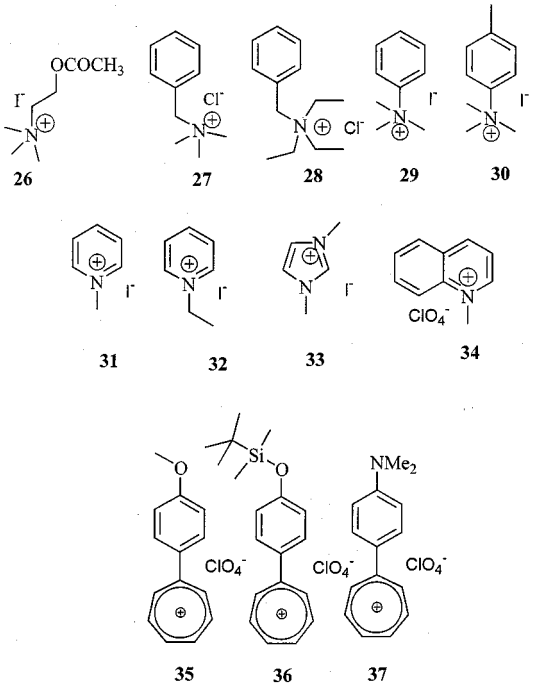
Figure 2. Schematic representation of inclusion geometries of different guests in the hosts **12** and **18**

are in the same range as those of **12** or **18**, thus indicating that it is the shape and not the cavity size that is the decisive parameter for efficient binding. On the other hand, a calix[4]arene fixed in the cone conformation by four propyl groups on the lower rim does not bind **34**.[11] This finding is in agreement with the results obtained with hosts **16** and **17**. On removing one cycloheptatrienyl group on the upper rim and one alkyl group at the lower rim (host **11**), the binding ability of the host decreases drastically (Table 2, Entries 8, 21).

(c) Calix[4]arenes in which the ring inversion is prevented (Entries 6, 7, 27, 28, 29, 35) do not bind cations such as **26**, **34** and **37**, although the cavity diameter of **10** (taken from the crystal structure) is large enough to include cations such as **26**. It seems that the fast interconversion of two flattened cone conformations assumed for these derivatives (see discussion above) hampers complexation. Substituents on the upper rim do not influence this behaviour.

(ii) Guest Variation

Three different types of organic cations, comprising quaternary ammonium ions, flat aromatic iminium ions and, for the first time, aromatic aryl tropylium ions, were chosen as guest molecules in order to explore the influence of the guest structure on the inclusion properties with a suitable calix[4]arene host (Scheme 3).



Scheme 3

The cavity formed by *O*-dialkylated cycloheptatrienyl calix[4]arenes is well suited for this purpose, and is characterised by two parallel cycloheptatrienylphenyl units which may facilitate a sandwich-like inclusion of flat aromatic guests. Two cycloheptatrienylphenyl units of the calix[4]arene are tilted away and open the cavity of the host. It is therefore expected that flat aromatic cations will be more strongly complexed than ammonium ions. Indeed, host **12** displays a moderate selectivity towards tropylium and iminium ions. Quaternary ammonium salts are less efficiently bound (see Table 2), but all of the salts investigated form complexes of definite stability with **12** in chloroform solution. Of the ammonium ions, the complex with acetylcholine exhibits the highest association constant (Entry 9). It can therefore be concluded that the phenyl groups in guests **27**−**30** do not contribute towards the binding ability of the ammonium ions.

(iii) Solvent Influence

As expected, weaker complexation is observed both in acetone solution and in chloroform solution containing acetonitrile (Table 2, Entries 20, 22, 25). The cation−π interaction has to overcome the substantial desolvation of guest and host, which is hindered by increasing solvent polarity.[12] In general, the association of cations and anions in media of low polarity plays an important role and may affect complexation; it is also known that ion pairs of aryl tropylium salts are destroyed in acetonitrile.[31] At the pre-

sent level of knowledge it is not clear which effect mainly occurs on changing the solvent.

Aryltropylium Ions as Guests

To the best of our knowledge, aryltropylium ions have never been used as organic cations to study cation−π interactions in solution. Guest **35** has, however, been reported to form complexes with crown ethers in the gas phase.[32]

Aryltropylium ions are of special interest because both the colour and the localisation of the positive charge can be tuned by the donor strength of the aryl group attached to the tropylium moiety. The longest wavelength absorption transition of aryltropylium ions involves a strong intramolecular charge transfer transition.[33] Therefore the question arises as to whether complexation of these guests by calixarene hosts is influenced by the π-donor strength of the aryl substituent connected with the tropylium entity. In addition to this, a bulky substituent was introduced onto the phenyl ring (guest **36**) in order to prevent the inclusion of this part of the aryl tropylium ion.

In the line from **35** to **37**, the absorption band is shifted towards the red and the corresponding reduction potential is shifted to more negative values, due to increasing charge transfer from the aryl moiety to the tropylium ring.[17] Despite the diminished positive charge of the seven-membered ring, the association constants do not vary significantly (see Table 2). Therefore, it is concluded that the charge transfer interaction between the host and the guest is negligible. The main role is played by the electrostatic attraction between the positive charge of the guest, which is more or less delocalised, and the aromatic wall of the host; apart from the charge, the shape of the guest has to match the cavity of the host. Comparison of hosts **12** and **18** permits some conclusions to be drawn about the influence of the substituents on the upper rim. Because of steric interference, the tropylium ion **36**, bearing a bulky substituent at the phenyl group, is more strongly bound by host **18**, with a free upper rim (Table 2, Entry 32). In contrast, **37** exhibits a preference towards hosts **12** and **13**, due to the enlarged π-basic wall of the cavity (compare Entries 21, 24, 30).

The colour of aryltropylium salts originates from the intramolecular charge transfer. Actually, it is the intensity, not the wavelength, of this absorption band that is drastically changed upon complexation. As can be seen from Figure 3, where some UV/Vis spectra of solutions used for the NMR titration experiments of the complex **14/37** are presented, the absorption band of **37**, around 570 nm, becomes smaller with increasing complexation.

Using the absorbance instead of the CIS value as a parameter to calculate the association constant by means of the algorithm used in the NMR titration experiment (see Exp. Sect.), a K value of 160 M^{-1} was obtained; this agrees, within error limits, with the value determined by NMR titration (Table 2, Entry 26). The limiting absorbance of **37** when fully saturated by **12** is less than half the absorbance of the free tropylium ion. Accordingly, the molar extinction coefficient of **37** decreases from 4.7×10^5 dm^2 mol^{-1} [34] to 2×10^5 dm^2 mol^{-1}. Such tropylium ion behaviour also holds true in the complex **11/37**. Correspondingly, hosts that do not bind the tropylium salt **37** do not lessen the absorption of the latter.

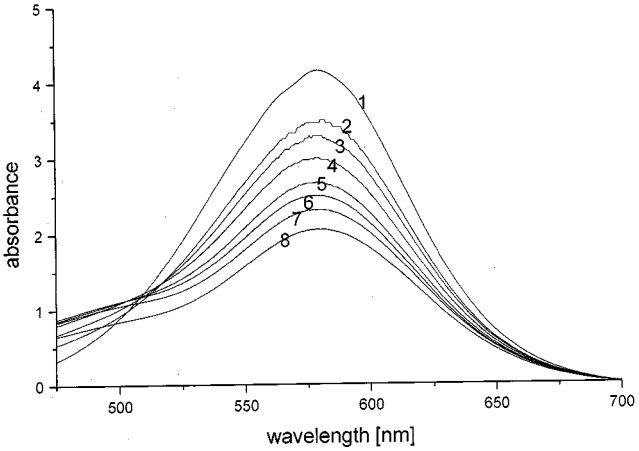


Figure 3. UV/Vis titration of the tropylium salt **37** with the host **14**: **1**: $R = 0.00$, Abs = 4.15; **2**: $R = 1.86$, Abs = 3.49; **3**: $R = 4.66$, Abs = 3.29; **4**: $R = 8.94$, Abs = 2.99; **5**: $R = 16.76$, Abs = 2.67; **6**: $R = 24.03$ Abs = 2.49; **7**: $R = 39.86$ Abs = 2.31; **8**: $R = 52.71$, Abs = 2.05; R = [**14**]/[**37**]

We attribute the diminished extinction coefficient of tropylium ions complexed by calixarenes to an enhanced torsion angle between the two aromatic units. According to the X-ray structure determination of single crystals of the guest **37** (see Figure 4), which we have carried out for the first time, the aryltropylium ion is almost planar (the torsion angle between the aromatic units is only 3°). Quantum mechanical calculations[35] have shown the oscillator strength of the S_0 Õ S_1 transition to be reduced on increasing the torsion angle between the two aromatic units.

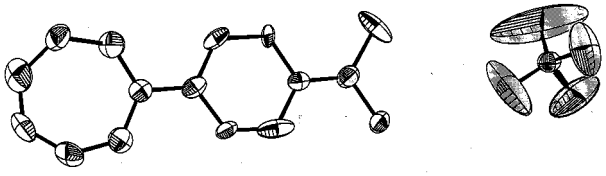


Figure 4. Molecular structure of the tropylium salt **37**

Complex Structure

The shift patterns observed in complexes of the ammonium ion **26** suggest a rather disordered complexation. According to the CIS values extrapolated to full complexation, both the ammonium head and the acetyl tail of **26** are bound to the cavity, with a clear preference for the head group. This indicates an exchange process leading to equilibrium (see Figure 2). The shift patterns of complexes of **35** and **36** strongly indicate that the tropylium moiety is closely bound to the cavity, whereas the aryl group is pointed towards the exterior.

In principle, complexation can induce chemical shift changes in the ^1H NMR spectra of both the guest and the host. Although the latter effect is small in the case of hosts **12** and **13**, the protons of the cycloheptatrienyl substituents

on the upper rim provide a probe for the mode of interaction between guest tropylium ions and the upper part of the cavity wall of the host. As discussed above, two sets of cycloheptatriene substituents can be discerned. The separation of these two pairs of cycloheptatrienyl groups is increased by complexation with cationic guests such as **26**, **34** and **37**, because the hydrogen resonances of the two sets of subunits of hosts **12** and **13** − namely (alkoxyphenyl)- and (hydroxyphenyl)cycloheptatriene subunits − are shifted, to a small extent, in the opposite direction, indicating different interactions between the pairs of distal subunits and the cationic guests (see Figure 5).

The proton signals of the alkylated subunits are shifted upfield, those of the subunits with free hydroxy groups are shifted downfield (see Figure 6). According to the larger

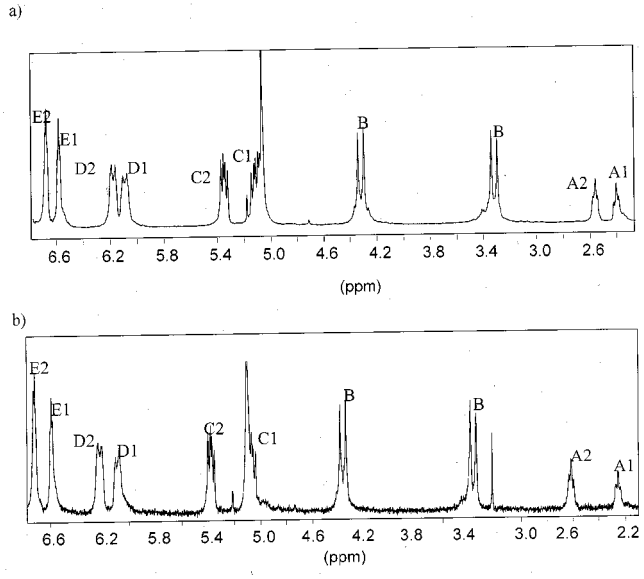


Figure 5. ^{1}H NMR spectra of the host **13** in the absence (a) and in the presence (b) of the guest **37**: A1: CHT, H-1; A2: CHT, H-1; B: $ArCH_2Ar$ (eq), $ArCH_2Ar$ (ax); C1: CHT, H-2,7; C2: CHT, H-2,7; D1: CHT, H-3,6; D2: CHT, H-3,6; E1: CHT, H-4,5; E2: CHT, H-4,5; CHT = 2,4,6-cycloheptatrienyl

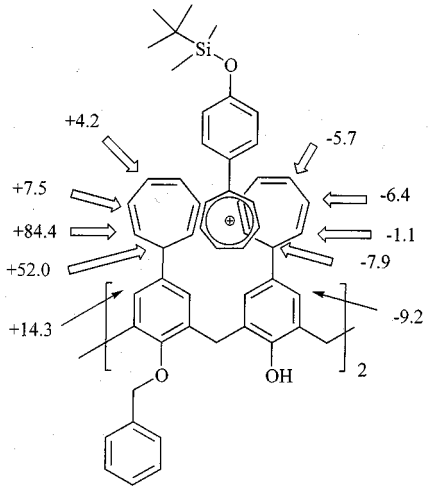


Figure 6. CIS values [Hz] observed for different protons in the complex **12/36** (300 MHz, ^{1}H NMR)

CIS values observed for the cycloheptatrienyl protons, compared to those of the aromatic protons, the cationic guest is located in the upper part of the calixarene cavity. Free horizontal rotation of the tropylium ion is suppressed, thus avoiding an averaging of the different shielding effects.

Conclusions

(1) Calix[4]arenes with different numbers of cycloheptatrienyl substituents on their upper rims are introduced here as a new class of hosts with enlarged hydrophobic cavities. The influence of the cycloheptatrienyl substituents on the complexation behaviour of the host depends on the guest. With the aryltropylium ion **37**, the complexation is enhanced by substituents on the upper rim in the order cycloheptatriene > H> *t*Bu. Apart from this function, the cycloheptatrienyl group may serve as a probe to monitor both the interaction with suitable guests and the conformation of the host, with the aid of induced chemical shifts of the different protons in the seven-membered ring.

(2) Generally, the number of substituents on the lower rim of calix[4]arenes has a large influence on the ligating properties of the host. The more rigid conformation, as exhibited by hosts such as those with two distal alkyl substituents and two free hydroxy groups on the lower rim, best matches the binding requirements.

(3) Cations of three families, quite different with respect to their shape and their charge distribution − namely ammonium, iminium and aryltropylium salts − are complexed by these hosts, with a clear preference shown for iminium and aryl tropylium salts; the latter being used in complexation studies of calixarenes for the first time. The intensity of the colour of the aryltropylium salts is strongly reduced on complexation; this affords an independent method for the determination of the association constants of these complexes.

(4) The acceptor strength of the aryltropylium ions has no influence on the strength of complexation. It is therefore assumed that π−π interactions such as the charge transfer interaction do not contribute substantially to the host-guest attraction.

Experimental Section

General Methods: Commercially available chemicals were used as received unless otherwise noted, solvents were dried according to standard procedures and all reactions were carried out under argon. − Column chromatography was carried out on 200 mesh silica gel (Merck). − All NMR spectra were recorded in $CDCl_3$ solution (TMS as internal standard), unless otherwise indicated, using a Bruker DPX 300 (300.13 MHz and 75.47 MHz, for ^{1}H and ^{13}C, respectively) spectrometer. CHT = cycloheptatrienyl substituent. − Mass spectra were obtained with a Concept 1H spectrometer (MSI).

NMR Studies: Binding studies were carried out by means of ^{1}H NMR titrations of guest solutions, usually at a concentration of 1 mM. Increasing amounts of the host were added, up to a host/guest ratio of 50:1 to 200:1 (20−80% saturation). Upfield shifts of

the resonances of different protons of the guest were monitored in order to calculate binding constants K and the upfield shift δ_{GC} of signals of the guests fully saturated by the host. Titration data points $\delta = f(R)$ were fitted to Equation (1) with $b = 1 + R + 1/K[H_0]$, $R = [H]/[G]$ (H = host, G = guest) and $\Delta\delta = \delta_G - \delta_{GC}$.[36]

$$\delta = \delta_G - (\Delta\delta/2)\,[b - (b^2 - 4R)^{1/2}] \quad (1)$$

Best fit parameters K and δ_{GC} were obtained in a nonlinear least-squares fitting procedure. Maximum errors for the K values were estimated as ± 15%.

X-ray Crystallographic Studies: Crystal data are given in Table 3. Compound **10** was obtained in monocrystalline form by slow concentration of the *tert*-butyl methyl ether solution, while suitable crystals of **21** were obtained by slow concentration of a $CHCl_3$ solution at room temperature. Single crystals of **37** were obtained by crystallisation from acetonitrile/ethyl acetate.

Data were collected with a STOE diffractometer, using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[38] The hydrogen atoms were included at calculated positions. All other non-hydrogen atoms were refined anisotropically. The X-STEP program was used for structure representations.

Syntheses: The syntheses of calixarenes **8** and **17** were described earlier.[16] Compounds **18** and **22** were synthesised according to procedures given in the relevant literature.[39]

5,11,17-Tri-*tert*-butyl-23-(cyclohepta-2,4,6-trienyl)-25,26,27,28-tetrahydroxycalix[4]arene (5): 5,11,17,23-tetra-*tert*-butylcalix[4]arene (Aldrich) was dealkylated according to ref.[40] A solution of 5,11,17-tri-*tert*-butylcalix[4]arene[41] (645 mg, 1.09 mmol) and 10 drops of acetic acid in toluene (50 mL) was treated with 7-methoxycyclohepta-1,3,5-triene (440 mg, 3.60 mmol), heating the mixture at 55 °C for 4 h with vigorous stirring. Stirring was continued for an additional 12 h at room temperature. The solution was concentrated under vacuum to a volume of about 10 mL. Methanol (100 mL) was added and the precipitate was filtered, washed with methanol and dried under vacuum. The crude product was recrystallised from methanol/toluene; yield 581 mg (78%), m.p. 280 °C. – ^{1}H NMR ($CDCl_3$): δ = 10.33 (s, 4 H, Ar-OH), 7.05 (m, 8 H, aromatic H), 6.70 (t, ^3J = 3 Hz, 2 H, CHT, H-4,5), 6.18 (m, 2 H, CHT, H-3,6), 5.27 (m, 2 H, CHT, H-2,7), 4.26 [br. m, 4 H, Ar-CH_2-Ar (ax)], 3.50 [d, 4 H, Ar-CH_2-Ar (eq)], 2.50 (t, ^3J = 5 Hz, 1 H, CHT, H-1), 1.21 [s, 18 H, C(CH_3)$_3$], 1.20 [s, 9 H, C(CH_3)$_3$]. – ^{13}C NMR ($CDCl_3$): δ = 147.7, 146.6, 144.5 (*Ar*-OH), 137.4 (*Ar*-CHT), 130.8 (CHT, C-4,5), 128.6, 127.9, 127.6, 127.4 (*Ar*-CH_2-*Ar*), 128.1 (CHT, C-3,6), 126.6, 126.1, 125.9, 125.8 (*Ar*-H), 124.2 (CHT, C-2,7), 44.6 (CHT, C-1), 34.0, 33.9 [*C*(CH$_3$)$_3$], 32.5, 32.4 (Ar-*C*H$_2$-Ar), 31.4, 31.3 [C(*C*H$_3$)$_3$]. – $C_{47}H_{54}O_4$ (682.95): calcd. C 82.66, H 7.97; found C 82.29, H 8.14.

5,17-Di-*tert*-butyl-11,23-bis(cyclohepta-2,4,6-trienyl)-25,26,27,28-tetrahydroxycalix[4]arene (6): 7-Methoxycyclohepta-1,3,5-triene (475 mg, 3.5 mmol) and 10 drops of acetic acid were added to a suspension of 5,17-di-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene[41] (500 mg, 0.9 mmol) in toluene (50 mL). The mixture was heated to 50 °C for 2 h, stirred at room temperature for an additional 20 h and then poured into methanol (1 L) to give **6** (450 mg, 72%); m.p. 160–162 °C. – ^{1}H NMR ($CDCl_3$): δ = 10.31 (s, 4 H,

Table 3. Crystallographic details for the X-ray analyses of **10**, **21** and **37**[37]

Compound	**10**	**21**	**37**
Empirical formula	$C_{84}H_{116}O_{14}$	$C_{60}H_{80}O_{12}$	$C_{15}H_{16}ClNO_4$
Molecular mass	1349.77	993.24	309.74
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	*C*2/*c*	*C*2/*c*	*P*21*cn*
Unit cell			
a [Å]	26.667(4)	25.432(6)	10.2084(14)
b [Å]	14.785(3)	12.0131(15)	6.6872(7)
c [Å]	21.220(4)	25.550(6)	20.961(3)
α [°]	90	90	90
β [°]	100.57(2)	133.041(16)	90
γ [°]	90	90	90
Unit cell volume [Å^3]	8225(13)	5705(2)	1430.9(3)
d (calcd.) [g·cm^{-3}]	1.090	1.156	1.438
Z	4	4	4
Temperature [K]	180	180	180
Linear absorption μ [mm^{-1}]	0.073	0.079	0.282
F(000)	2928	2144	648
Radiation [Å]	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)
Monochromator	graphite		
Crystal size [mm]	0.44 × 0.20 × 0.18	0.96 × 0.94 × 0.54	0.52 × 0.12 × 0.08
Transmission range	0.9870–0.9687	0.9585–0.9278	0.9778–0.8671
θ range for data coll. [°]	2.26–25.25	1.74–25.25	2.79–25.25
Reciprocal lattice segment	$-31 \le h \le 32$	$-30 \le h \le 30$	$-12 \le h \le 12$
	$-18 \le k \le 18$	$0 \le k \le 14$	$-8 \le k \le 8$
	$-25 \le l \le 25$	$-30 \le l \le 30$	$-25 \le l \le 25$
Data/restraints/parameters	8017/10/450	5160/0/446	2576/11/190
No. of refls. collected	25882	5244	8838
No. of refls. unique	8017	5160	2576
R_{int}	0.0775	0.0298	0.0575
Goodness-of-fit on F^2	0.939	1.079	0.985
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0651	*R*1 = 0.0563	*R*1 = 0.0876
	*wR*2 = 0.1604	*wR*2 = 0.1356	*wR*2 = 0.2230
Final *R* indices (all)	*R*1 = 0.1182	*R*1 = 0.0801	*R*1 = 0.1130
	*wR*2 = 0.1858	*wR*2 = 0.1613	*wR*2 = 0.2511
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e Å^{-3}]	0.661, −0.400	0.450, −0.349	1.123, −0.343

Ar-O*H*), 7.06 (s, 4 H, aromatic H), 7.04 (s, 4 H, aromatic H), 6.69 (m, 4 H, CHT, H-4,5), 6.18 (m, 4 H, CHT, H-3,6), 5.26 (m, 4 H, CHT, H-2,7), 4.28 [d, ^1J = 14 Hz, 4 H, Ar-CH_2-Ar (ax)], 3.51 [d, ^1J = 14 Hz, 4 H, Ar-CH_2-Ar (eq)], 2.49 (t, ^3J = 10 Hz, 2 H, CHT, H-1), 1.21 [s, 18 H, C(CH_3)$_3$]. − ^{13}C NMR ($CDCl_3$): δ = 153.1 (*Ar*-OH), 148.8 (*Ar*-CHT), 141.4 [*Ar*-C(CH$_3$)$_3$], 130.8 (CHT, C-4,5), 128.9, 128.1 (*Ar*-CH$_2$-*Ar*) 126.7, (*Ar*-H) 125.8 (CHT, *C*-3,6), 124.1 (CHT, C-*2*,7), 44.4 (CHT, C$_1$), 31.6 (Ar-*C*H$_2$-Ar), 31.4 [C(*C*H$_3$)$_3$]. − $C_{50}H_{52}O_4 \times H_2O$ (734.98): calcd. C 81.70, H 7.42; found C 81.44, H 7.73.

5,17-Bis(cyclohepta-2,4,6-trienyl)-25,26,27,28-tetrahydroxy-11,23-bis(2-propenyl)calix[4]arene (7): 7-Methoxycyclohepta-1,3,5-triene (850 mg, 6.96 mmol) and 10 drops of acetic acid were added to a suspension of 5,17-bis(2-propenyl)-25,26,27,28-tetrahydroxycalix[4]arene[42] (976 mg, 1.93 mmol) in toluene (80 mL). The mixture was heated to 50 °C for 14 h with stirring and then concentrated under vacuum to a volume of 10 mL. MeOH (100 mL) was added, affording **7**; yield 910 mg (69%), m.p. 184−190 °C. − ^{1}H NMR ($CDCl_3$): δ = 10.24 (s, 4 H, Ar-O*H*), 7.04 (s, 4 H, aromatic H), 6.85 (s, 4 H, aromatic H), 6.71 (m, 4 H, CHT, H-4,5), 6.21 (m, 4 H, CHT, H-3,6), 5.85 (m, 2 H, CH$_2$C*H*=CH$_2$), 5.29 (m, 4 H, CHT, *H*-2,7), 5.05 (m, 4 H, CH$_2$CH=C*H*$_2$), 4.26 [br. d, 4 H, Ar-C*H*$_2$-Ar (ax)], 3.50 [br. d, 4 H, Ar-C*H*$_2$-Ar (eq)], 3.17 (d, ^3J = 6 Hz, 4 H, C*H*$_2$CH=CH$_2$), 2.53 (t, ^3J = 5 Hz, 2 H, CHT, H-1). − ^{13}C NMR ($CDCl_3$): δ = 147.6, 147.0 (*Ar*-OH), 137.5 (CH$_2$*C*H=CH$_2$), 137.4, 133.6, 128.4, 128.2 (Ar), 130.9 (CHT, C-4,5), 129.0, 128.0 (*Ar*H), 126.6 (CHT, C-2,7), 124.2 (CHT, C-3,6), 115.6 (CH$_2$CH=*C*H$_2$), 44.6 (CHT, *C*-1), 39.3 (*C*H$_2$CH=CH$_2$), 32.0 (Ar*C*H$_2$Ar). − $C_{48}H_{44}O_4 \times H_2O$ (702.89): calcd. C 82.02, H 6.60; found C 81.75, H 6.49.

25,26,27,28-Tetrabutoxy-5,11,17-tri-*tert*-butyl-23-(cyclohepta-2,4,6-trienyl)calix[4]arene (9): Aqueous NaOH (0.5 mL, 50%) was added to **5** (100 mg, 0.15 mmol) in toluene (12 mL). The mixture was treated with *n*-bromobutane (685 mg, 5 mmol) in the presence of tetrabutylammonium bromide (24 mg, 0.074 mmol), with stirring, and heated to 55 °C for 14 h. After addition of water (100 mL), neutralisation (HCl), extraction of the aqueous phase with dichloromethane, drying of the combined organic phases ($MgSO_4$), and solvent removal, the crude product was purified by column chromatography (eluent dichloromethane/hexane, 1:9) to give **9**, yield 60 mg (44%), m.p. 66−70 °C. − ^{1}H NMR ($CDCl_3$) δ = 6.95 (m, 4 H, Ar-*H*), 6.63 (m, 2 H, CHT, H-4,5), 6.58 (s, 2 H, aromatic H), 6.46 (s, 2 H, aromatic H), 6.07 (m, 2 H, CHT, H-3,6), 5.05 (m, 2 H, CHT, H-2,7), 4.45 [d, ^1J = 12 Hz, 2 H, Ar-C*H*$_2$-Ar (ax)], 4.42 [d, ^1J = 12 Hz, 2 H, Ar-C*H*$_2$-Ar (ax)], 3.97 (t, ^3J = 8 Hz, 4 H, Ar-OC*H*$_2$-), 3.81 (m, 4 H, Ar-OC*H*$_2$-), 3.13 [d, ^1J = 12 Hz, 2 H, Ar-C*H*$_2$-Ar (eq)], 3.11 [d, ^1J = 12 Hz, 2 H, Ar-C*H*$_2$-Ar (eq)], 2.18 (t, ^3J = 5 Hz, 1 H, CHT, H-1), 1.99 (m, 8 H, OCH$_2$C*H*$_2$-), 1.54 (m, 8 H, -OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.23 [s, 18 H, C(CH_3)$_3$], 1.01 (t, 12 H, *J* = 7 Hz, OCH$_2$CH$_2$CH$_2$C*H*$_3$), 0.81 [s, 9 H, C(CH_3)$_3$]. − $C_{63}H_{86}O_4 \times H_2O$ (925.39): calcd. C 81.77, H 9.59; found C 81.98, H 9.43.

25,26,27,28-Tetrakis[(*tert*-butoxycarbonyl)methoxy]-5,17-di-*tert*-butyl-11,23-bis(cyclohepta-2,4,6-trienyl)calix[4]arene (10): NaH (0.3 g, 12 mmol) was added to **6** (0.60 g, 0.8 mmol) in DMF (15 mL) and THF (75 mL) under argon. The mixture was heated to 70 °C and *tert*-butyl bromoacetate (2.9 g, 14.9 mmol) was slowly added, with vigorous stirring. After refluxing for 20 h, the suspension was worked up as reported for compound **9**. The residue obtained after concentration under vacuum was recrystallised from *tert*-butyl methyl ether (MTBE) to give **10**; yield 470 mg, 50%, m.p. > 350 °C. − ^{1}H NMR ($CDCl_3$): δ = 6.91 (s, 8 H, aromatic H), 6.54 (m, 4 H, CHT, H-4,5), 5.99 (m, 4 H, CHT, H-3,6), 4.90 (m, 4 H, CHT, H-2,7), 4.89 [d, ^1J = 13 Hz, 4 H, Ar-C*H*$_2$-Ar (ax)], 4.88 (s, 4 H, O-C*H*$_2$-CO), 4.64 (s, 4 H, OC*H*$_2$-CO), 3.21 [d, ^1J = 13 Hz, 4 H, Ar-C*H*$_2$-Ar (eq)], 2.25 (t, ^3J = 6 Hz, 2 H, CHT, H-1), 1.49 [s, 18 H, C(C*H*$_3$)$_3$], 1.44 [s, 18 H, C(C*H*$_3$)$_3$], 1.19 [s, 18 H, C(C*H*$_3$)$_3$]. − ^{13}C NMR ($CDCl_3$): δ = 170.6 (C=O), 170.5 (C=O), 151.4 (*Ar*-O), 150.7 (*Ar*-O), 148.8 (*Ar*-CHT), 141.4 [*Ar*-C(CH$_3$)$_3$], 134.8, 134.0 (*Ar*-CH$_2$-*Ar*), 130.9 (CHT, C-4,5), 128.2, 126.2 (*Ar*-H),125.2 (CHT, C-3,6), 124.5 (CHT, C-2,7), 81.9, 81.7 [O*C*(CH$_3$)$_3$], 61.9, 61.3 (O*C*H$_2$CO), 44.4 (CHT, C-1), 34.9 [Ar-*C*(CH$_3$)$_3$], 34.4 [Ar-*C*(CH$_3$)$_3$], 30.4 (Ar-*C*H$_2$-Ar), 28.1 [OC(*C*H$_3$)$_3$]. − $C_{74}H_{92}O_{12} \times$ 2MTBE (1349.84): calcd. C 74.72, H 8.73; found C 74.68, H 8.41.

25-[(*tert*-Butoxycarbonyl)methoxy]-5,11,17-tris(cyclohepta-2,4,6-trienyl)-26,27,28-trihydroxycalix[4]arene (11): 26-(*tert*-Butoxycarbonyl)calix[4]arene[43] (200 mg, 0.37 mmol) in MeCN (80 mL) was treated with 7-methoxycycloheptatriene (300 mg, 2.46 mmol) as reported for compound **5**. After evaporation of the solvent, the residue was immediately subjected to flash chromatography (eluent: dichloromethane/hexane/ethyl acetate, 1:1:0.1) to give 224 mg (75%) **11**; m.p. 97 °C. − ^{1}H NMR ($CDCl_3$): δ = 10.06 (s, 1 H, Ar-O*H*), 9.28 (s, 2 H, Ar-O*H*), 7.06 (m, 8 H, aromatic H), 6.89 (t, ^3J = 7 Hz, 1 H, aromatic H), 6.69 (m, 6 H, CHT, *H*-4,5), 6.17 (m, 6 H, CHT, *H*-3,6), 5.30 (m, 6 H, CHT, H-2,7), 4.80 (s, 2 H, OC*H*$_2$-CO), 4.55 [d, ^1J = 13 Hz, 2 H, Ar-C*H*$_2$-Ar (ax)], 4.35 [d, ^1J = 13 Hz, 2 H, Ar-C*H*$_2$-Ar (ax)], 3.47 [d, ^1J = 13 Hz, 2 H, Ar-C*H*$_2$-Ar (eq)], 3.46 [d, ^1J = 13 Hz, 2 H, Ar-C*H*$_2$-Ar (eq)], 2.49 (br. t, ^3J = 5 Hz, 3 H, CHT, H-1), 1.64 [s, 9 H, C(C*H*$_3$)$_3$]. − ^{13}C NMR ($CDCl_3$): δ = 168.7 (-COO, *C*-51), 152.5, 149.2, 148.5 (*C*-25,26,27,28), 136.8, 136.2, 134.1, 128.8, 128.6, 128.5 (C- 1,3,5,7,9,11,13,15,17,19,21), 130.8, 130.7 (*C*-32,33,39,40,46,47), 129.5, 128.0, 127.9, 127.4, 126.2 (C-4,6,10,12,16,18,22,23,24), 126.8, 126.7, 126.6, (C-30,35,37,42,44,49), 124.0 (C-31,34,38,41,45,48), 83.4 [*C*(CH$_3$)$_3$], 72.7 (ArO-*C*H$_2$-CO), 44.5 (C-29,36,43), 32.3, 31.9 (Ar-*C*H$_2$-Ar, C-2,8,14,20), 28.2 [C(*C*H$_3$)$_3$, C-53,54,55]. − $C_{55}H_{52}O_6$ (809.02): calcd. C 81.62, H 6.48; found C 81.65, H 6.64.

25,27-Bis(benzyloxy)-5,11,17,23-tetrakis(cyclohepta-2,4,6-trienyl)-26,28-dihydroxycalix[4]arene (12): Compound **8** (0.6 g, 0.765 mmol) in MeCN (180 mL) was treated with K_2CO_3 (140 mg) under reflux. Benzyl bromide (432 mg, 2.5 mmol) was added and the reaction mixture was heated for 4 h. After further stirring for 14 h at room temperature, the solvent was removed under vacuum. The residue was purified by column chromatography (eluent: *n*-hexane/dichloromethane, 1:1); yield 373 mg (51%), m.p. 111−113 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.92 (s, 2 H, Ar-O*H*), 7.66 (m, 4 H, *Ar*-benzyl), 7.36 (m, 6 H, *Ar*-benzyl), 7.02 (s, 4 H, aromatic H), 6.92 (s, 4 H, aromatic H), 6.69 (m, 4 H, CHT, H-4,5), 6.60 (m, 4 H, CHT, H-4,5), 6.19 (m, 4 H, CHT, H-3,6), 6.11 (m, 4 H, CHT, H-3,6), 5.36 (m, 4 H, CHT, H-2,7), 5.14 (m, 4 H, CHT, H-2,7), 5.09 (s, 4 H, benzyl), 4.34 [d, ^1J = 13 Hz, 4 H, Ar-C*H*$_2$-Ar (ax)], 3.34 [d, ^1J = 13 Hz, 4 H, Ar-C*H*$_2$-Ar (eq)], 2.58 (t, ^3J = 5 Hz, 2 H, CHT, H-1), 2.43 (t, ^3J = 5 Hz, 2 H, CHT, H-1). − ^{13}C NMR ($CDCl_3$): δ = 151.9 (*Ar*-OR) 150.9 (*Ar*-OH), 140.2 (*C*H$_2$-benzyl), 136.7 (*Ar*-CHT), 134.3 (*Ar*-CH$_2$-*Ar*), 130.8 (CHT, C-4,5), 130.7 (CHT, C-4,5), 128.7 (*Ar*-H), 128.07 (*Ar*-H), 127.6 (CHT, C-3,6), 127.5 (CHT, C-3,6), 127.2, 126.0 (benzyl), 124.1 (CHT, C-2,7), 124.0 (CHT, C-2,7), 78.4 (*C*H$_2$-benzyl), 44.4 (CHT, C-1), 44.4 (CHT, C-1), 31.6 (Ar-*C*H$_2$-Ar). − MS (FAB, nitrophenyl octyl ether): 965 [M + 1]$^+$. − $C_{70}H_{60}O_4$ (965.25): calcd. C 87.10, H 6.27; found C 86.75, H 6.55.

25,27-Bis[(*tert*-butoxycarbonyl)methoxy]-5,11,17,23-tetrakis(cyclohepta-2,4,6-trienyl)-26,28-dihydroxycalix[4]arene (13): Compound **8** (0.60 g, 0.765 mmol), *tert*-butyl bromoacetate (0.5 g, 2.5 mmol) and

K_2CO_3 (0.15 g, 0.765 mmol) were treated as for compound **12**. Column chromatography was performed with *n*-hexane/dichloromethane (1:3) as eluent; yield 0.51 g (51%), m.p. 135−140 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.81 (s, 2 H, Ar-O*H*), 7.02 (s, 4 H, aromatic H), 6.92 (s, 4 H, Ar-*H*), 6.70 (m, 4 H, CHT, H-4,5), 6.61 (m, 4 H, CHT, H-4,5), 6.22 (m, 4 H, CHT, H-3,6), 6.12 (m, 4 H, CHT, H-3,6), 5.38 (m, 4 H, CHT, H-2,7), 5.15 (m, 4 H, CHT, H-2,7), 4.65 (s, 4 H, -OCH_2CO), 4.54 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (ax)], 3.38 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (eq)], 2.56 (t, ^3J = 5 Hz, 2 H, CHT, H-1) 2.43 (t, ^3J = 5 Hz, 2 H, CHT, H-1), 1.48 [s, 18 H, C(CH_3)$_3$]. − ^{13}C NMR ($CDCl_3$): δ = 168.0 (C=O), 151.8 (Ar-OR), 140.2 (Ar-OH), 134.2, 133.2 (*Ar*-CH_2-*Ar*), 130.8, 130.8 (CHT, C-4,5), 128.2 (*Ar*-CHT), 127.5, 127.2 (CHT, C-3,6), 126.1 (*Ar*-H), 124.2, 124.0 (CHT, C-2,7), 82.4 [*C*(CH_3)$_3$], 73.2 (-O*C*H_2CO-), 44.5 (CHT, C-1), 44.4 (CHT, C-1), 32.0 (Ar-*C*H_2-Ar), 28.2 [-OC(*C*H_3)$_3$]. − $C_{68}H_{68}O_8 \times 2H_2O$ (1049.32): calcd. C 77.83, H 6.91; found C 77.55, H 7.06.

25,27-Dibutoxy-5,11,17,23-tetrakis(cyclohepta-2,4,6-trienyl)-26,28-dihydroxycalix[4]arene (14): As for compound **12**, by refluxing a mixture of **8** (1.2 g, 1.5 mmol), 1-bromobutane (0.7 g, 5.1 mmol) and K_2CO_3 (0.56 g, 4.053 mmol) in MeCN (200 mL) for 20 h; column chromatography (eluent: *n*-hexane/dichloromethane, 1:2); yield 0.4 g (30%); m.p. > 350 °C. − ^{1}H NMR ($CDCl_3$): δ = 8.40 (s, 2 H, Ar-O*H*), 6.96 (s, 4 H, aromatic H), 6.90 (s, 4 H, aromatic H), 6.63 (s, 4 H, CHT, H-4,5), 6.56 (s, 4 H, CHT, H-4,5), 6.11 (m, 4 H, CHT, H-3,6), 6.05 (m, 4 H, CHT, H-3,6), 5.30 (m, 4 H, CHT, H-2,7), 5.13 (m, 4 H, CHT, H-2,7), 4.30 [d, ^1J = 12 Hz, 4 H, Ar-CH_2-Ar (ax)], 3.97 (t, ^1J = 5 Hz, 4 H, -OCH_2CH$_2$-), 3.32 [d, ^1J = 12 Hz, 4 H, Ar-CH_2-Ar (eq)], 2.49 (t, ^3J = 5 Hz, 2 H, CHT, H-1), 2.36 (t, ^3J = 5 Hz, 2 H, CHT, H-1), 2.01 (m, 4 H, -CH_2CH$_2$CH$_3$), 1.73 (m, 4 H, -CH_2CH$_3$), 1.04 (t, ^3J = 7 Hz, 6 H, -CH$_3$). − ^{13}C NMR ($CDCl_3$): δ = 152.0 (Ar-O-), 140.2 (Ar-OH), 134.4, 133.7 (*Ar*-CH_2-*Ar*), 130.8 (CHT, C-4,5), 130.7 (CHT, C-4,5), 127.5 (CHT, C-3,6), 127.3 (CHT, C-4,5), 126.0 (*Ar*-H), 124.1 (CHT, C-2,7), 124.0 (CHT, C-2,7), 75.5 (Ar-O-*C*H$_2$), 44.5 (CHT, C-1), 32.3 (Ar-*C*H_2-Ar), 26.9 (*C*H_2-CH$_2$-CH$_3$), 19.4 (*C*H_2-CH$_3$), 14.1 (-CH$_3$). − $C_{64}H_{64}O_4 \times 5H_2O$ (987.29): calcd. C 77.86, H 7.56; found C 77.39, H 7.27.

5,11,17,23-Tetrakis(cyclohepta-2,4,6-trienyl)-25,27,26,28-tetrakis-[(ethoxycarbonyl)methoxy]calix[4]arene (15): A suspension of **8** (0.52 g, 0.66 mmol), ethyl bromoacetate (0.83 g, 5.35 mmol) and K_2CO_3 (0.55 g, 3.98 mmol) in dry acetone (40 mL) was heated under reflux for 6 d. After cooling and filtration, the solvent was removed under vacuum. The residue was purified by recrystallisation from ethanol to give 0.46 g of **15** (62%), m.p. 165−7 °C. − ^{1}H NMR ($CDCl_3$): δ = 6.75 (s, 8 H, aromatic H), 6.62 (m, 8 H, CHT, H-4,5), 6.10 (m, 8 H, CHT, H-3,6), 5.11 (m, 8 H, CHT, H-2,7), 4.92 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (ax)], 4.82 (s, 8 H,-OCH_2CO), 4.23 (q, ^3J = 7 Hz, 8 H, -CH_2CH$_3$), 3.25 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (eq)], 2.45 (t, ^3J = 7 Hz, 4 H, CHT, H-1) 1.31 (t, ^3J = 7 Hz, 12 H, -CH$_3$). − ^{13}C NMR ($CDCl_3$): δ=170.3 (C=O), 154.2 (Ar-O), 138.1 (*Ar*-CH_2-*Ar*), 134.4 (*Ar*-CHT), 130.8 (CHT, C-4,5), 127.5 (CHT, C-3,6), 126.6 (*Ar*-H), 124.2 (CHT, C-2,7), 71.4 (O*C*H$_2$CO), 60.5 (CO*C*H$_2$CH$_3$), 44.0, (CHT, C-1), 31.7 (Ar-*C*H$_2$-Ar), 14.2 (OCH$_2$*C*H$_3$). − $C_{72}H_{72}O_{12}$ (1129.36): calcd. C 76.57, H 6.43; found C 76.65, H 6.51.

25,26,27,28-Tetrakis[(*tert*-butoxycarbonyl)methoxy]-5,11,17,23-tetrakis(cyclohepta-2,4,6-trienyl)calix[4]arene (16): Compound **8** (0.95 g, 1.21 mmol) in DMF (15 mL) and THF (75 mL) was deprotonated with NaH (0.8 g, 33.3 mmol). The refluxing mixture was treated with *tert*-butyl bromoacetate (7.3 g, 37.4 mmol) and refluxed for an additional 20 h. After cooling, dichloromethane (200 mL) and HCl (10%, 60 mL) were added. The organic phase was treated with NaCl solution (satd.) and water. The organic layer was dried ($MgSO_4$) and the solvent removed under vacuum. The residue was recrystallised from methanol to give 0.75 g (50%) of **16**, m.p. 173 °C. − ^{1}H NMR ($CDCl_3$): δ = 6.66 (s, 8 H, aromatic H), 6.55 (m, 8 H, CHT, H-4,5), 6.02 (m, 8 H, CHT, H-3,6), 5.04 (m, 8 H, CHT, H-2,7), 4.87 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (eq)], 4.68 (s, 8 H, O-CH_2CO), 3.17 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (ax)], 2.38 (t, ^3J = 6 Hz, 4 H, CHT, H-1), 1.41 [s, 36 H, C(CH$_3$)$_3$]. − ^{13}C NMR ($CDCl_3$): δ = 169.4 (C=O), 154.5 (Ar-O), 137.8 (*Ar*-CH_2-*Ar*), 134.5 (*Ar*-CHT), 130.8 (CHT, C-4,5), 127.3 (CHT, C-3,6), 126.8 (Ar-H), 124.1 (CHT, C-2,7), 80.9 [*C*(CH$_3$)$_3$], 72.0 (O*C*H$_2$CO), 44.1, (CHT, C-1), 31.9 (Ar-*C*H$_2$-Ar), 28.2 [-OC(*C*H$_3$)$_3$]. − $C_{80}H_{88}O_{12} \times 4H_2O$ (1313.64): calcd. C 73.15, H 7.37; found C 73.18, H 7.27.

25,26,27,28-Tetrabutoxy-5,11,17,23-tetrakis(cyclohepta-2,4,6-trienyl)calix[4]arene (17): Compound **8** (0.1 g, 0.235 mmol) in DMF (10 mL) was deprotonated with NaH (0.3 g, 7.5 mmol) at 70 °C. 1-Bromobutane (0.3 g, 2.97 mmol) was added. The reaction mixture was stirred for 1 h at 70 °C and for an additional 12 h at room temperature. The reaction was quenched by addition of methanol (3 mL). The solution was poured into water (50 mL), saturated with NaCl, and extracted with diethyl ether. After drying of the organic layer, the solvent was removed. The residue was purified by column chromatography (eluent: dichloromethane/*n*-hexane, 3:4) to give 0.17 g (73%) of **17**, m.p. > 350 °C, − ^{1}H NMR (C_6D_6): δ = 6.89 (s, 8 H, aromatic H), 6.55 (m, 8 H, CHT, H-4,5), 6.10 (m, 8 H, CHT, H-3,6), 5.32 (m, 8 H, CHT, H-2,7), 4.61 [d, ^1J = 12 Hz, 4 H, Ar-CH_2-Ar (eq)], 3.97 (t, ^3J = 7 Hz, 8 H, -O-CH_2CH$_2$CH$_2$CH$_3$), 3.20 [d, ^1J = 12 Hz, 4 H, Ar-CH_2-Ar (ax)], 2.78 (t, ^3J = 5 Hz, 4 H, CHT, H-1), 2.01 (m, 8 H, -CH_2-CH$_2$-CH$_3$), 1.43 (m, 8 H, -CH_2-CH$_3$), 1.01 (t, ^3J = 7 Hz, 12 H, CH$_3$). − ^{13}C NMR ($CDCl_3$): δ= 138.0 (*Ar*-CHT), 135.2 (*Ar*-H), 131.1 (CHT, C-4,5), 127.0 (CHT, C-3,6), 124.6 (CHT, C-2,7), 75.4 (Ar-O-*C*H$_2$), 44.8 (CHT, C-1), 32.8 (-*C*H$_2$-CH$_2$-CH$_3$), 31.9 (Ar-*C*H$_2$-Ar), 19.7 (*C*H$_2$-CH$_3$), 14.3 (-CH$_3$). − $C_{72}H_{72}O_4$ (1001.37): calcd. C 86.36, H 7.25; found C 86.12, H 7.63.

25,27-Bis[(*tert*-butoxycarbonyl)methoxy]-26,28-dihydroxycalix-[4]arene (19): As for compound **13**, from 25,26,27,28-tetrahydroxycalix[4]arene (0.212 g, 0.5 mmol), *tert*-butyl bromoacetate (0.33 g, 1.68 mmol) and K_2CO_3 (0.07 g, 0.5 mmol). The crude product was purified by column chromatography (eluent: dichloromethane/cyclohexane, 3:1) to give 0.25 g (75%) of **19**, m.p. 196 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.66 (s, 2 H, Ar-O*H*), 7.04 (d, ^3J = 7 Hz, 4 H, Ar-H), 6.88 (d, ^3J = 7 Hz, 4 H, Ar-H), 6.73 (t, ^3J = 7, 2 H, Ar-H), 6.64 (t, ^3J = 7 Hz, 2 H, Ar-H), 4.58 (s, 4 H, -OCH$_2$CO), 4.47 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (ax)], 3.37 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (eq)], 1.56 [s, 18 H, -C(CH$_3$)$_3$]. − ^{13}C NMR: δ = 167.8 (C=O), 153.1 (Ar-OH), 152.5 (Ar-O), 133.0 (*Ar*-CH_2-*Ar*), 129.0, 128.4 (Ar-H), 128.0 (*Ar*-CH_2-*Ar*), 125.4 (Ar-H), 118.7 (Ar-H), 82.5 [O-*C*(CH$_3$)$_3$], 73.2 (O-*C*H$_2$-CO), 31.5 (Ar-*C*H$_2$-Ar), 28.1 [-OC(*C*H$_3$)$_3$]. − $C_{40}H_{44}O_8 \times H_2O$ (670.80): calcd. C 71.62, H 6.91; found C 71.78, H 6.95.

26,28-Dibutoxy-5,17-di-*tert*-butyl-25,27-dihydroxycalix-[4]arene (20): According to the literature,[42] 25,27-dibutoxy-5,11,17,23-tetra-*tert*-butyl-26,28-dihydroxycalix[4]arene (1.012 g, 1.33 mmol) was added to a suspension of $AlCl_3$ (0.500 g, 3.7 mmol) in anhydrous toluene (75 mL), and the mixture was stirred for 6 h at room temperature. The reaction was quenched by addition of water (200 mL) and extracted with dichloromethane. After drying of the organic layer, the solvent was removed. The residue was purified by column chromatography (eluent: dichloromethane/cyclohexane, 1:2) to give 0.479 g (56%) of **20**, m.p. 176 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.99 (s, 2 H, Ar-O*H*), 6.96 (d, ^3J = 7 Hz, 4 H, aromatic H), 6.79 (s, 4 H, aromatic H), 6.55 (t, ^3J = 7 Hz, 2 H, ArH), 4.24 [d, ^1J = 12 Hz,

4 H, ArCH_2Ar (ax)], 3.92 (t, ^3J = 6 Hz, 4 H, OCH_2), 3.27 [d, ^1J = 12 Hz, 4 H, ArCH_2Ar (eq)], 1.96 (m, 4 H, OCH$_2$CH_2), 1.67 (m, 4 H, O(CH$_2$)$_2$CH_2), 1.00 (t, ^3J = 7 Hz, 6 H, O(CH$_2$)$_3$CH_3), 0.96 (s, 18 H, C(CH$_3$)$_3$]. – ^{13}C NMR (CDCl$_3$): δ = 153.1(Ar-OH), 150.1 (Ar-OR), 147.0 [*Ar*-C(CH$_3$)$_3$], 132.7, 128.5 (*Ar*CH$_2$*Ar*), 128.2, 125.6 (ArH), 119.0 (ArH), 76.3 (O*C*H$_2$), 34.0 [*C*(CH$_3$)$_3$], 32.2 (OCH$_2$*C*H$_2$), 31.6 (Ar*C*H$_2$Ar), 31.2 [C(*C*H$_3$)$_3$], 19.4 [O(CH$_2$)$_2$*C*H$_2$], 14.1 [O(CH$_2$)$_3$*C*H$_3$]. – $C_{44}H_{56}O_4$ (648.93): calcd. C 81.44, H 8.70; found C 81.19, H 8.42.

5,17-Di-*tert*-butyl-25,26,27,28-tetrakis[(*tert*-butoxycarbonyl)-methoxy]calix[4]arene (21): According to the procedure for the synthesis of compound **16**, from 5,17-di-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene[41] (0.90 g, 1.7 mmol), *tert*-butyl bromoacetate (4.3 g, 21.9 mmol) and NaH (0.40 g, 16.7 mmol). The crude product was recrystallised from *tert*-butyl methyl ether to give **20**, yield 0.7 g (45%), m.p. 203–205 °C. – ^{1}H NMR (CDCl$_3$): δ = 7.02 (s, 4 H, aromatic H), 6.28 (t, ^3J = 7 Hz, 2 H, aromatic H), 6.12 (d, ^3J = 7 Hz, 4 H, Ar-H), 4.85 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (ax)], 4.77 (s, 4 H, -OCH_2COO), 4.45 (s, 4 H, -OCH_2COO), 3.18 [d, ^1J = 13 Hz, 4 H, Ar-CH_2-Ar (ax)], 1.49 (s, 18 H, -OC(CH$_3$)$_3$], 1.42 (s, 18 H, -OC(CH$_3$)$_3$ 1.31 [s, 18 H -C(CH$_3$)$_3$]. – ^{13}C NMR (CDCl$_3$): δ = 169.9, 168.9 (C=O), 155.3, 154.3 (Ar-O), 144.8 [Ar-*C*(CH$_3$)$_3$], 135.2, 133.3 (*Ar*-CH$_2$-*Ar*), 127.6, 125.8 (Ar-H), 122.6 (Ar-H), 81.2, 80.5 [-O-*C*(CH$_3$)$_3$], 72.4, 71.3 (O-*C*H$_2$-CO), 34.0 [Ar-*C*(CH$_3$)$_3$], 31.9 (Ar-*C*H$_2$-Ar), 31.7 [Ar-C(*C*H$_3$)$_3$], 28.1 [-O-C(*C*H$_3$)$_3$]. – $C_{60}H_{56}O_{12}$ (969.10): calcd. C 74.36, H 5.83; found C 74.12, H 5.85.

Aryl Tropylium Salts: Compounds **24**, **25**, **35** and **37** were obtained according to ref.[44]

{4-[(*tert*-Butyldimethylsilyl)oxy]phenyl}tropylium Perchlorate (36). – (a) 1-Bromo-4-[(*tert*-butyldimethyl)silyloxy]benzene: 4-Bromophenol (29 g, 168 mmol) in THF (60 mL) was treated with *tert*-butylchlorodimethylsilane (25.5 g, 169 mmol) and triethylamine (25 mL). After refluxing for 6 h and cooling to room temperature, the solution was poured into a mixture of water (60 mL) and dichloromethane (200 mL). The combined organic layers were treated with NaOH (0.1 M), dried and concentrated under vacuum. The residue was purified by distillation, b.p. 92 °C (1.4 × 10^{-2} mbar), yield 40 g (83%). – ^{1}H NMR (CDCl$_3$): δ = 7.32 (d, 2 H, aromatic H), 6.72 (d, 2 H, aromatic H), 0.99 [s, 9 H, C(CH$_3$)$_3$], 0.21 (s, 6 H, CH$_3$). – ^{13}C NMR (CDCl$_3$): δ = 165.8, 132.3, 121.9, 113.6 (Ar), 25.6 18.1, [*C*(CH$_3$)$_3$], –4.5 (CH$_3$). – MS: 288 [M$^+$]. – **(b) 4-{4-[(*tert*-Butyldimethylsilyl)oxy]phenyl}-1,3,5-cycloheptatriene:** The Grignard compound from 1-bromo-4-[(*tert*-butyldimethylsilyl)oxy]benzene (30 g, 104 mmol) and Mg (2.55 g, 104 mmol) in THF (80 mL) was treated with 7-methoxy-1,3,5-cycloheptatriene at 60 °C. The reaction mixture was worked up by addition of a dilute NaHCO$_3$ solution. The aqueous solution was extracted with dichloromethane. The organic layer was separated, dried and concentrated. The residue was distilled to give 18.5 g (61%) of the product, b.p. 158 °C (1.6 × 10^{-2} mbar). – ^{1}H NMR (CDCl$_3$): δ = 7.32 (d, 2 H, aromatic H), 6.85 (d, 1 H, CHT, H-5), 6.81 (d, 2 H, aromatic H), 6.40 (d, 1 H, CHT, H-3), 6.23 (m, 1 H, CHT, H-6), 5.44 (m, 2 H, CHT, H-1,7), 2.29 (t, 2 H CHT, H-1), 0.99 [s 9 H, C(CH$_3$)$_3$], 0.20 (s, 6 H, CH$_3$). – ^{13}C NMR δ = 155.1 (Ar-OSi-), 142.5 (CHT, C-3), 135.4, 127.9, (Ar), 127.4 (CHT, C-5), 126.6 (CHT, C-3,6), 121.3 (CHT, C-2,7), 119.9 (Ar-H), 27.9, (CHT, C-1), 25.7, 18.2 [*C*(CH$_3$)$_3$], –4.4 (CH$_3$). – MS: 298 [M$^+$]. – $C_{19}H_{26}OSi$ (298.51): calcd. C 76.45, H 8.78; found C 76.35, H 8.80. – **(c) 36:** 4-{4-[(*tert*-Butyldimethylsilyl)oxy]phenyl}-1,3,5-cycloheptatriene (13 g, 43.5 mmol) was dissolved in dichloromethane (30 mL) and trityl perchlorate (14.9 g) was added. After refluxing for 3 h and cooling to room temperature, *tert*-butyl methyl ether (600 mL) was added. The precipitate was separated, dissolved in acetonitrile and again precipitated with *tert*-butyl methyl ether to give 13 g (75%) of **36**, m.p. 161–164 °C. – ^{1}H NMR (CD$_3$CN): δ = 9.25 (d, 2 H, tropylium); 8.93 (m, 4 H, tropylium); 7.94 (d, ^3J = 9 Hz, 2 H, aromatic H), 7.18 (d, ^3J = 9 Hz 2 H, aromatic H), 1.02 [s, 9 H, C(CH$_3$)$_3$], 0.31 (s, 6 H, CH$_3$). – ^{13}C NMR (CD$_3$CN): δ = 168.6 (Ar-OSi-), 152.52, 152.8, 153.24 (tropylium), 133.8 (Ar-H), 132.5 (*Ar*-tropylium), 122.8 (Ar-H), 25.8 [C(*C*H$_3$)$_3$], 18.86), –4.3 (CH$_3$). – FAB-MS (nitrophenyl octyl ether): 297 [M$^+$ – ClO$_4^-$]. – UV/Vis (acetonitrile): λ_{max} = 448 nm.

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