Synthesis of *C*-Alkylcalix[4]arenes, 6[‡] The Interaction of Resorcin[4]arenes with Fe^{III} in Chloroform

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Resorcinarene octamethyl ethers, bearing carboalkyloxy groups in the side chains, have been shown to interact with Fe^{III} in organic media. ^{1}H-NMR studies, carried out using Ga^{III} instead of Fe^{III}, suggest that these systems have two active sites of interaction, the first located at the aromatic moiet and the other in the vicinity of the carbonyl groups. As a confirmation of this, resorcinarenes without carbonyl groups in the side chains have been found to exhibit only one active site. Notably, in the latter case the interaction results in configurational changes.

Introduction

Our recent studies have been focused on the introduction of various functionalities at the "outside periphery" of the resorcinarene skeleton[1–3] with the aim of generating appropriate binding sites for various substrates. Unsubstituted calixarenes are not effective cation receptors, but their derivatives bearing amide, ketone, and ester substituents at the lower rim have shown significant cation affinity.[4–10] For example, ketones and esters of calix[4]arenes[11][12] selectively bind Li^I in preference to other alkali metal cations in acetonitrile, while amide derivatives form stable complexes with Eu^{III}, Tb^{III}, and Gd^{III} chlorides in aqueous or alcoholic media.[13–15] Resorcin[4]arenes have also been extensively investigated with regard to their applications in molecular recognition, supramolecular chemistry, and materials science.[16–19]

This paper deals with complexation studies carried out in organic media using resorcinarene octamethyl ethers as hosts and Fe^{III} as the guest.

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Results and Discussion

The *C*-alkylcalix[4]resorcinarene octamethyl ethers **1a**–**1c** (Figure 1) were obtained by $BF_3{\cdot}Et_2O$-catalyzed tetramerization of (*E*)-2,4-dimethoxycinnamic isopropyl ester.[1]

Addition of an equimolar amount of $FeCl_3{\cdot}H_2O$ to a solution of the isopropyl ester **1a** in $CHCl_3$ immediately resulted in a magenta solution, the UV spectrum of which showed absorption maxima at 330, 568, and 628 nm, along with those present in the spectra of the individual components, **1a** and $FeCl_3$. In the course of 24 h, the solution underwent a colour change through purple to blue, as the absorption maximum at 628 nm increased at the expense of that at 568 nm. This is illustrated in Figure 2

In order to better understand these phenomena, we performed a series of experiments at various temperatures, in which the concentrations of both the host and the guest were varied. The best result, in terms of saturation time, was obtained using 3×10^{-4} M concentrations of both **1a** and $FeCl_3$ at a temperature of 50 °C.

A 2:1 ratio, corresponding to a molar fraction of 0.33 for Fe^{III} was calculated for a **1a**/$FeCl_3$ complex at $\lambda = 330$ nm by Job's method[20] (Figure 3).

In order to confirm the key role of the macrocyclic structure in the host–guest interaction, compound **5** was prepared by catalytic reduction of the corresponding (*E*)-2,4-dimethoxycinnamic acid isopropyl ester. When **5** was treated with $FeCl_3$, under the same conditions as used with **1a**, no additional band was detected in the UV spectrum.

To confirm the above results, ^{1}H-NMR titration experiments, in which $FeCl_3$ was replaced by $GaCl_3$, were performed on **1a**. Diamagnetic gallium derivatives have been used previously in NMR studies;[21][22] the replacement of Fe^{III} by Ga^{III} is justified by the physicochemical similarity

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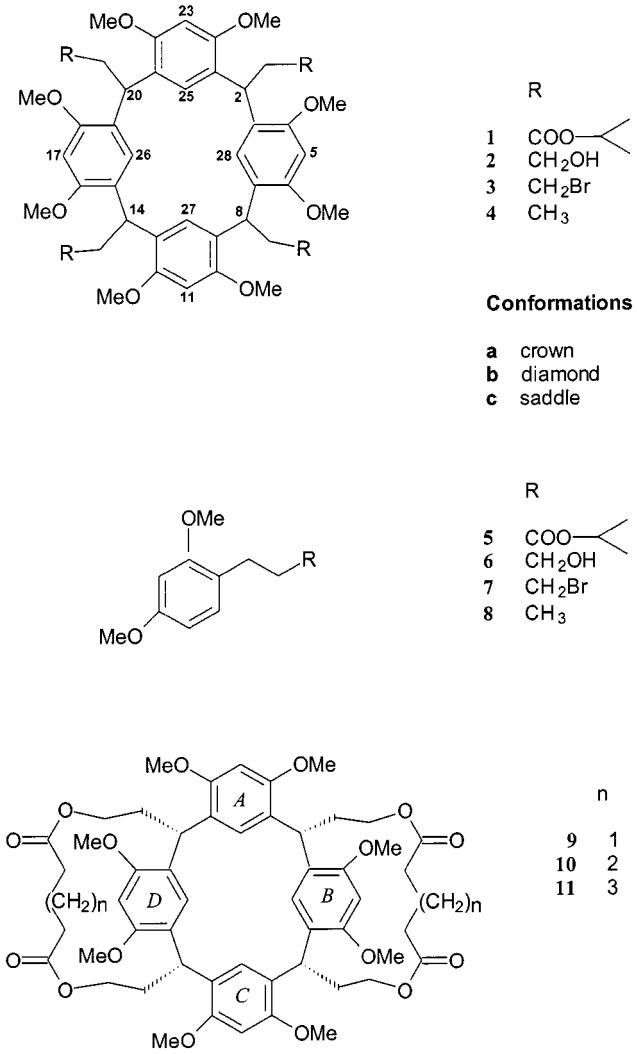

Figure 1. Resorcin[4]arene derivatives and monomer models synthesized

of the two cations, which have the same charge and similar ionic radii in hexacoordinate complexes.[23]

To a solution of **1a** (20 mg, 0.020 mmol) in $CDCl_3$ (0.8 mL), a solution of $GaCl_3$ in $CDCl_3$ (14 mg in 2 mL) was added portionwise (0.2 mL aliquots, 0.007 mmol each). After each addition, the chemical shift variations ($\Delta\delta$ in Hz) of the proton signals were measured with reference to the values in the ^{1}H-NMR spectrum of the pure resorcin[4]arene. The ^{1}H-NMR spectra of the mixtures were recorded at 60 °C, at which the complex is more soluble and the signals are better resolved. As a result, a series of plots showing $\Delta\delta$ as a function of the amount of metal ion added could be constructed. The signals of the isopropyl CH and of the bridge CH were most affected, shifting to higher and lower fields, respectively, as shown in Figure 4.

In the ^{13}C-NMR spectrum of a mixture of **1a**/$GaCl_3$ obtained following the addition of an excess of the salt, the resonances appeared at the shifts reported in Table 1. These data were interpreted in terms of the formation of a host–guest complex between the macrocycle and the cation, the observed NMR signals being attributable to an averaging of those due to the free and the complexed forms. Similar results were obtained with the stereoisomers **1b** and **1c**, whereas addition of $GaCl_3$ in $CDCl_3$ solution did not change the ^{1}H- and ^{13}C-NMR spectra of the model compound **5**, other than through dilution effects.

The molar ratio of the cation to the resorcin[4]arene in the complex could not be determined as there was no well-defined change in the slope of the curve (Figure 4). However, the different effects of the Ga^{III} cation on the protons (Figure 4) and the carbons (Table 1) of the macrocycle suggested the existence of different interaction sites.

Examination of CPK molecular models showed that for **1a** (crown conformation) these sites could be located: (i) in the cavity defined by the four side chains, (ii) at the external periphery of the ester functions, (iii) in the space defined by the aromatic methoxy groups, and (iv) at the centre of the aromatic rings.

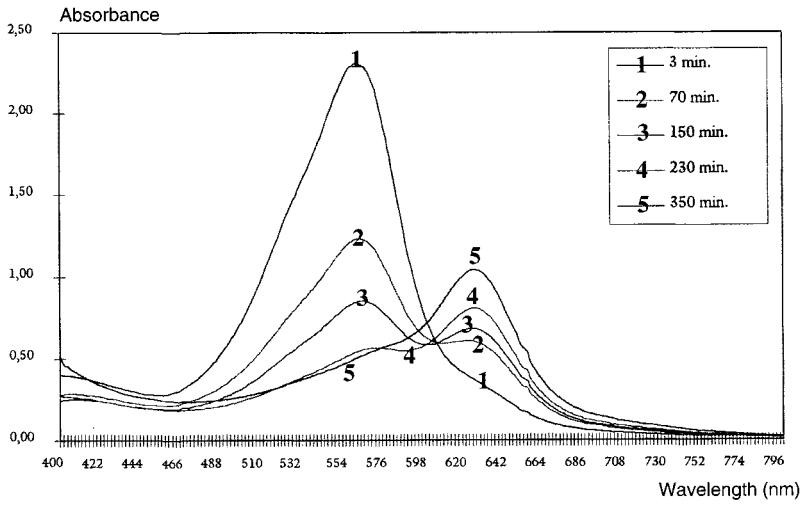

Figure 2. Absorption maxima in the visible region of compound **1a**

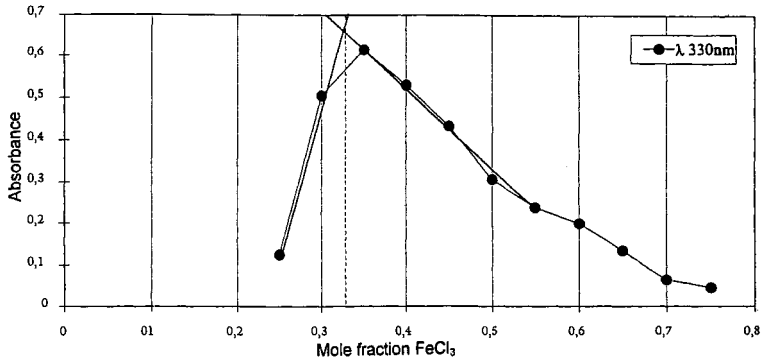

Figure 3. Stoichiometry of complex **1a**/$FeCl_3$ calculated according to the Job method at λ = 330 nm in the UV/Vis spectrum

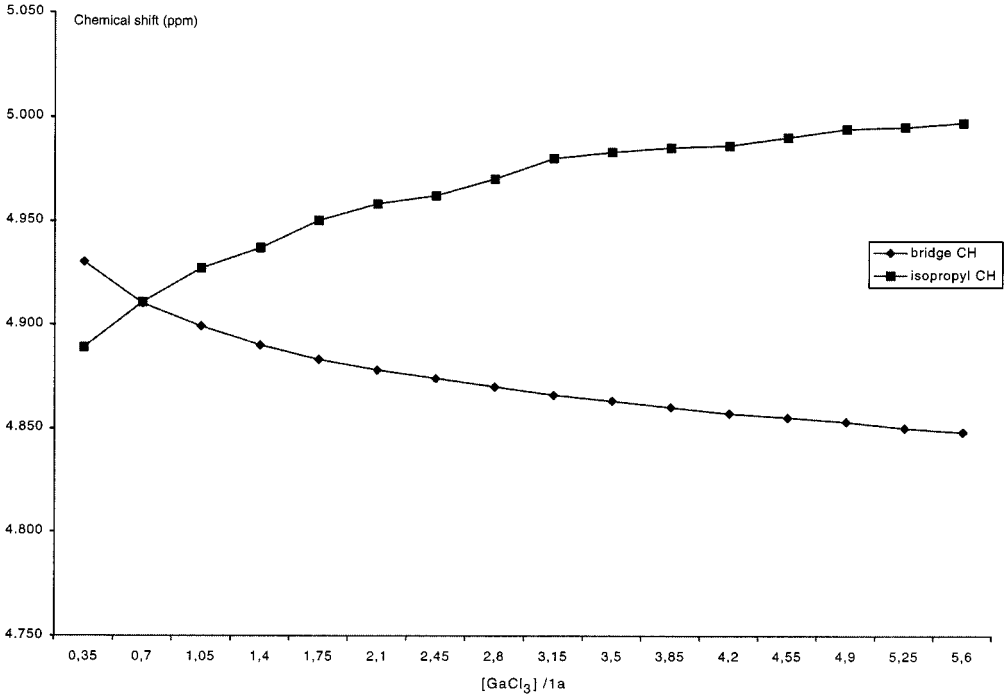

Figure 4. Chemical shift variations in the signals due to the bridge CH (υ) and isopropyl CH (ν) protons of **1a** upon addition of $GaCl_3$

Table 1. Chemical shift variations in the ^{13}C-NMR signals of resorcinarenes **1a** and **4a** upon addition of excess $GaCl_3$ (3:1)

Carbon type	Δδ (in Hz)			
	1a		**4a**	
	lowfield	highfield	lowfield	highfield
CH_e	42.75		129.79	
C_{ar}–O		10.70		33.96
OMe	26.48		70.93	
C_{ar}–C	9.04		65.65	
CH_i		34.23		18.11
CH	4.08			13.58
CH_2	51.34			11.32
CO	266.90		–	
OCH	174.06		–	
Me		9.16		19.62

In order to verify the importance of the side chains and of the carbonyl functions, two further derivatives **2a** and **4a** (Figure 1) were synthesized. The tetraalcohol **2a** was prepared, as previously reported,[1] by reduction of the tetraester **1a** with $LiAlH_4$ in THF. Treatment of **2a** with CBr_4 and PPh_3 in CH_2Cl_2 gave the tetrabromo derivative **3a** (Figure 1), subsequent treatment of which with Bu_3SnH and AIBN[24] in dry benzene under reflux for 3 h afforded **4a**.

The low solubility of **2a** in $CHCl_3$ prevented any study of its interaction with Fe^{III} cations. On the other hand, the UV spectrum of compound **4a** in $CHCl_3$, upon portionwise addition of $FeCl_3$, again showed two additional bands at 568 and 632 nm (Figure 5), while the colour of the solution changed from magenta through purple to blue. Accordingly, as shown in Figure 5, the 632 nm shoulder of the absorption centred at 568 nm increased with time and eventually reached the same intensity as the maximum at 568 nm. Notably, the UV/Vis spectrum of the **4a**/$FeCl_3$ mixture did not exhibit any absorption at λ = 330 nm.

The UV/vis spectrum of the monomer **8** (Figure 1), synthesized from **5** via the alcohol **6** and the bromo derivative **7** (see Experimental Section), did not show any additional

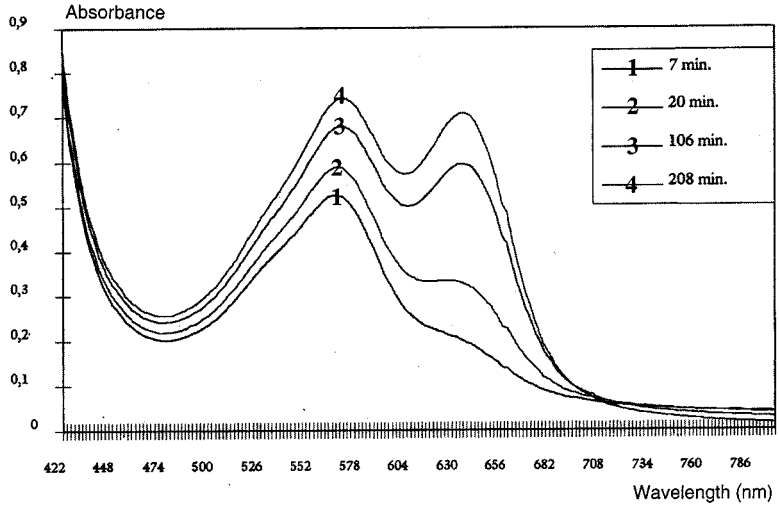

Figure 5. Absorption maxima in the visible region of compound **4a**

band upon addition of $FeCl_3$, again confirming the structural importance of the macrocyclic system.

After treating the mixture **1a**/$FeCl_3$ with MeOH and subjecting the resulting mixture to chromatography on silica gel, the resorcinarene **1a** was recovered in the free form. In contrast, on analogous treatment of the **4a**/$FeCl_3$ mixture, not only the free resorcinarene **4a** was isolated (67% of the starting material), but also the stereoisomer **4b** (22%). The diamond configuration of **4b** was confirmed by synthesizing this compound starting from **1b** and following the same procedure as used for the synthesis of **4a** from **1a**. When pure **4b** was treated with $FeCl_3$ in $CHCl_3$, the resulting UV/Vis spectrum was the same as that observed for the **4a**/$FeCl_3$ mixture. Treatment of the **4b**/$FeCl_3$ mixture with methanol as described above again led to the isolation of free **4b** (59% of the starting material) along with **4a** (29%). It must be emphasized that both the conversions **4a** → **4b** and **4b** → **4a** involve a configurational change, i.e. scission of the C(13)–C(14) or C(14)–C(15) bonds prior to ring closure.[1] The above results clearly suggested that the absorption at $\lambda = 330$ nm, observed only in the UV/Vis spectrum of **1a**/$FeCl_3$, could be attributed to an interaction between the carboxylic groups and Fe^{III}. Consequently, the absorption bands at 568 nm and 620 nm, which are present in the UV/Vis spectra of both **1a**/$FeCl_3$ and **4a**/$FeCl_3$ in $CHCl_3$, could be assigned to the other active site, involving an interaction between Fe^{III} and the upper rim of the macrocycle. To validate the above hypotheses, ^{1}H-NMR titration experiments using $GaCl_3$ [21–23] were repeated on **4a**.

Figure 6 shows the chemical shift variations in the signals due to the external aromatic protons (in the 5, 11, 17, and 23 positions) and the methoxy groups, which were affected the most markedly, as a function of the number of mmol of metal ions added.

A change in the slopes of the two curves corresponding to a 1:1 molar ratio suggested the formation of a 1:1 complex between the calixarene and $GaCl_3$. The chemical shift variation after this point would seem to be less pronounced and may be attributed simply to dilution of the system. Indeed, when the solvent was evaporated after 4 mmol $GaCl_3$ per mmol of macrocycle had been added and the residue was redissolved in 0.8 mL of $CDCl_3$, the chemical shifts observed for the H_i and OMe signals were comparable with those observed at the 1:1 molar ratio. The changes in the ^{13}C-NMR spectrum of **4a**, as compared with that of **1a** (Table 1), support the hypothesis of the formation of a **4a**/$GaCl_3$ complex through interaction at the upper rim, whereas the nuclei of the side chain do not exhibit any downfield shift in their signals. Accordingly, it would appear that here the alkyl substituent is not involved in any interaction with the cation.

Following the addition of excess $GaCl_3$ (ratio ca. 2:1), the ^{1}H-NMR spectrum recorded after 1 h featured signals attributable to a new compound; after leaving overnight, these intensified to account for ca. 25% of the material balance (by integration). These signals were attributed to the formation of a **4b**/$GaCl_3$ complex. This was corroborated by the fact that treatment of the mixture with MeOH and subsequent separation by preparative TLC gave both free **4a** and **4b** (ratio 3:1). Analogously, titration of **4b** with $GaCl_3$ led to the generation of new signals, which were coincident with the "shifted" signals seen for the pair **4a**–**4b**/$GaCl_3$. Free **4a** and **4b**, in a ratio of ca. 1:2 (by integration), were again obtained upon decomposing the complexes with MeOH.

Next, we extended our investigation to the host–guest properties of the more rigid resorcinarenes **9–11** (Figure 1), which we have synthesized previously.[3] The double-spanned resorcinarenes **9–11** are characterized by a frozen boat conformation corresponding to one of the two equivalent forms in equilibrium in the crown configuration.[23] Compounds **9–11**, having C_{2v} symmetry, feature two parallel polymethylene bridges, along with two opposite (B and D) and two in-plane (A and C) aromatic rings. Notably, the arrangement of the B and D rings in these compounds leads to highfield shifts of the signals due to 25-H and 27-H and the C-4, C-6, C-16, and C-18 methoxy groups. As a result, these resorcinarenes would seem to display all the pre-

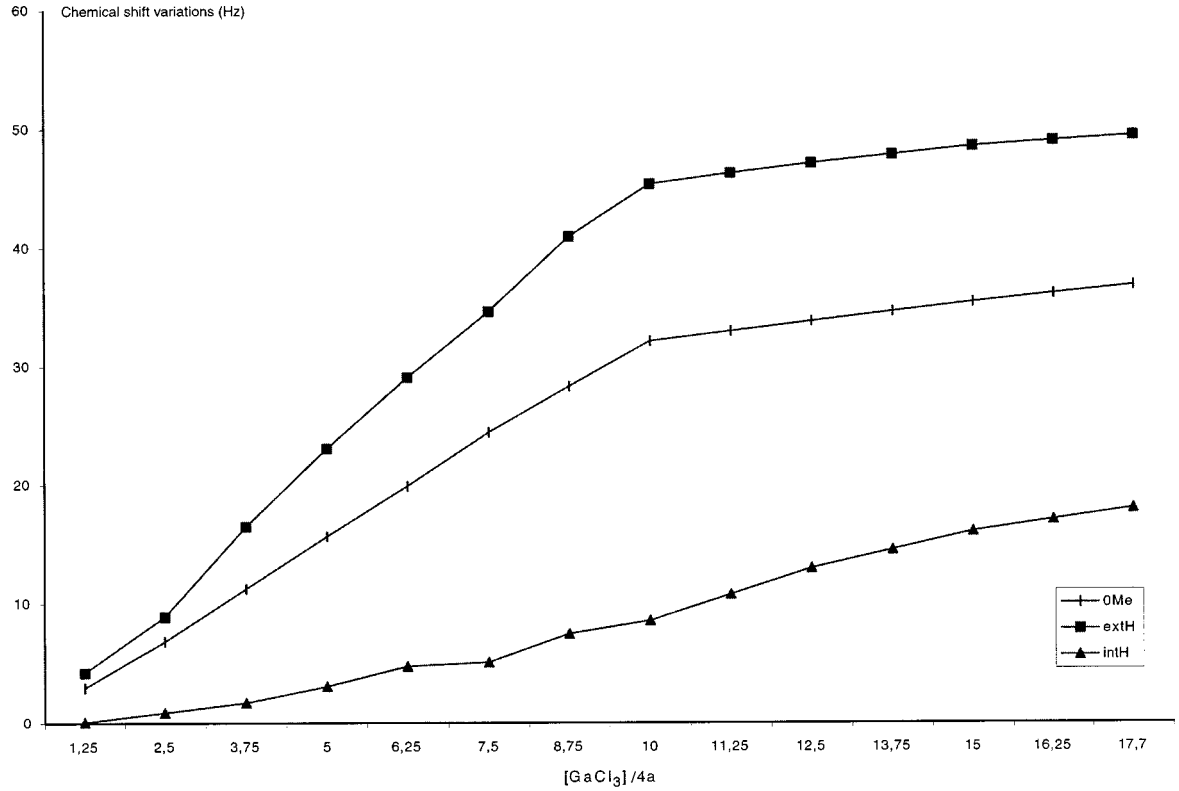

Figure 6. Chemical shift variations in the signals due to OMe (υ), H_e (ν), and H_i (σ) upon addition of $GaCl_3$ to **4a** in $CDCl_3$

requisites enabling a study of the interactions with $FeCl_3$ and/or $GaCl_3$.

Titration of the adipoyl derivative **10** with a 2.5×10^{-3} M solution of $GaCl_3$ in $CDCl_3$ at 60 °C gave the results presented in Table 2.

Table 2. Chemical shift variations in the ^{13}C-NMR signals of resorcinarene **10** upon addition of excess $GaCl_3$ (2:1)

Position	Carbon type	$\Delta\delta_C$ (Hz)		$\Delta\delta_H$ (Hz)	
		lowfield	highfield	lowfield	highfield
1,9,13,21	C_{ar}–C	86.4			
2,8,14,20	CH	7.2		4.4	
3,7,15,19	C_{ar}–C	0.4			
4,6,16,18	C_{ar}–O		8.4		
5,17	CH_e	156.0		86.9	
10,12,22,24	C_{ar}–O	8.4			
11,23	CH_e		5.6	16.0	
25,27	CH_i		31.6		66.9
26,28		4.8		0.6	
4-,6-,16-,18-	OMe	112.0		96.1	
10-,12-,22-,24-	OMe	3.6		17.2	
2-,8-,14-,20-	CH_2		10.4		0.6
chain	CH_2O	56.8		A: 31.8	B: 6.3
chain	C=O	110.0			
chain	CH_{2e}	12.8		56.2	
chain	CH_{2i}	8.8		C: 21.6; D: 17.8	

The different effects on the signals in the ^{1}H- and ^{13}C-NMR spectra suggested that one site of interaction is located among the methoxy groups of the two face-to-face aromatic nuclei.

Moreover, the ^{1}H- and ^{13}C-NMR chemical shift variations showed that with regard to the side chains the carbonyl and the adjacent CH_2O groups were the most influenced by the interaction with $GaCl_3$. Notably, the two geminal protons (A and B in Table 2) of the oxymethylene group became non-equivalent and their respective signals were shifted in opposite directions. The signals due to the methylene units of the adipoyl bridge were seen to be less influenced by the interaction of **10** with $GaCl_3$. For instance, those due to the geminal protons of CH_{2i} (C and D in Table 2) were slightly shifted downfield. The above results suggested that Ga^{III} had to be located in a second active site, orthogonal to the carboxylic groups and not between the two spanning chains. Considering the signal shifts of carbons C-1/C-21 and C-9/C-13, we surmised that the

cation was most probably located between two resorcinarene molecules.

The inclusion of $GaCl_3$ in resorcinarene **10** was confirmed by the deep-blue colour of the solutions, associated with absorption maxima at 560 and 620 nm in the UV/vis spectrum, and by peaks in the FAB-MS spectrum at *m/z* = 1136 and 1101, attributable to the fragments $[M + GaCl_2]^+$ and $[M + GaCl]^+$, respectively. The homologous resorcinarenes **9** and **11** produced comparable results.

Conclusions

The above results have shown that *C*-alkyl-resorcinarene octamethyl ethers, synthesized in our laboratories,[1–3] are capable of interacting with $FeCl_3$ and $GaCl_3$ in organic solvents. Resorcinarenes lacking carboxylic groups in the side chains (such as **4a** and **4b**) possess only one active site located at the upper part of the aromatic moiet. Resorcinarenes bearing carboxylic groups, either in a freely rotating side chain (as in **1a**) or in the polymethylene bridge of the basket compound **10**, possess a second interaction site. In the latter case, on the basis of the different influences on the chemical shifts in the ^{1}H-NMR spectrum, the cation was hypothesized to reside external to the two "handles", between two molecules of **10**.

Experimental Section

General Remarks: Melting points (uncorrected): Kofler apparatus. – ^{1}H- and ^{13}C-NMR spectra (300 MHz and 75 MHz, TMS at δ = 0 as internal standard in $CDCl_3$ solution): Varian Gemini 300 spectrometer. – EI-MS (direct inlet): VG7070 EQ spectrometer. – UV/vis spectra: Cary 4 spectrophotometer. – Column chromatography: Merck Kieselgel 60.

Tetrabromoresorcinarenes 3a and 3b: A solution of PPh_3 (12.4 mmol) in CH_2Cl_2 (8 mL) was added dropwise to a solution of the calixarene tetraalcohol (**2a** or **2b**,[1] 3.5 mmol) and CBr_4 (1.4 mmol) in CH_2Cl_2 (10 mL). The resulting mixture was stirred at room temperature for 20 h and then the solvent was evaporated. Purification of the residue by column chromatography (CH_2Cl_2) afforded the tetrabromoresorcinarene **3a** or **3b** in 58% and 54% yield, respectively.

3a (Crown): m.p. 263–265 °C. – ^{1}H NMR ($CDCl_3$): δ = 6.52 (br. s, 4 H, 25-, 26-, 27-, 28-H), 6.31 (s, 4 H, 5-, 11-, 17-, 23-H), 4.63 (t, 4 H, *J* = 7.5 Hz, 2-, 8-, 14-, 20-H), 3.62 (s, 24 H, 8 × OMe), 3.37 (t, 8 H, *J* = 7.5 Hz, 4 × CH_2Br), 2.42 (q, 8 H, *J* = 7.5 Hz, 4 × CH_2). – ^{13}C NMR: δ = 156.40 (s, C-4, C-6, C-10, C-12, C-16, C-18, C-22, C-24), 125.46 (d, C-25, C-26, C-27, C-28), 124.76 (s, C-1, C-3, C-7, C-9, C-13, C-15, C-19, C-21), 97.03 (d, C-5, C-11, C-17, C-23), 56.08 (q, OMe), 38.31 (t, CH_2), 34.63 (d, C-2, C-8, C-14, C-20), 31.45 (t, CH_2Br).

3b (Diamond): m.p. 214–216 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.37 (s, 2 H, 25-, 28-H), 6.46 (s, 2 H, 5-, 23-H), 6.43 (s, 2 H, 26-, 27-H), 6.38 (s, 2 H, 11-, 17-H), 5.21 (t, 1 H, *J* = 8 Hz, 2-H), 4.77 (dd, 2 H, *J* = 7.5 and 6.5 Hz, 8-, 20-H), 4.73 (t, 1 H, *J* = 8 Hz, 14-H), 3.87 (s, 2 H, 4-, 24-OMe), 3.86 (s, 2 H, 6-, 22-OMe), 3.78 (s, 2 H, 10-, 18-OMe), 3.67 (s, 2 H, 12-, 16-OMe), 3.36 (m, 4 H, 2 × CH_2Br), 3.29 (t, 2 H, *J* = 7.5 Hz, CH_2Br), 2.81 (t, 2 H, *J* = 8 Hz, CH_2Br), 2.48 (q, 2 H, *J* = 7.5 Hz, 2-CH_2), 2.42 (m, 4 H, 8-CH_2, 20-CH_2), 1.65 (q, 2 H, *J* = 8 Hz, 14-CH_2). – ^{13}C NMR: δ = 155.96 (s, C-10, C-18), 155.86 (s, C-12, C-16), 156.56 (s, C-6, C-22), 156.51 (s, C-4, C-24), 126.94 (d, C-26, C-27), 126.79 (d, C-25, C-28), 125.46 (s, C-7, C-21), 124.21 (s, C-13, C-15), 123.63 (s, C-1, C-3), 122.97 (s, C-9, C-19), 96.92 (d, C-11, C-17), 95.94 (d, C-5, C-23), 56.47 (q, 4-, 24-OMe), 56.23 (q, 6-, 22-OMe), 55.83 (q, 10-, 18-OMe), 55.79 (q, 12-, 16-OMe), 40.59 (t, 2-CH_2), 39.65 (t, 14-CH_2), 37.76 (t, 8-, 20-CH_2), 34.60 (d, C-8, C-20), 32.00 (t, 2 × CH_2Br), 31.69 (t, CH_2Br), 31.59 (t, CH_2Br), 31.40 (d, C-2), 31.12 (d, C-14).

Tetraethylresorcinarenes 4a and 4b: A solution of **3a** or **3b** (0.16 mmol), Bu_3SnH (0.24 mmol), and a catalytic amount of AIBN in dry benzene (1.5 mL) was refluxed for 3 h under N_2. The solvent was then evaporated and the residue was washed several times with hexane. Purification by column chromatography ($CHCl_3$/MeOH, 97:3) afforded pure **4a** or **4b** in quantitative yield.

4a (Crown): m.p. 260–262 °C. – ^{1}H NMR ($CDCl_3$): δ = 6.65 (s, 4 H, 25-, 26-, 27-, 28-H), 6.32 (s, 4 H, 5-, 11-, 17-, 23-H), 4.38 (t, 4 H, *J* = 7.5 Hz, 2-, 8-, 14-, 20-H), 3.60 (s, 24 H, 8 × OMe), 1.85 (quint, 8 H, *J* = 7 Hz, 4 × CH_2), 0.92 (t, 8 H, *J* = 7 Hz, Me). – ^{13}C NMR: δ = 155.86 (s, C-4, C-6, C-10, C-12, C-16, C-18, C-22, C-24), 125.99 (d, C-25, C-26, C-27, C-28), 126.08 (s, C-1, C-3, C-7, C-9, C-13, C-15, C-19, C-21), 96.98 (d, C-5, C-11, C-17, C-23), 56.17 (q, 8 × OMe), 27.76 (t, 4 × CH_2), 36.95 (d, C-2, C-8, C-14, C-20), 12.76 (t, 4 × Me). – EI-MS: *m/z* (%) = 712 $[M]^+$ (29), 683 $[M – Et]^+$ (100), 327 $[M – 2 × Et]^{2+}$ (16).

4b (Diamond): m.p. 205–206 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.60 (s, 2 H, 25-, 28-H), 6.46 (s, 2 H, 26-, 27-H), 6.43 (s, 2 H, 5-, 23-H), 6.38 (s, 2 H, 11-, 17-H), 5.01 (t, 1 H, *J* = 8 Hz, 2-H), 4.56 (t, 1 H, *J* = 8 Hz, 14-H), 4.53 (dd, 2 H, *J* = 10 and 5.5 Hz, 8-, 20-H), 3.86 (s, 2 H, 4-, 24-OMe), 3.84 (s, 2 H, 6-, 22-OMe), 3.76 (s, 2 H, 10-, 18-OMe), 3.56 (s, 2 H, 12-, 16-OMe), 2.98 (quint, 2 H, *J* = 8 Hz, 2-CH_2), 1.86 (m, 4 H, 8-CH_2, 20-CH_2), 1.03 (quint, 2 H, *J* = 8 Hz, 14-CH_2), 0.92 (t, 4 H, *J* = 7.5 Hz, 2 × Me), 0.86 (t, 2 H, *J* = 7.5 Hz, Me), 0.33 (t, 2 H, *J* = 7.5 Hz, Me). – ^{13}C NMR: δ = 156.38 (s, C-6, C-22), 155.92 (s, C-4, C-24), 155.35 (s, C-10, C-18), 155.35 (s, C-12, C-16), 127.01 (d, C-26, C-27), 127.89 (s, C-7, C-21), 126.85 (d, C-25, C-28), 126.14 (s, C-1, C-3), 125.72 (s, C-13, C-15), 124.81 (s, C-9, C-19), 97.04 (d, C-11, C-17), 96.11 (d, C-5, C-23), 56.71 (q, 4-, 24-OMe), 56.48 (q, 6-, 22-OMe), 55.91 (q × 2, 10-, 12-, 16-, 18-OMe), 37.00 (d, C-8, C-20), 33.13 (d, C-14), 32.66 (d, C-2), 30.49 (t, 2-CH_2), 29.49 (t, 14-CH_2), 27.55 (t, 8-, 20-CH_2), 13.03 (t, 2 × Me), 12.55 (t, Me), 12.05 (t, Me). – EI-MS: *m/z* (%) = 712 $[M]^+$ (27), 683 $[M – Et]^+$ (100), 327 $[M – 2 × Et]^{2+}$ (19).

3-(2,4-Dimethoxyphenyl)propyl Alcohol (6): The alcohol was prepared by $LiAlH_4$ reduction of the 3-(2,4-dimethoxyphenyl)propanoic acid isopropyl ester (**5**), which, in turn, was synthesized by reduction of 2,4-dimethoxycinnamic acid isopropyl ester with H_2 in the presence of Pd/C.

Isopropyl Ester 5: Oil. – ^{1}H NMR ($CDCl_3$): δ = 7.02 (d, 1 H, *J* = 8 Hz, 6-H), 6.42 (d, 1 H, *J* = 2 Hz, 3-H), 6.38 (dd, 1 H, *J* = 8 and 2 Hz, 5-H), 3.77 (s, 3 H, OMe), 3.75 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 2.86 (t, 2 H, *J* = 7.5 Hz, 7-H), 2.56 (t, 2 H, *J* = 7.5 Hz, 8-H). – ^{13}C NMR: δ = 173.59 (s, C=O), 159.33 (s, C-4), 158.07 (s, C-2), 129.07 (d, C-6), 120.87 (s, C-1), 103.50 (d, C-5), 98.17 (d, C-3), 54.98 (q, OMe), 54.89 (q, OMe), 51.16 (q, OMe), 34.02 (t, C-8), 25.28 (t, C-7). – EI-MS: *m/z* (%) = 224 $[M]^+$ (67), 164 $[M – HCOOMe]^+$ (13), 151 $[M – CH_2COOMe]^+$ (100), 121 $[151 – OCH_2]^+$ (49), 91 $[121 – OCH_2]^+$ (25).

Alcohol 6: Oil. – ^{1}H NMR ($CDCl_3$): δ = 7.04 (d, 1 H, *J* = 8 Hz, 6-H), 6.45 (d, 1 H, *J* = 2 Hz, 3-H), 6.44 (dd, 1 H, *J* = 8 and 2 Hz, 5-H), 3.81 (s, 3 H, OMe), 3.79 (s, 3 H, OMe), 3.59 (t, 2 H, *J* = 6 Hz, CH_2OH), 2.65 (t, 2 H, *J* = 7 Hz, 7-H), 1.81 (tt, 2 H, *J* = 7 and 6 Hz, 8-H). – ^{13}C NMR: δ = 159.17 (s, C-4), 158.20 (s, C-2), 130.25 (d, C-6), 122.23 (s, C-1), 104.15 (d, C-5), 98.47 (d, C-3), 61.92 (t, CH_2OH), 55.35 (q, 2 × OMe), 33.10 (t, C-8), 25.21 (t, C-7). – EI-MS: *m*/*z* (%): 196 $[M]^+$ (40), 165 $[M - CH_2OH]^+$ (4), 151 $[M - CH_2 - CH_2OH]^+$ (100), 121 (40), 91 (13).

1-Bromo-3-(2,4-dimethoxyphenyl)propane (7) and 1-(2,4-Dimethoxyphenyl)propane (8): Compounds **7** (60% yield) and **8** (quantitative yield) were obtained according to the procedures described for the preparation of **3a** and **4a**, respectively.

Bromide 7: Oil. – ^{1}H NMR ($CDCl_3$): δ = 7.04 (d, 1 H, *J* = 8 Hz, 6-H), 6.44 (d, 1 H, *J* = 2 Hz, 3-H), 6.41 (dd, 1 H, *J* = 8 and 2 Hz, 5-H), 3.79 (s, 6 H, OMe), 3.38 (t, 2 H, *J* = 7 Hz, CH_2Br), 2.68 (t, 2 H, *J* = 7 Hz, 7-H), 2.10 (p, 2 H, *J* = 7 Hz, 8-H). – ^{13}C NMR: δ = 159.39 (s, C-4), 158.29 (s, C-2), 130.33 (d, C-6), 121.20 (s, C-1), 103.72 (d, C-5), 98.49 (d, C-3), 55.31, 55.18 (q, 2 × OMe), 33.75 (t, CH_2Br), 32.84 (t, C-8), 28.19 (t, C-7).

Alkane 8: Oil. – ^{1}H NMR ($CDCl_3$): δ = 7.01 (d, 1 H, *J* = 8 Hz, 6-H), 6.44 (d, 1 H, *J* = 2 Hz, 3-H), 6.41 (dd, 1 H, *J* = 8 and 2 Hz, 5-H), 3.79 (s, 6 H, OMe), 2.51 (dd, 2 H, *J* = 8 and 7 Hz, 7-H), 1.60 (m, 2 H, 8-H), 0.92 (t, 3 H, *J* = 7 Hz, Me). – ^{13}C NMR: δ = 158.86 (s, C-4), 158.23 (s, C-2), 129.86 (d, C-6), 123.43 (s, C-1), 103.53 (d, C-5), 98.35 (d, C-3), 55.26 (q, OMe), 55.18 (q, OMe), 31.58 (t, C-8), 23.14 (t, C-7), 14.00 (q, Me). – EI-MS: *m*/*z* (%) = 180 $[M]^+$ (45), 151 $[M - Et]^+$ (100), 121 $[151 - OCH_2]^+$ (38), 91 $[121 - OCH_2]^+$ (21).

General Procedure for ^{1}H-NMR Titrations with $GaCl_3$: The initial concentrations of the solutions of pure host (resorcin[4]arene) and guest ($GaCl_3$) in $CDCl_3$ were 2.5 × 10^{-3} M. The resorcinarene solution (0.8 mL) was titrated with aliquots (0.1, 0.2, and 0.4 mL) of the $GaCl_3$ solution. After each addition of the salt, the ^{1}H-NMR spectrum was recorded at 60 °C and the complexation shifts of the signals (Δδ) relative to those of the pure compounds were evaluated. The final solutions obtained from each experiment were concentrated and the ^{13}C-NMR spectra were recorded.

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