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ORIGINAL ARTICLE

Calix[4]arenes bearing a tropylium substituent as hosts for organic cations

M. Fehlinger · W. Abraham

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Abstract Four novel calix[4]arenes bearing one cycloheptatrienyl substituent and two calix[4]arenes with one tropylium substituent at the wider rim were synthesized. Cycloheptatrienyl- and tropylium-calixarenes represent two states of a potentially photoswitchable calixarene host. The complexation of selected hosts with organic cations such as quinolinium, ammonium and tropylium ions was studied. It was found that the complexation of organic cations by the tropylium-substituted host was much stronger in $CDCl_3$ solution than by the related cycloheptatrienyl-host. Aryltropylium ions are bound by tropylium hosts. Accordingly, dimers of the host itself are formed both in $CDCl_3$ solution and in the gas phase. Because of the intramolecular charge transfer tropyliumcalix[4]arenes are qualified as chromogenic hosts. These undergo two acid-base equilibriums depending on the concentration and the solvent.

Keywords Calix[4]arenes · Cycloheptatriene · Tropylium · Complexation · NMR-titration · Isomeric complexes

Introduction

Calixarenes [1] belong to important building blocks for supramolecular assemblies [2] and molecular recognition, and are widely used as receptors for inorganic cations [3], anions [4] and also organic cations [5] and neutral compounds [6]. Molecular recognition arises from different forces acting on complementary faces of the calixarene host and the guest inside the cavity. *Endo*-cavity inclusion complexes with organic cations such as quaternary ammonium ions and the iminium and tropylium ions may be favoured by cation-π-interaction and π-stacking [7].

Previously, we found that the binding properties of the π-basic cavity of calix[4]arene can be improved by introducing cycloheptatrienyl substituents at the upper rim [7]. Furthermore, the cycloheptatrienyl substituents offer the possibility of their conversion into the related tropylium ions, thus drastically changing the properties of the cavity. We questioned whether the tropylium ion at the upper rim diminishes the binding constants of organic cations relative to the neutral cycloheptatrienyl substituent. We were interested in studying the complexation behaviour of calixarene hosts having cycloheptatriene and tropylium substituents, respectively, at the upper rim. Previously, we reported on the synthesis of calix[4]arenes bearing four tropylium substituents at the upper rim [8]. Because of the low solubility, the complexation properties of these calixarenes could not be investigated.

Here we report on the synthesis of calix[4]arenes with only one cycloheptatrienyl (compounds **6**, **7**) or one tropylium substituent (compounds **9** and **10**) at the upper rim and on their complexation behaviour.

Experimental

Apparatus and materials

Commercially available chemicals were used as received unless otherwise noted, solvents were dried

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M. Fehlinger · W. Abraham (✉)
Institut für Chemie, Humboldt-Universität, Brook-Taylor-Str. 2, 12489 Berlin, Germany
e-mail: Abraham@chemie.hu-berlin.de

according to standard procedures and all reactions were carried out under argon. Column chromatography was carried out on *200 mesh* silica gel (Merck).

The syntheses of calixarenes **11** and **13** were described earlier [7].

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 ^1H and ^{13}C, respectively) spectrometer. *J* values are given in Hz.

Mass spectra were obtained with a Concept ^1H spectrometer (MSI).

Determination of stability constants

Self-association

A 5 mMol solution of compound **10** was sequentially diluted to a final concentration of 0.0004 Mol, and the chemical shift of the tropylium proton (γ) was monitored. The observed shifts (δ_{obs}) were applied to the equation $\delta_{obs} = \delta_{dimer} + \{(\delta_{monomer-} \delta_{dimer})[(- 1 + (1 + 8K_aC)^{1/2}]/4K_aC)\}$, where *C* corresponds to the concentration of **10** and K_a, $\delta_{monomer}$, and δ_{dimer} are the calculated parameters.

Binding constants

Binding studies were carried out by means of ^1H NMR titrations of guest solutions usually at a concentration of 1 mmol. Increasing amounts of the host were added up to host: guest of 50:1–200:1 ratio (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 of the guests fully saturated by the host δ_{GC}.

Titration data points $\delta = f(R)$ were fitted to the equation

$$\delta = \delta_G - (\Delta\delta/2)(b - \sqrt{b^2 - 4R}) \quad [9]$$

with $b = 1 + R + 1K[H_0]$ and $R = [H][G]$

H = host , G = guest, $\Delta\delta = \delta_G - \delta_{GC}$

Best fit parameters K and δ_{GC} were obtained in a nonlinear least-square fitting procedure using the curve fitting program ''Sigma Plot'' (Jandel Scientific Software).

Maximum errors for the *K* values were estimated as ±15%. In order to determine complexation constants of **10** with cationic guests, the self-association had to be considered. For this purpose, the concentration of the host was corrected for the self-association. The molar fraction of the dimer was obtained from the observed proton signal of the tropylium moiety of compound **10** and the calculated CIS-values at the infinitesimal and infinite high concentration of **10** known from the NMR titration of the self-complexation:

$$[dimer] = \frac{\delta_{observed} - \delta_{dimer}}{\delta_{monomer} - \delta_{dimer}}[10]$$

X-Ray crystallographic studies

Compounds **7** and **11** were obtained in monocrystalline form by slow cooling of the warm acetonitrile-solution. Data were collected with a STOE-diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least squares techniques against F_2 (SHELXL-97) [10]. The hydrogen atoms were included at calculated positions. All other nonhydrogen atoms were refined anisotropically. The X-STEP-Program was used for structure representations. (Table 1)

Synthesis

Compound **3**

A solution of **4** [12] (0.8 g, 1.0 mmol) in methanol (20 cm^3) and conc. H_2SO_4 (1 cm^3) was refluxed for 2 h and then quenched with water (100 cm^3). The reaction mixture was extracted with dichloromethane: the combined extracts were dried ($MgSO_4$) and the solvent was removed under vacuum. The crude product was chromatographed (silica gel, dichloromethane/methanol 100:1) to give **3** (0.51 g, 77%) as a colourless solid, mp 61 °C; found: C, 68.95; H, 5.66; $C_{37}H_{36}O_{10}$ requires C, 69.36; H 5.66;

^1H NMR (δ, ppm): 7.11 (2 H, d, *J* 7, ArH), 7.05 (2 H, d, *J* 8, ArH), 6.93 (1 H, t, *J* 8, ArH), 6.71 (1 H, t, *J* 8, ArH), 6.56–6.46 (6 H, m, ArH), 5.98 (1 H, s, OH), 5.13 (2 H, s, OCH_2), 4.92 [2 H, d, *J* 14, $ArCH_2Ar$ (ax.)], 4.61 (2 H, d, *J* 16, OCH_2CO_2), 4.52 (2 H, d, *J* 16, OCH_2-CO_2), 4.36 [2 H, d, *J* 14, $ArCH_2Ar$ (ax.)], 3.82 (6 H, s, CO_2Me), 3.70 (3 H, s, CO_2Me), 3.32 [2 H, d, *J* 14, $ArCH_2Ar$ (eq.)], 3.31 [2 H, d, *J* 14, $ArCH_2Ar$ (eq.)]; ^{13}C NMR δ_C) 171.4, 169.7 (CO), 155.6, 153.8, 153.2 (Ar), 135.9, 133.1, 132.8, 129.3 ($ArCH_2Ar$), 129.5, 128.5, 128.3, 124.0, 123.3, 118.8 (ArH), 71.8, 70.0 (OCH_2CO_2), 51.9, 51.3 (CH_3), 31.7, 31.0 ($ArCH_2Ar$).

Compound **5**

A solution of **2** [13] (0.645 g, 1.09 mmol), 1-methoxycyclohepta-2,4,6-triene **1** [14] (0.44 g, 3.60 mmol) and

Table 1 Crystallographic details for the X-ray analysis of 7 and 11

Compound	**7**	**11** × CH_3CN
Empirical formula	$C_{53}H_{60}O_{10}$	$C_{70}H_{71}NO_8$
Molecular mass	857.01	1054.28
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell a [Å]	11.224(4)	13.482(3)
b [Å]	13.873(3)	14.496(3)
c [Å]	16.770(3)	18.641(4)
α [°]	91.173(16)	67.74(3)
β [°]	108.92(3)	88.82(3)
γ [°]	104.42(2)	63.69(3)
Unit cell volume [$Å^3$]	2377.7(11)	2974.6(12)
d (calcd.) [g*cm^{-3}]	1.197	1.177
Z	2	2
Temperature [K]	180	180
Linear absorption. μ [mm^{-1}]	0.082	0.076
F(000)	916	1124
Crystal size [mm]	0.88 × 0.60 × 0.40	0.64 × 0.36 × 0.12
θ-range for data coll. [°]	1.52–25.95	2.26–25.25
Limiting indices	–13 ≤ h ≤ 13	–16 ≤ h ≤ 16
	–17 ≤ k ≤ 17	–17 ≤ k ≤ 17
	–20 ≤ l ≤ 20	–21 ≤ l ≤ 21
Data/restraints/ parameters	9286/0/569	10103/2/904
No. of refls. collected	12752	19867
No. of refls. unique	9286	10103
R_{int}	0.0564	0.0383
Goodness-of-fit on F^2	1.076	0.886
Final R indices [I > 2σ(I)]	*R*1 = 0.0643	*R*1 = 0.0522
	w*R*2 = 0.1607	w*R*2 = 0.1251
Final R indices (all)	*R*1 = 0.1110	*R*1 = 0.0996
	w*R*2 = 0.1968	w*R*2 = 0.1433
$\Delta\rho_{max}$, $\Delta\rho_{min}$ [e $Å^{-3}$]	0.820, –0.249	0.499, –0.263

10 drops glacial acetic acid in dry toluene (50 cm^3) was stirred for 4 h at 55 °C and then at room temperature overnight. The solution was evaporated, and the oily residue was treated with methanol (100 cm^3). The precipitated product was washed with methanol and dried to give **5** (0.58 g, 78%); mp 280 °C, found: C, 82.29; H 8.14; $C_{47}H_{54}O_4$ requires C, 82.66; H 7.97; ^{1}H NMR (δ, ppm): 10.33 (4 H, s, ArOH), 7.09–7.01 (8 H, m, ArH), 6.70 (2 H, t, *J* 3, cycloheptatrienyl = CHT, H-4,5), 6.23–6.14 (2 H, m, CHT, H-3,6), 5.31–5.23 (2 H, m, CHT, H-2,7), 4.27 [4 H, br m, $ArCH_2Ar$ (ax.)], 3.50 [4 H, br d, $ArCH_2Ar$ (eq.)], 2.50 (1 H, t, *J* 6, CHT, H-1), 1.21 (18 H, s, $C(CH_3)_3$), 1.20 (9 H, s, $C(CH_3)_3$); ^{13}C NMR δ_C) 147.7, 146.6, 146.4 (ArOH), 144.5, 144.4, 137.4 ($ArC(CH_3)_3$ and ArCHT), 130.8 (CHT, C-4,5), 128.6, 127.9, 127.6, 127.4 ($ArCH_2Ar$), 128.1 (CHT, C-3,6), 126.6, 126.1, 125.9, 125.8 (ArH), 124.2 (CHT, C-2,7), 44.6 (CHT, C-1), 34.0, 33.9 ($C(CH_3)_3$), 32.5, 32.4 ($ArCH_2Ar$), 31.4, 31.3 ($C(CH_3)_3$).

Compound **6**

A solution of **3** (0.4 g, 0.62 mmol), **1** (0.205 g, 1.67 mmol) and 30 drops glacial acetic acid in dry acetonitrile (120 cm^3) was stirred at 60 °C for 1 day.

The solvent was evaporated and the oily residue was purified by column chromatography (CC) (SiO_2, CH_2Cl_2/MeOH 100:3) to give **6** (0.37 g, 81%), mp 45 °C, found: C, 72.31; H, 6.23; $C_{44}H_{42}O_{10}$ requires C, 72.31; H 5,79; ^{1}H NMR (δ, ppm): 7.08 (2 H, d, *J* 7, ArH), 7.00 (2 H, s, ArH), 6.90 (1 H, t, *J* 7, ArH), 6.75 (2H, t, *J* 3 Hz, CHT, H-4,5), 6.58–6.50 (6 H, m, ArH), 6.29–6.21 (2 H, m, CHT, H-3,6), 5.98 (1 H, s, OH), 5.47–5.39 (2 H, m, CHT, H-2,7), 5.10 (2 H, s, OCH_2CO_2), 4.91 [2 H, d, *J* 13, $ArCH_2Ar$ (ax.)], 4.64 (2 H, d,^{1}*J* 16, OCH_2CO_2), 4.53 (2 H, d, *J* 16, OCH_2CO_2), 4.38 [2 H, d, *J* 14, $ArCH_2Ar$ (ax.)], 3.82 (6 H, s, CO_2Me), 3.71 (3 H, s, CO_2Me), 3.32 [4 H, d, *J* 14, $ArCH_2Ar$ (eq.)], 2.59 (^{1}H, t, *J* 6, CHT, H-1); ^{13}C NMR δ_C)171.3, 169.8 (CO), 155.5, 154.0, 151.8 (ArOH and ArOR), 135.8, 133.2, 132.8, 129.4 ($ArCH_2Ar$), 134.1 (ArCHT), 130.9, 129.4, 128.5, 128.4, 127.4, 127.2, 124.0, 123.9, 123.4 (ArH und CHT, C-2-7), 71.8, 70.0 (OCH_2CO_2), 51.9, 51.3 (CH_3), 44.5 (CHT, C-1), 31.7, 31.2 ($ArCH_2Ar$, $C(CH_3)_3$).

Compound **7**

To a solution of **4** [12] (0.3 g, 0.39 mmol) and **1** (0.14 g, 1.17 mmol) in dry acetonitrile (60 cm^3) 10 drops glacial acetic acid were added, and the solution was then stirred at 55 °C overnight.

The solution was evaporated and the oily residue was recrystallized from ethanol to give **7** (0.22 g, 67%), mp 87 °C, found: C, 73.21; H 7.39; $C_{53}H_{60}O_{10}$ requires C, 73.50; H 7.10; ^{1}H NMR (δ, ppm): 7.03 (2 H, d, *J* 8, ArH), 6.97 (2 H, s, ArH), 6.85 (1 H, t, *J* 8 Hz, ArH), 6.74 (2 H, t, *J* 3 Hz, CHT, H-4,5), 6.59–6.47 (6 H, m, ArH), 6.29–6.20 (3 H, m, OH and CHT, H-3,6), 5.46–5.37 (2 H, m, CHT, H-2,7), 4.96 (2 H, s, OCH_2CO_2), 4.89 [2 H, d,^{1}*J* 14, $ArCH_2Ar$ (ax.), 4.63 (2 H, d, *J* 16, OCH_2CO_2), 4.48 [2 H, d, *J* 14, $ArCH_2Ar$ (ax.)], 4.38 (2 H, d, *J* 16, OCH_2CO_2), 3.29 [4 H, d, *J* 14, $ArCH_2Ar$ (eq.)], 2.56 (1 H, t, *J* 6, CHT, H-1), 1.51 (18 H, s, $C(CH_3)_3$), 1.42 (9 H, s, $C(CH_3)_3$); ^{13}C NMR δ_C) 69.8, 168.6 (CO), 155.5, 154.7, 151.8 (ArOH and ArOR), 135.8, 133.4, 132.9, 129.4 ($ArCH_2Ar$), 133.8 (ArCHT), 130.8 (CHT, C-4,5), 129.1, 128.4, 128.3, 127.3, 127.2, 123.9, 123.7, 123.0 (ArH and CHT, C-2,3,6,7), 81.8, 80.7 ($C(CH_3)_3$), 72.7, 70.7 (OCH_2CO_2), 44.5 (CHT, C-7), 31.9, 31.3 ($ArCH_2Ar$), 28.1, 28.0 ($C(CH_3)_3$).

Conversion of compound **6** *into* **8**

A solution of compound **6** (0.3 g) in toluene (100 cm^3) was refluxed for 15 h. The solvent was removed under vacuum to give the isomer **8** (0.3 g), mp 75 °C, found: C, 72.17; H 6.05; $C_{44}H_{42}O_{10}$ requires C, 72.31; H 5,79; ^{1}H NMR (δ, ppm): 7.24 (1 H, s, OH), 7.2 (2 H, s, ArH), 7.1 (2 H, d, *J* 7, ArH), 6.90 (2 H, m, CHT, H-2), 6.40 (1 H, d, *J* 10, CHT, H-7), 6.58–6.48 (6 H, m, ArH), 6.28 (1 H, m, CHT, H-3), 5.55 (1 H, m, CHT, H-6), 5.45 (1 H, m, CHT, H-4), 5.10 (2 H, s, OCH_2CO_2), 4.90 [2 H, d, *J* 14, $ArCH_2Ar$ (ax.)], 4.37 (2 H, d, *J* 16, OCH_2CO_2), 4.54 (2 H, d, *J* 16, OCH_2CO_2), 4.35 [2 H, d, *J* 14, $ArCH_2Ar$ (ax.)], 3.80 (6 H, s, CO_2Me), 3.68 (3 H, s, CO_2Me), 3.31 [4 H, d, *J* 14, $ArCH_2Ar$ (eq.)], 2.36 (1 H, t, *J* 6, CHT, H-5).

Compound **9**

A solution of **5** (0.19 g, 0.28 mmol) in dry dichloromethane (5 cm^3) was treated with a solution of tritylhexafluorophosphate (217 mg, 0.56 mmol) in dry dichloromethane (3 cm^3). The mixture was stirred overnight.

The product precipitated by addition of methyl-*tert*butylether (MTBE, 5 cm^3) was separated by centrifugation and washed with MTBE to give **9** (0.202 g, 88%), mp > 360 °C, found C, 65.65; H, 6.60; $C_{47}H_{53}F_6O_4P{\cdot}2H_2O$ requires C 65.42, H 6.66; ^{1}H NMR (δ, ppm): 9.13 (2 H, d, *J* 10, Tropylium = Trop, H-2,7), 8.93–8.82 (4 H, m, Trop, H-3–6), 7.93 (2 H, s, TropArH), 7.29–7.24 (6 H, m, ArH), 4.20–3.13 (8 H, m, $ArCH_2Ar$), 1.18, 1.17 (9H; 18H, 2× s, $C(CH_3)_3$); ^{13}C NMR (δ_C)168.19 (Trop, C-1), 155.75 (ArTrop), 152.82, 152.62 (Trop, C-2-7), 147.01, 146.47, 145.95 (ArOH), 133.38, 131.79, 129.64, 128.71 ($ArCH_2Ar$), 132.47, 127.24, 126.58, 126.33 (ArH), 34.67, 34.61 ($C(CH_3)3$), 31.57 ($ArCH_2Ar$), 31.42, 31.37 ($C(CH_3)_3$).

Compound **10**

A solution of **6** (0.23 g, 0.31 mmol) in dry acetonitrile (10 cm^3) was treated with tritylhexafluorophosphate (0.137 g, 0.35 mmol) and was stirred at room temperature for 4 h.

The solution was evaporated, and the residue was dissolved in dichloromethane. The product was precipitated by adding MTBE and afterwards washed with toluene to give **10** (0.26 g, 97%,), mp 139 °C, found: C, 60.03; H 4.93; $C_{44}H_{41}F_6O_{10}P$ requires C, 60.41; H 4.72; λ_{max}(acetonitrile)/nm 267 (ϵ/dm^3 mol^{-1} cm^{-1} 19857 l mol^{-1} cm^{-1}); ^{1}H NMR (δ, ppm): 9.25 (2 H, d, *J* 10, Trop, H-2,7), 8.86–8.64 (4 H, m, Trop, H-3-6), 7.92 (2 H, s, ArH), 7.20 (2 H, d, *J* 8, ArH), 6.96–6.60 (7 H, m, ArH), 5.05 (2 H, s, OCH_2CO_2), 4.82 [2 H, $ArCH_2Ar$ d, *J* 13, (ax.)], 4.71 (2 H, d, *J* 16, OCH_2CO_2), 4.51 (2 H, d, *J* = 16, OCH_2CO_2), 4.40 [2 H, d, *J* 14, $ArCH_2Ar$ (ax.)], 3.81 (6 H, s, CO_2Me), 3.67 (3 H, s, CO_2Me), 3.59 [2 H, d, *J* 14, $ArCH_2Ar$ (eq.)], 3.37 [2 H, d, *J* 13 Hz, $ArCH_2Ar$ (eq.)]; ^{13}C NMR δ_C) 170.4, 168.7 (CO), 167.0, 159.0, 154.7 (ArOH und ArOR), 152.6 (Trop, C-1), 150.2, 149.7, 149.4 (Trop, C-2-7), 134.6, 133.2, 131.0, 130.1 ($ArCH_2Ar$), 131.4 , 128.6, 128.4, 127.6 (ArH), 128.1 (ArTrop), 123.5, 122.9 (ArH), 71.0, 69.6 (OCH_2CO_2), 50.8, 50.2 (CH_3), 30.2, 29.8 ($ArCH_2Ar$).

Compound **12**

2,6-Dimethylphenol (2 g, 16 mmol) was mixed with **1** (2.2 g, 18 mmol) and acetic acid (0.4 cm^3) was added. The mixture was heated to 65 °C for 6 h. After cooling, the mixture was dissolved in dichloromethane (50 cm^3). The solution was washed with water, dried and the solution was evaporated under vacuum. The crude product was purified by column chromatography (silica gel, dichloromethane) to give 7-(4-hydroxy-2,6-dimethylphenyl)-1,3,5-cycloheptatriene as an oil (1.6 g, 64%).

This product was used without further characterization for the oxidation procedure: 1.6 g (10 mmol) in acetonitrile (50 cm^3) was treated with trityl perchlorate (3.4 g, 10 mmol). The solution was stirred for 3 h at room temperature. The solvent was evaporated and the residue was washed several portions of MTBE. The remaining solid was dissolved in acetonitrile (1 cm^3) and compound **12** (1.3 g, 60%) was obtained by adding of MTBE, mp 218 °C, found: C, 58.06; H, 4.97; $C_{15}H_{15}ClO_5$ requires C, 57.98; H, 4.87; ^{1}H NMR (δ, ppm, CD_3CN): 9.15 (2 H, d, *J* 10, Trop, H-2,7), 8.83 (2 H, m, Trop, H-5,6), 8.72 (2 H, m, Trop, H-3,4), 7.68 (2 H, s, ArH), 2.37 (6 H, s, methyl).

Compound **16** *was prepared in three steps:*

7-(4-Isopropylaminophenyl)-cyclohepta-1,3,5-triene **1** (3.3 g, 24 mmol) in acetonitrile solution (10 cm^3) was added to N-isopropylaniline (3 g, 22 mmol) in acetonitrile (10 cm^3). After addition of 30 drops acetic acid, the reaction mixture was stirred for 3 days. The solution was evaporated, and the residue was purified by CC (silica gel, MTBE/hexane 2.5:100) to give a yellow oil (3.3 g, 66%). Found: C, 85.14; H, 8.81; N 6.14; $C_{16}H_{19}N$ requires C, 85.29; H, 8.50; N, 6.22; ^{1}H NMR (δ, ppm): 7.16 (2 H, d, *J* 9, ArH), 6.74–6.70 (2 H, m, CHT, H-3,4), 6.60 (2 H, d, *J* 9, ArH), 6.27–6.16 (2 H, m,

CHT, H-2,5), 5.45–5.35 (2 H, m, CHT, H-1,6), 3.63 (septet, *J* 6, 1 H, isopropyl), 3.42 (1 H, br s, NH), 2.58 (1 H, t, *J* = 6 Hz, CHT, H-1), 1.22 (6 H, d, *J* 6, isopropyl).

3-(4-Iisopropylaminophenyl)-cyclohepta-1,3,5-triene

A solution of 7-(4-Isopropylaminophenyl)-cyclohepta-1,3,5-triene (1 g) in toluene (50 cm^3) was refluxed for 24 h. The solvent was removed under vacuum to give an oil (0.9 g, 90%) which was used for the oxidation without further purification, found: C, 84.95; H, 8.83, N, 6.15; $C_{16}H_{19}N$ requires C, 85.29; H, 8.50, N, 6.22; ^1H NMR (δ, ppm): 7.31 (2 H, d, *J* 9, ArH), 6.86 (1 H, d, *J* 6, CHT, H-4), 6.58 (2 H, d, *J* 9, ArH), 6.37–6.24 (2 H, m, CHT, H-2,5), 5.59–5.39 (2 H, m, CHT, H-1,6), 3.65 (1 H, septet, *J* 6, isopropyl), 3.51 (1 H, br s, NH), 2.33 (1 H, t, *J* 7, CHT, H-7), 1.22 (6 H, d, *J* 6, isopropyl).

(4-Iisopropylaminophenyl)-tropylium perchlorate 16

3-(4-Iisopropylaminophenyl)-cyclohepta-1,3,5-triene (0.9 g, 4 mmol)) dissolved in dichloromethane (60 cm^3) was treated with trityl perchlorate (1.4 g, 4.2 mmol). The solution was stirred for 1 day. After removing the solvent under vacuum, the oily residue was treated with toluene. The resulting solid was washed with toluene and MTBE to give **16** (0.8 g, 63%), mp > 360 °C, found: C, 59.67; H, 5.96; N, 4.03; $C_{16}H_{18}ClNO_4$ requires C, 59.36; H, 5.60; N, 4.33); λ_{max} (acetonitrile)/nm 550 (ϵ/$dm^3\ mol^{-1}\ cm^{-1}$ 33800); ^1H NMR (δ, ppm): 8.56 (2 H, d, *J* 11, Trop, H-2,7), 8.12–8.00 (2 H, m, Trop, H-3,6), 7.91–7.82 (4 H, m, Trop, H-4,5; ArH), 6.83 (2 H, d, *J* 9 , ArH), 6.35 (1 H, br s, NH), 3.85 (1 H, m, isopropyl), 1.34 (6 H, d, *J* 6, isopropyl).

Results and discussion

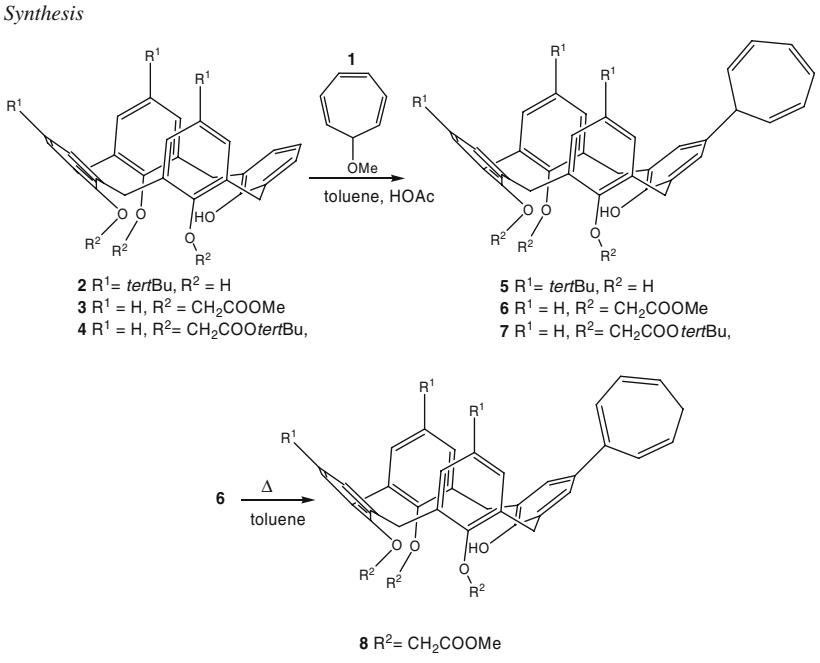
Host syntheses

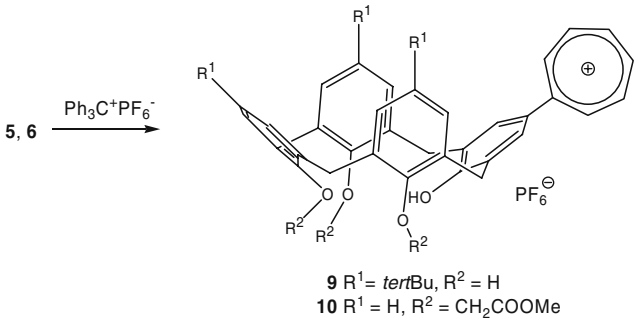
The synthesis pathway leading to cycloheptatrienyl compounds **5**–**8** is outlined in Scheme 1. In order to introduce only one seven-membered substituent at the wider rim three positions have to be protected such as in compound **2**. In order to introduce only one substituent at the wider rim the selective reaction of 7-methoxycycloheptatriene **1** with the phenolic unit of the calix[4]arene can be used as a key step. Consequently, the reaction of calixarenes **3** and **4** with three phenol ether units results in calixarenes **6** and **7** monosubstituted at the wider rim.

The 7-(4-hydroxyphenyl)-cycloheptatriene moiety within the calix[4]arene **6** can thermally be isomerized by a 1,5-hydrogen shift (Scheme 1). The resulting conjugative connection between the aryl substituent and the seven-membered ring may influence both the conformation and the complexation behaviour of the calix[4]arene.

The oxidation of the cycloheptatrienylcalixarenes was performed by the hydride transfer to the trityl salt, yielding the hosts bearing one tropylium substituent at the upper rim (Scheme 2)

Scheme 1 Synthesis of cycloheptatrienylcalixarenes





Scheme 2 Synthesis of tropylium calixarenes

Conformation

According to the ^{13}C-NMR signals of the methylene groups (31 ppm), all calix[4]arenes possess a cone conformation [15]. The partially alkylated hosts **6** and **7** adopt a pinched-cone conformation, which is inferred from the resonance of one of the axial methylene protons that exhibits a strong downfield-shift. Compound **7** exhibits this conformation also in the solid state as it is demonstrated in the crystal structure (Fig. 1).

The cycloheptatriene ring is strongly twisted against the plane of the adjacent phenyl group (71°). Such behaviour of cycloheptatriene rings was also observed in the related calix[4]arene **11** with four cycloheptatriene substituents at the upper rim. Compound **11** has been described recently [7]; however, crystals were obtained in the current work (see Fig. 2). The calixarene **11** adopts a pinched-cone conformation in which the non-alkylated cycloheptatrienylphenol units are tilted away from the cavity (opening angle 86°). This finding differs from those of the conformation inferred from NMR-data in $CDCl_3$ solution [7]. The two cycloheptatrienylphenyl subunits with alkylated OH-groups are more parallel (opening angle 37°). Only one cycloheptatrienyl group of the paralleled units is twisted (angle 72°); the other one is nearly in the plane of the aryl group (9°) to avoid steric interference.

The tropylium-substituted arene unit and the opposite phenyl ring in calix[4]arene **10** are less tilted away from the cavity, as was inferred from the smaller difference of the resonances of the equatorial and axial

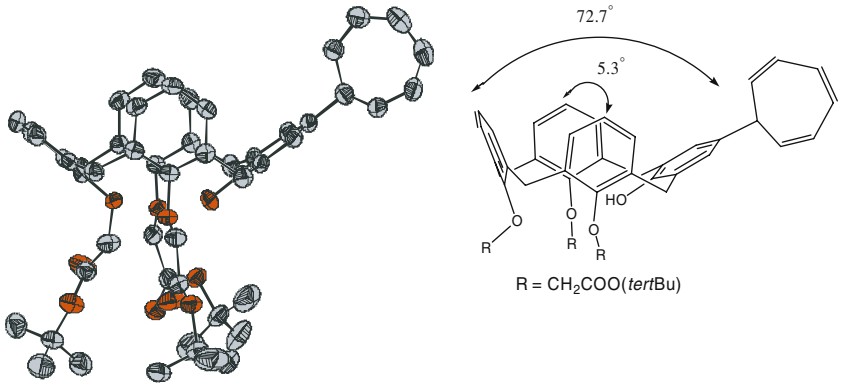


Fig. 1 View of the molecular structure and angles of the pinched-cone conformation of compound **7** (all hydrogen atoms are omitted for clarity)

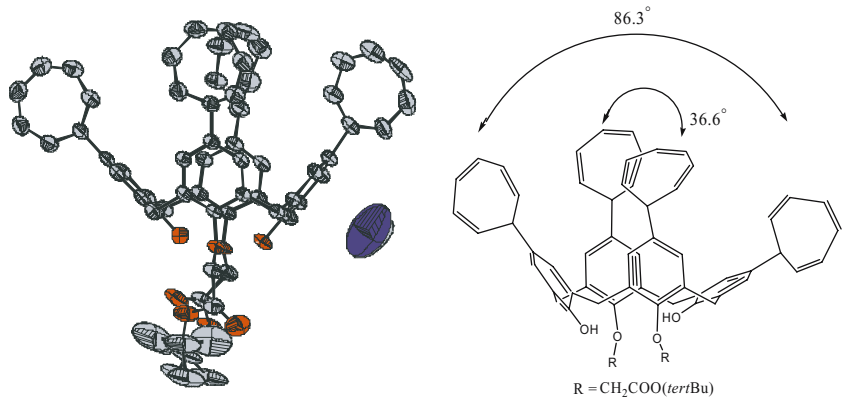


Fig. 2 Molecular structure of compound **11** including one molecule of acetonitrile and angles of the pinched-cone conformation

Compound **11**

protons of the methylene bridges (0.45 versus 0.53 ppm).

Solvatochromism and acidity of tropylium calix[4]arenes

The tropylium substituent increases the acidity of the p-OH-group considerably [8] and it may serve as a probe of the processes occurring at the lower rim. Two acid-base equilibriums control the absorption spectra (Scheme 3), and the three components that are involved in these equilibriums have strongly separated long-wavelength absorption spectra. The phenolate ion possesses a quinoid structure (**10_a**) with a long wavelength absorption band around 550 nm (equilibrium I) [14] while the corresponding acid absorbs around 450 nm. Tropylium ions themselves are acids, too. In protic solvents, the pseudo base hydroxycycloheptatriene (**10_b**) is formed [14].

The equilibrium II does not involve a pure proton transfer. Because the base hydroxyphenylcycloheptatriene additionally forms a water molecule in the reaction with a proton, the acid constant differs from the pK_a of Brönsted acids by the activity of water in acetonitrile. Also, other nucleophilic solvents, such as methanol, attack the tropylium moiety to form cycloheptatrienes characterized by absorption maxima around 300 nm. The pK_a-values of **9**, **10**, and **12** (see Scheme 3), which we included for comparison, are 3.0, 4.6, and 4.9 respectively. These constants reflect the properties of the lower rim. Compound **9** has the highest acidity because the three remaining hydroxyl groups, which are much weaker acids than that of the tropylium unit, stabilize **9_a** by intramolecular hydrogen bonds.

Accordingly, for the calixarene **9**, even in aprotic solvents such as acetone and acetonitrile, the equilibrium I is detectable by the appearance of two absorption bands attributed to **9** and **9_a**.

(See Supporting Information for the longest wavelength absorption maxima in different solvents.)

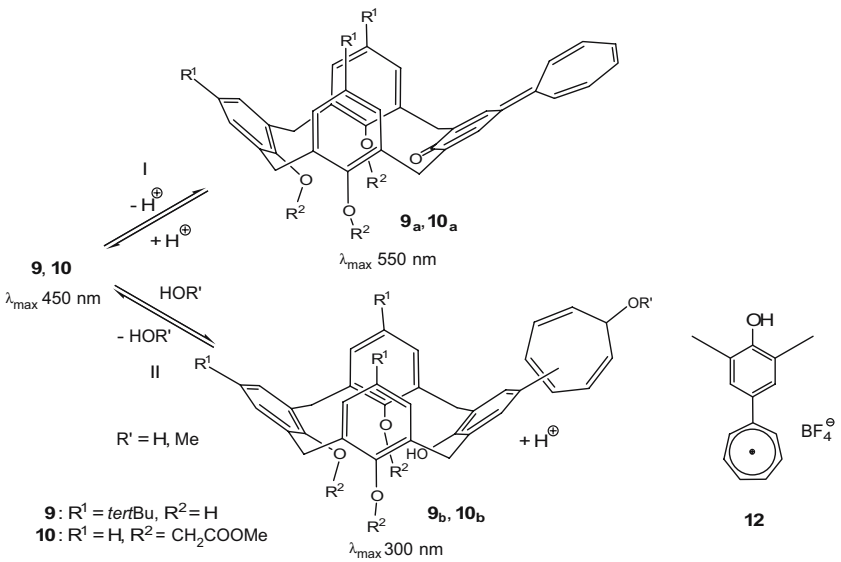
Due to lower acidity, both **10** and **12** exhibit, contrary to **9**, the absorption band of the quinoid base only in aqueous solution. Absorption maxima of compounds **9**, **10**, and **12** in different solvents are given in the Supporting Information.

Complexation studies

Complexation in the gas phase

Up to now, the complexation behaviour of calixarenes bearing a tropylium ion as a substituent at the wider rim has not been studied. Therefore, it would be interesting to evaluate the influence of the positively charged substituent at the calixarene cavity on the complexation of organic cations. One could expect that the repulsion of the positive charges results in very weak interaction between the host and the guest.

The unsubstituted tropylium ion forms capsule with neutral calixarenes [16] and resorcarenes [17, 18]. Previously [7], we have shown that aryltropylium ions are bound by uncharged calixarene hosts. Therefore, the question arises as to whether compound **10** can serve as a guest for other calixarenes such as compound **11** [7] (Scheme 4), with a cavity extended by cycloheptatrienyl substituents, and compound **13**, which lacks any substituent at the upper rim. Indeed, the mass spectra (ESI-MS) exhibit a peak of low



Scheme 3 Equilibriums of tropylium calix[4]arenes observed in protic solvents

intensity with the mass of $[\mathbf{11}/\mathbf{10}\text{-}PF_6^-]^+$ and $[\mathbf{13}/\mathbf{10}\text{-}PF_6^-]^+$ apart from the peak of the positively charged $[\mathbf{10}\text{-}PF_6^-]^+$ ion with high intensity.

Moreover, a self-complexation of compound **10** can be detected by the appearance of the $[(\mathbf{10})_2\text{-}PF_6^-]^+$ ion (see also Supporting Information).

Self-association in $CDCl_3$ solution

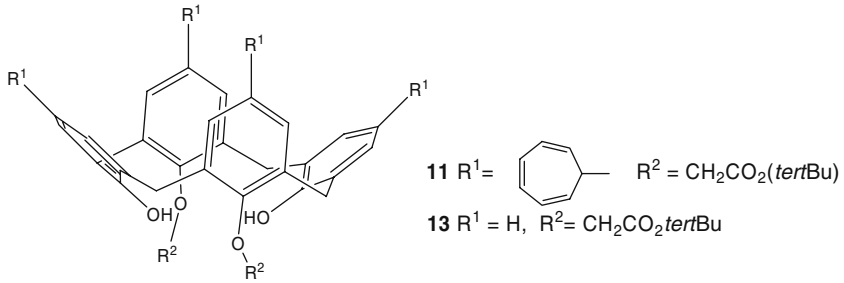
Aryltropylium salts are known to form ion pairs in weakly polar solvents such as dichloromethane [19]. The relatively high association constants of the *p*-tolyl tropylium salts are only slightly dependent on the nature of the anion. Therefore, one can expect that ion pairs are also formed in the case of calix[4]arene **10**. Unfortunately, we were not able to obtain crystals suitable for crystallographic studies in order to detect where the anion is located.

Inspired from the observed self-association of compound **10** in the gas phase, we considered the concentration dependent shifts of proton resonances of compound **10** in $CDCl_3$ solution. The resonances of protons 4/5 (see Scheme 5 and Table 2) are stronger upfield-shifted compared with the other protons of the tropylium ring; this shift was achieved by increasing the concentration of **10**. We have checked whether the increased ion pair concentration gives rise to this shift. For this purpose $NaBF_4$ was added to a solution of compound **11** in $CDCl_3/CD_3CN$ (3:1) solution. Only a small down-field shift of the tropylium protons was observed. Therefore the observed upfield shift can be attributed to the self-association of **11** involving insertion of the positively charged seven-membered ring of one molecule **10** into the cavity of the another (Scheme 5).

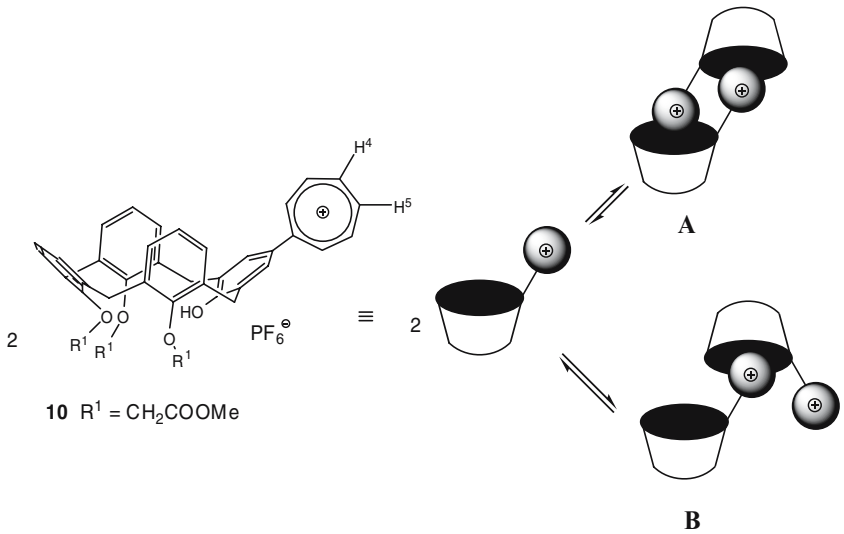
Apart from the tropylium protons, the proton resonances of the methylene groups of the calixarene ring also are dependent on the concentration of **10**. As the difference between the axial and the equatorial proton resonances of one pair increases with increasing concentration, the difference of the other pair is diminished. This relationship can be explained by a more pronounced pinched-cone conformation within the dimeric complex.

The systematic shift of the resonances of the tropylium protons upon dilution consistent with the for-

Scheme 4 Chemical structures of the hosts **11** and **13**

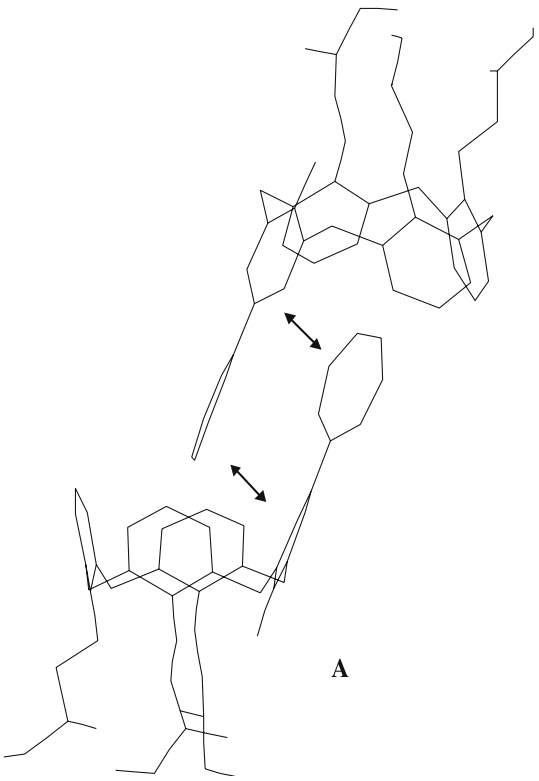


Scheme 5 Schematic representation of the proposed models of the dimers



mation of a dimer was used to calculate the association constant to be 230 M^{-1}. The satisfying agreement between the calculated chemical shift depending on the calixarene concentration and the experimental values excludes the formation of oligomeric complexes. In addition, mass spectroscopy indicates the presence of the dimer (see above). Two conceivable structures of the complex are pictured in Scheme 5. It should be more likely that both tropylium substituents are included in the two cavities of the calixarenes (structure A in Scheme 5). Accordingly, only one set of proton signals of the tropylium group is observed. For B, two different tropylium substituents may be expected even at rapid exchange between monomer and dimer because in every case two different tropylium substituents are in exchange with one tropylium substituent in the monomer.

The surprising finding of the dimers with two positive charges demonstrates that the attraction forces resulting from complementary cation-π interaction according to the model shown in Scheme 6 are stronger than the repulsion of the two charges. At present the role of the ion pairs is not clear.



Scheme 6 Energy-minimized structure of the dimeric structure A obtained by molecular modelling (M^+-calculation performed by Hyperchem, version 4.5 (Hypercube, Inc.); arrows denote the cation-π-interactions

Binding of organic cations

Taking into account that dimers of the cationic host **10** are observed, other cationic guests are also expected to bind in the cavity of **10**. To compare the binding properties of neutral and cationic hosts, compounds **3**, **4**, **6**–**8**, and **10** were studied regarding their complexation with three types of organic cations (Scheme 7).

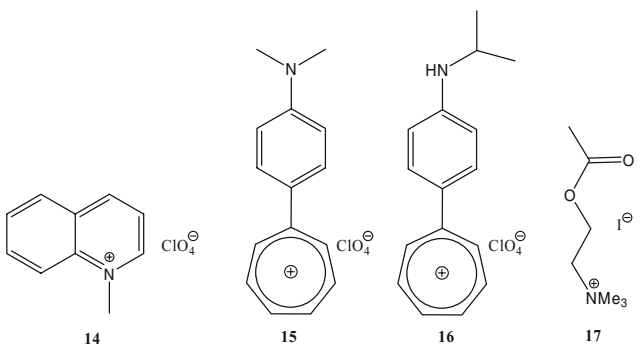
Binding constants were determined based on NMR-titration experiments using different proton resonances of the guests (see Table 3).

One cycloheptatrienyl substituent at the upper rim of calix[4]arene does not improve the binding of organic cations (compare rows 2 and 4 in Table 3). In contrast, we have found that four cycloheptatrienyl groups at the upper rim clearly improve the binding properties of the calixarene host [7].

The cycloheptatrienyl substituent in host **6** is bound with its sp^3-carbon at the calixarene rim. It may be expected that by connecting the cycloheptatriene moiety with a sp^2-carbon, as in host **8**, the π-basic cavity is improved. However, no significantly stronger binding by the host **8** compared with host **6** has been measured.

However, taking into consideration the binding constants given in Table 2, one tropylium substituent at the upper rim of the calix[4]arene significantly improves the binding of all investigated organic cations. This outcome is probably the result of complementary cation-π interaction, charge transfer interaction, and π-stacking. Probably anions contribute to this phenomenon.

The binding of guests by host **10** competes with the self-complexation of the host. Because the NMR-titration was carried out with variable concentrations of the host, the concentration of the free host available for the guest must be corrected (see Table 3). This was carried out only for the guest **14** because both for guest



14 15 16 17

Scheme 7 Organic cations used as guests in complexation studies

Table 2 Chemical induced shift ($\Delta\delta$/ppm) of various proton resonances of the tropylium calixarene **10** due to self-association

Concentration of compound **10**	0.39 mmol δ/ppm	45 mmol δ/ppm	$\Delta\delta$/ppm
Tropylium-H4/5	7.80	6.68	1.12
Tropylium-H3/6	8.44	7.85	0.59
Tropylium-H2/7	8.97	8.74	0.23
Calixarene (ArH)	7.71	7.67	0.04
Calixarene ($ArCH_2Ar$, axial)	4.85/4.42	4.88/4.33	–0.04/0.1
Calixarene ($ArCH_2Ar$, equatorial)	3.57/3.35	3.53/3.35	0.04/0
OCH_2COO	4.92 (s)/4.86/4.53	5.03 (s)/4.78/4.48	–0.12(s)/0.08/0.05
CO_2CH_3	3.87/3.71	3.86/3.73	0.01/–0.02

Table 3 Association constants calculated based on chemical shifts of guest protons in the 1:1 complexes

Host	Guest			
	14	15	16	17
	K (M^{-1})	K (M^{-1})	K (M^{-1})	K (M^{-1})
3	23 ± 0.5	15 ± 4/21 ± 5	–	11 ± 2/11 ± 1
4	41 ± 8	9 ± 1/24 ± 1	52 ± 2	–
6	19 ± 4	8 ± 3/6 ± 4	–	–
7	41 ± 3	21 ± 3/24 ± 1	–	–
8	30 ± 3	–	–	–
10	416 ± 58 540 ± 133[4]	163 ± 20/446 ± 43[1]	122 ± 6[2]	1090 ± 76/293 ± 24[3]

[1] NMe_2/H2 and H6 of tropylium

[2] H2 and H6 of tropylium

[3] NMe_2/CH_3CO

[4] Binding constant corrected with respect to self-complexation of **10**

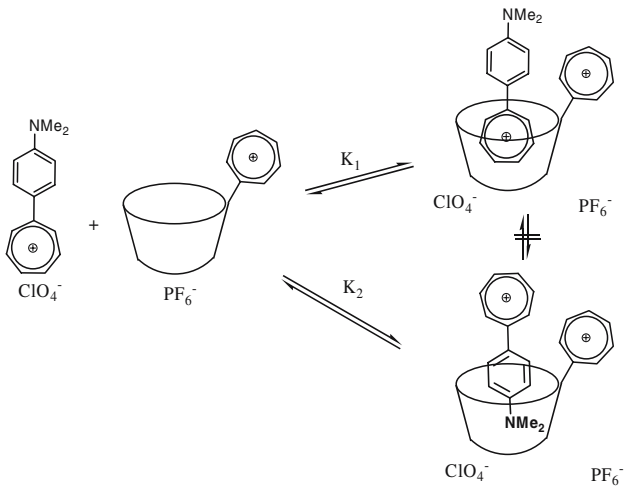
–, Not determined

15 and guest **17** the microscopic complexation constants could not be determined (see below). Generally, the observed complexation constants are rather low. However, the structure of the complexes in solution concluded from the CIS-values is more important than the binding constant itself. In general, the observed proton resonances are upfield-shifted because of the shielding effect by the aryl groups of the host. The positively charged parts of the guests get inserted into the cavity of the calix[4]arenes, forming *endo*-complexes. This process is inferred from the CIS-values of the proton resonances of the methyl group of compounds **14** and **17** and the tropylium protons at C-2,6 of **15**. Also in the case of the quinolinium ion **14** as guest, the largest upfield shift up to 3 ppm is observed for the protons at C2.

However, according to the observed CIS-values (see Supporting Information), the complexation affects significantly the protons of the dimethylamino group in guest **15** and those of the acetyl group of **17** indicating the contact with the π-basic cavity.

The NMR-titration experiments carried out with guests **15** and **17** result in hyperbolic dependencies of the proton resonances on the ratio of host to guest concentration (see Supporting Information). In contrast to the complex **10**/**14** binding constants for guests **15** and **17** obtained with different proton resonances differ considerably (see Table 3) despite the satisfying fit between the experimental and calculated values. Job-plots using the two proton resonances show that 1:1-complexes are formed (see Supporting Information). The large deviations of the calculated binding constants cannot be explained by experimental errors. Rather isomeric complexes have to be taken into account. The existence of isomeric 1:1 complexes (see Scheme 8) would result in the observed deviations of the binding constants by using of the simple complexation model [20]. In such case the determination of the microscopic association constants K_1 and K_2 is not possible. In the same way, the CIS-values given in Supporting Information do not represent the microscopic CIS-value of the two isomeric complexes.

Opposite to guest **14**, guests **15** and **17** have more elongated shape with two different groups at the ends. Therefore, the isomeric complexes may differ by the group inserted into the cavity of the host



Scheme 8 Possible isomeric complexes.

(see Scheme 8). To check this presumption of isomeric inclusion complexes, the guest **16** with a bulky amino group was studied both with the host **10** and with **13** without the tropylium substituent. The upfield shift of the proton resonances of the methyl group is rather low in this case; nevertheless, this shift can be used to calculate the complexation constant. Indeed, the complexation constants obtained with signals of the tropylium part and of the *iso*-propyl group do not differ for the host–guest complex **10**/**16**. The calculated high-field shift for the methyl group of the *i*-propyl moiety is small (–28 Hz) but not negligible. We interpret this finding with the interaction of the amino group with the tropylium substituent at the upper rim of **10**; e.g., the π-system of the tropylium ring shields the protons of the *i*-propyl group. Accordingly, there is no complexation-induced shift of the methyl protons of **16** with the host **13**. The obtained complexation constant for the complex **10**/**16** may represent to a certain extent, the binding strength of aryl tropylium ions, such as **15**.

Conclusions

Contrary to expectation, a positively charged substituent, such as tropylium group at the upper rim of calix[4]arene, binds organic cations like ammonium and the iminium or tropylium ions more strongly than the related host with a neutral cycloheptatriene substituent. The stronger binding is attributed to complementary cation-π interaction between the aryltropylium moiety of the host and the guest. Together with π-stacking effects and, probably, ion pairing with the anions, these interaction forces compensate the repulsion of the positive charges.

In the case of the dimethylaminophenyltropylium ion as the guest, isomeric complexes are formed including either the tropylium or the aryl part within the cavity of the calixarene host.

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