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Pavel Lhotak[a][b]; Ryoji Nakamura[a]; Seiji Shinkai[a]
[a] Department of Chemical Science & Technology, Faculty of Engineering, Kyushu University, Fukuoka, Japan [b] Department of Organic Chemistry, Prague Institute of Chemical Technology, Prague 6, Czech Republic

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Synthesis and ^{1}H NMR studies of vinyl-substituted calix[4]arene derivatives: Enhanced cation-π interactions with extended calix[4]arene π-systems

PAVEL LHOTAK[a,b], RYOJI NAKAMURA[a] AND SEIJI SHINKAI[a,*]

[a]*Department of Chemical Science & Technology, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan;*
[b]*Present address: Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic*

A new class of calix[4]arene derivatives bearing vinyl groups on the upper rim has been synthesized using the condensation of starting 5,17-diformyl-25,26,27,28-tetrapropoxycalix[4]arene with malonic acid in the presence of piperidine as a catalyst. The corresponding vinyl substituted derivative can be isolated directly in 40% yield and serves as a starting point for the preparation of calix[4]arene derivatives fixed either in the *cone* or *1,3-alternate* conformations. The complexation ability of such compounds towards Ag^+ cation has been studied with the help of ^{1}H NMR spectroscopy and MS spectroscopy. It was shown that the presence of the double bonds at upper rim can enhance binding constants as compared with unsubstituted derivatives due to their additional cation-π interactions. The significance of the double bonds for quaternary pyridinium salts has been also demonstrated by the enhanced binding ability.

INTRODUCTION

Calix[n]arenes[1,2] have become very well known for their unique molecular architecture and they have been attracting much attention of chemists, especially during the last decade. Because of their easy derivatization and possible fixing of the molecule in several different conformations, they have emerged as a "third class of host molecules" in supramolecular chemistry.[3] They have been recognized as very useful building blocks for the construction of more elaborated molecular systems possessing interesting functions.[4,5] In our previous papers we have shown that calix[n]arenes are able to bind suitable cations by the cation-π interactions.[6] For instance, derivatives of 1,3-alternate calix[4]arene is believed to bind Ag^+ by the cooperative effect of the cation-π interactions from aromatic subunits and cation-lone electron pairs interactions from oxygen atoms (Figure 1A).[6a,d] There are also interesting examples of organic ligands where Ag^+ is bound because of cation-π interactions from triple[7] (Figure 1B) or double[8] bonds (Figure 1C), the structure of which has been proved by X-ray results.

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*Corresponding author.

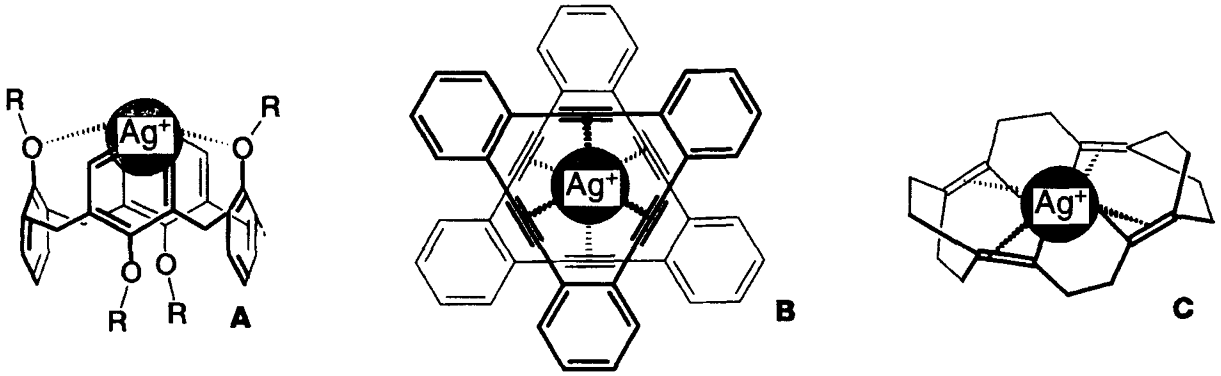

FIGURE 1 Examples of cation-π interactions.

As a consequence of our previous research we aimed at the synthesis of vinyl-substituted calix[4]arenes bearing double bonds on the upper rim. Such a type of calixarenes having multiple bonds within a molecule is very interesting from several points of view: (a) they can be used as a monomer for the preparation of calix[4]arene-based polymers or copolymers; (b) they are valuable intermediates for the synthesis of derivatives containing triple bonds; (c) last but not least, they are also interesting from theoretical points of view. Due to the presence of the wider π-system (double bonds are conjugated with calixarene's aromatic subunits), one can study their complexation ability for suitable cations and quantitatively estimate what is the contribution of multiple bonds to the cation-π interactions in overall binding process.

RESULTS AND DISCUSSION

This study has been "provoked" by an unexpected discovery achieved in our laboratory. We found that, contrary to our expectation, the Knoevenagel reaction[9] of diformyl calixarene **1** according to Figure 2 (after prolonged heating) does not yield cinnamic acid derivative **2a**, but compound **2b** can be isolated from the reaction mixture as a sole product in 41% yield. The production of the vinyl derivative seems to be really surprising. In fact, we could not find the similar reaction in literature. Decarboxylation of α,β-unsaturated carboxylic acids is usually carried out by heating with copper or cuprous oxide in quinolin,[10] but we could not find any example of such a decarboxylation reaction induced in a piperidine-pyridine system. Tetrapropoxy tetraformyl derivative **3** (Figure 2) did not yield any trace of the similar product and cinnamic acid derivative **4** was isolated in almost quantitative yield (98.5%). Therefore, we came into a conclusion that the presence of free hydroxyl groups in the molecule is essential for the course of this reaction. This is also supported by the fact that the reaction of a model compound, 4-ethoxybenzaldehyde **5a**, under the identical reaction conditions yields quantitatively (99%) the corresponding 4-ethoxycinnamic acid **6**, whereas in case of 4-hydroxybenzaldehyde **5b** 4-hydroxystyrene **7** was isolated in 10% yield from otherwise polymeric products. Fortunately, unlike the reaction of 4-hydroxystyrene,[11] it seems that the unique molecular structure of calix[4]arene derivatives protects the double bonds from additional polymerization during the course of this reaction.

Compound **2b** was then alkylated by propyl iodide in the presence of NaH to yield cone

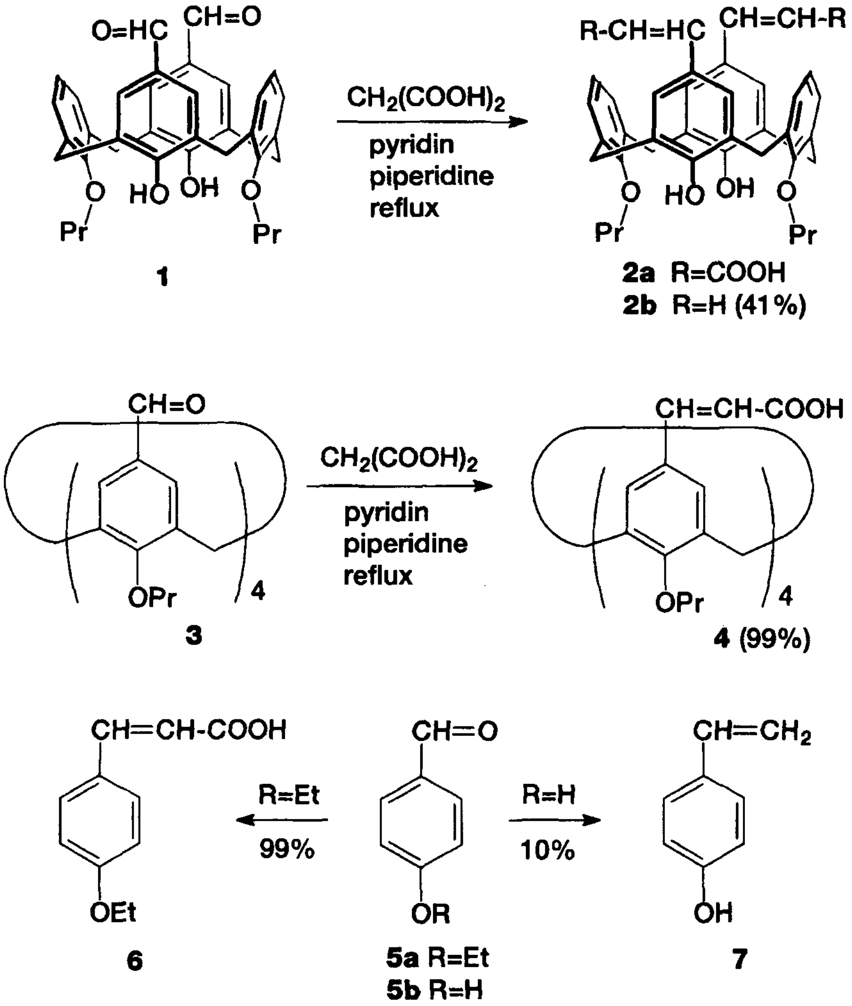

FIGURE 2 Preparation of vinyl derivatives.

derivative **10** in 82% (Figure 3). Alkylation with Cs_2CO_3/PrI in refluxing acetone has offered appropriate 1,3-alternate compound **9** (81% yield). To obtain a model compound with approximately the same substituent but without its possible cation-π contribution, we have carried out the reduction of diacetyl compound **12** (prepared from compound **8** by Friedel-Crafts alkylation followed by additional alkylation of OH groups) with the help of Et_3SiH-CF_3COOH mixture. The resultant diethyl derivative **13** has been isolated in 72% yield. The same product was also obtained by Pd/C catalyzed hydrogenation of **10** in 82% yield.

It is known that calixarenes can serve as π-base receptors for the selective binding of suitable cations (such as Ag^+) by cation-π interactions.[6] We have measured ^{1}H NMR spectra of several double bond containing calixarenes in the presence of silver triflate (AgTf) to specify the binding sites for silver cation. To obtain the consistent and hence comparable data, all measurements have been carried out in $CDCl_3$:CD_3OD = 4:1 v/v mixture at 25°C and the concentration of calixarene was kept at 5 mmol dm^{-3}.

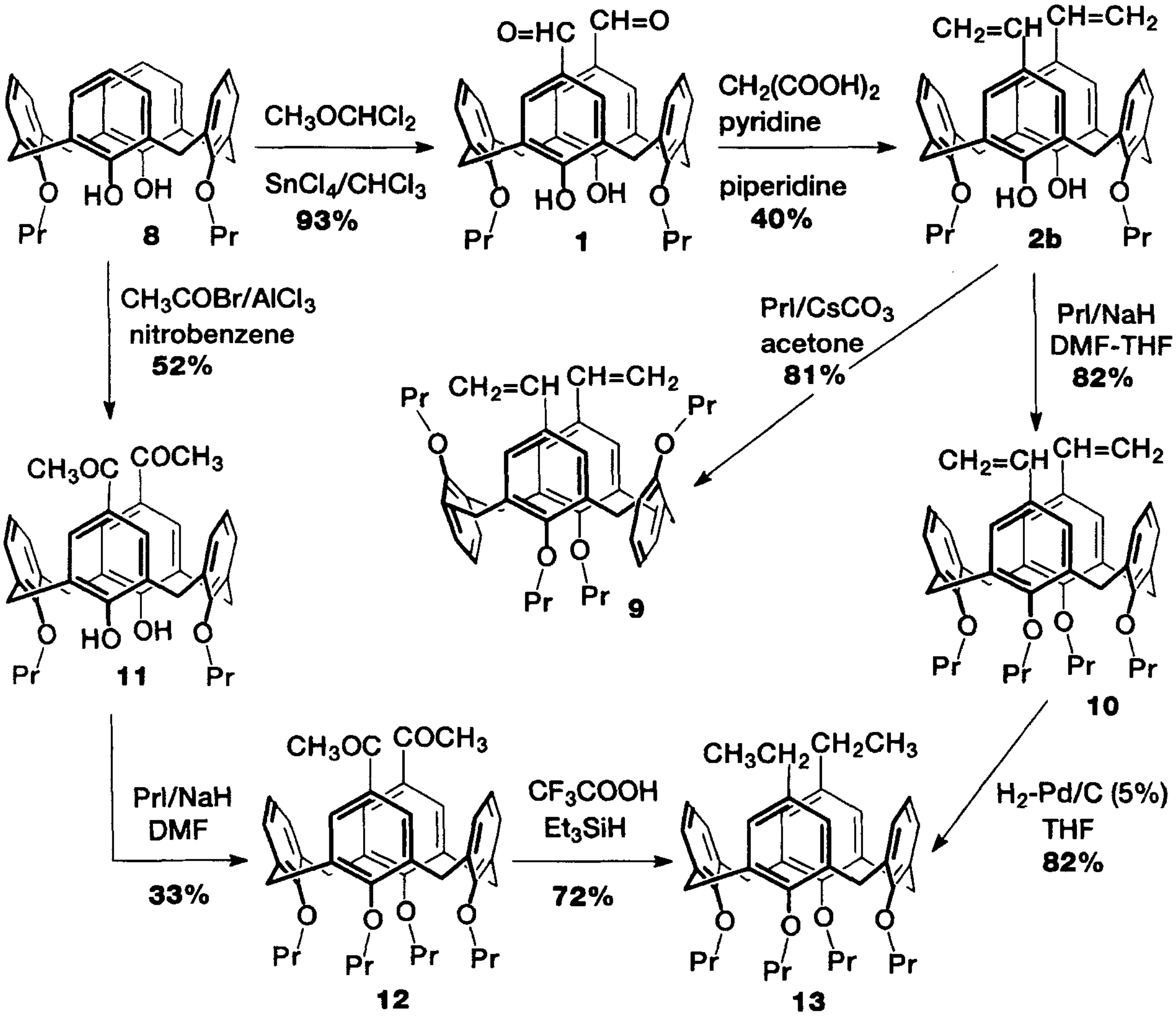

FIGURE 3 Synthesis of vinyl-substituted calix[4]arene derivatives.

The induced chemical shifts (after addition of 10 mmol of AgTf) are depicted in Figure 4. In all cases we can observe significant changes in the chemical shift of α-protons in the double bonds. In dipropoxy calixarene **2b** this is even far the most dramatic change (0.14 ppm) in the whole molecule confirming the importance of the double bonds in Ag^+ binding. Also, compound **10** exhibits very substantial changes; especially, those of unsubstituted aromatic rings (0.49 ppm for H-para and 0.42 for H-meta) along with α-protons in the double bonds (0.22 ppm) indicate a possible binding mode that Ag^+ is clasped by two opposite unsubstituted rings and the double bonds serve at the same time for holding of Ag^+ inside the cavity by additional cation-π interactions with the double bonds.

Figure 5 shows typical binding curves obtained by NMR titration. Typically, binding constants were estimated from the titration data obtained

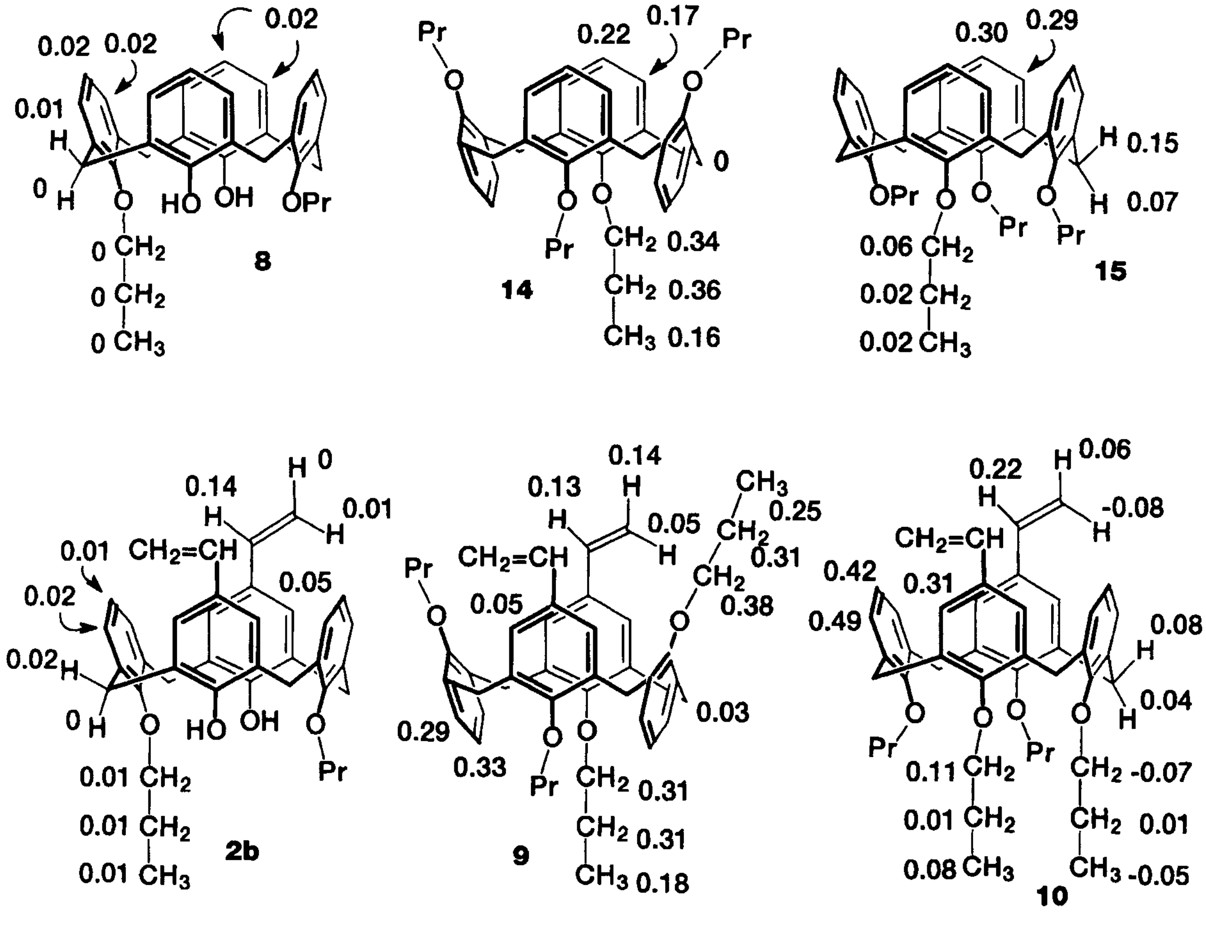

FIGURE 4 ^{1}H NMR induced chemical shifts after addition of 2 equivalents of AgTf, $CDCl_3$:CD_3OD = 4:1 v/v at 25°C; (–) denotes the up-field chemical shift.

for several different protons and compared for self-consistency of the results. Calix[4]arene protons (c = 0.005 mol dm^{-3}) were monitored in the presence of various guest (AgTf) concentrations (0.001–0.050 mol dm^{-3}). The complexation constants of calix[4]arene derivatives towards Ag^+ cation have been computed using original nonlinear regression curve-fitting program for the formation of a 1:1 complex. The stoichiometry of complexes has been evaluated by ^{1}H NMR experiments using continuous-variation plot[12] (Job plot) and assuming the induced chemical shift is a linear function of complexation. In all cases the stoichiometry has been determined as 1:1; the example of Job plot is depicted in Figure 6.

As can be seen from Table 1 the affinity towards Ag^+ has increased in all cases after the introduction of the double bonds into the upper rim: compare the following couples: **8** (15.8 ± 1.8 mol^{-1} dm^3) and **2b** (36.2 ± 1.5 mol^{-1} dm^3); **14** (1150 ± 120 mol^{-1} dm^3) and **9** (1730 ± 180 mol^{-1} dm^3); and **15** (1110 ± 145 mol^{-1} dm^3) and **10**[13] (K = 8000 mol^{-1} dm^3). These values clearly show that the double bond really plays an important role in enhancing the K_c due to its own contribution to the cation-π interactions. To further support

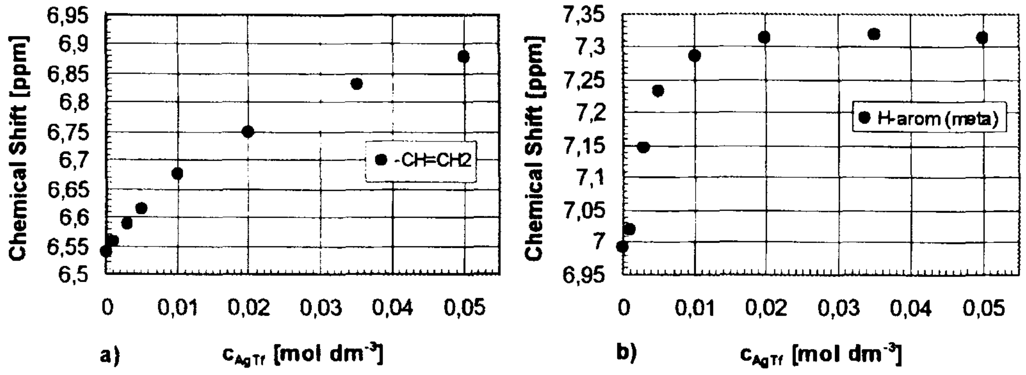

FIGURE 5 ^1H NMR titration curves of **2b** (Figure 5a) and **9** (Figure 5b) (c = 5 mmol dm^{-3}) with AgTf ($CDCl_3$:CD_3OD = 4:1 v/v, 25°C, 250 MHz).

this proposal, a complexation constant of diethyl derivative **13** has been measured. The value obtained (1852 ± 200 mol^{-1} dm^3) is much lower than that for vinyl derivative **10** (8000 mol^{-1} dm^3), indicating that in case of the ethyl-group only the simple electron-donating effect can operate to moderately enhance the K_c.

In the ^1H NMR titration of **10** a very unusual behavior was induced by the excess amount of silver cation. While in all other cases the titration curves exhibit a smooth saturation curvature in agreement with proposed hyperbolic function, derivative **10** shows a clear maximum or minimum (Figure 7) that indicates the presence of some additional calixarene-Ag^+ interactions. It is noteworthy that this phenomenon, induced at high Ag^+ concentration, is observable only for some parts of the molecule. As can be seen from Figure 7, axial or equatorial CH_2 protons do not show any uncommon change.

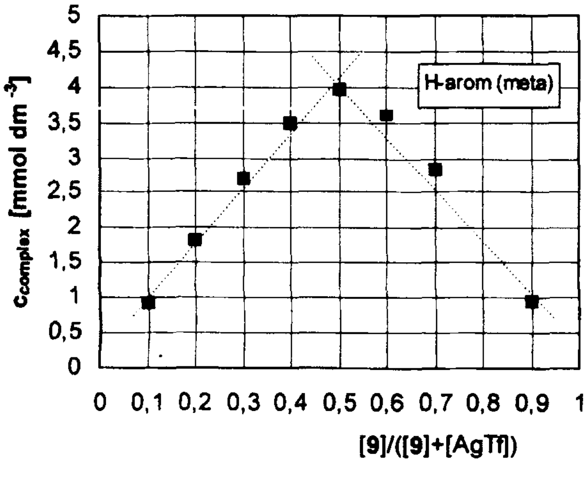

FIGURE 6 Job plot of derivative **9**, $c_{calix} + c_{AgTf}$ = 0.005 mol dm^{-3}

On the other hand, methyl groups, aromatic hydrogens, and *trans*-hydrogens in the double bonds possess a local extreme on the titration curves. Due to the uncommon course of titration curve the Job plot was found to be useless for proving of stoichiometry. Mass spectra of **10** (positive SIMS) in the presence of 1 and 10 equivs. of AgTf have been measured to find what phenomenon occurs in this system. In both cases, however, only one peak for the 1:1 complex (m/z = 753) has been observed. Low temperature ^1H NMR spectra of the **10**-Ag^+ system have been measured in CD_2Cl_2:CD_3OD = 4:1 v/v (Figure 8). Unfortunately, signals of complexed and uncomplexed species appeared separately only at lowest possible temperature (− 85°C) where they were very broadened. It is only recognizable that at high Ag^+ concentration there is some other species apart of 1:1 complex, that could not be assigned due to extensive line broadening. We now consider that **10** and Ag^+ form additional species with higher

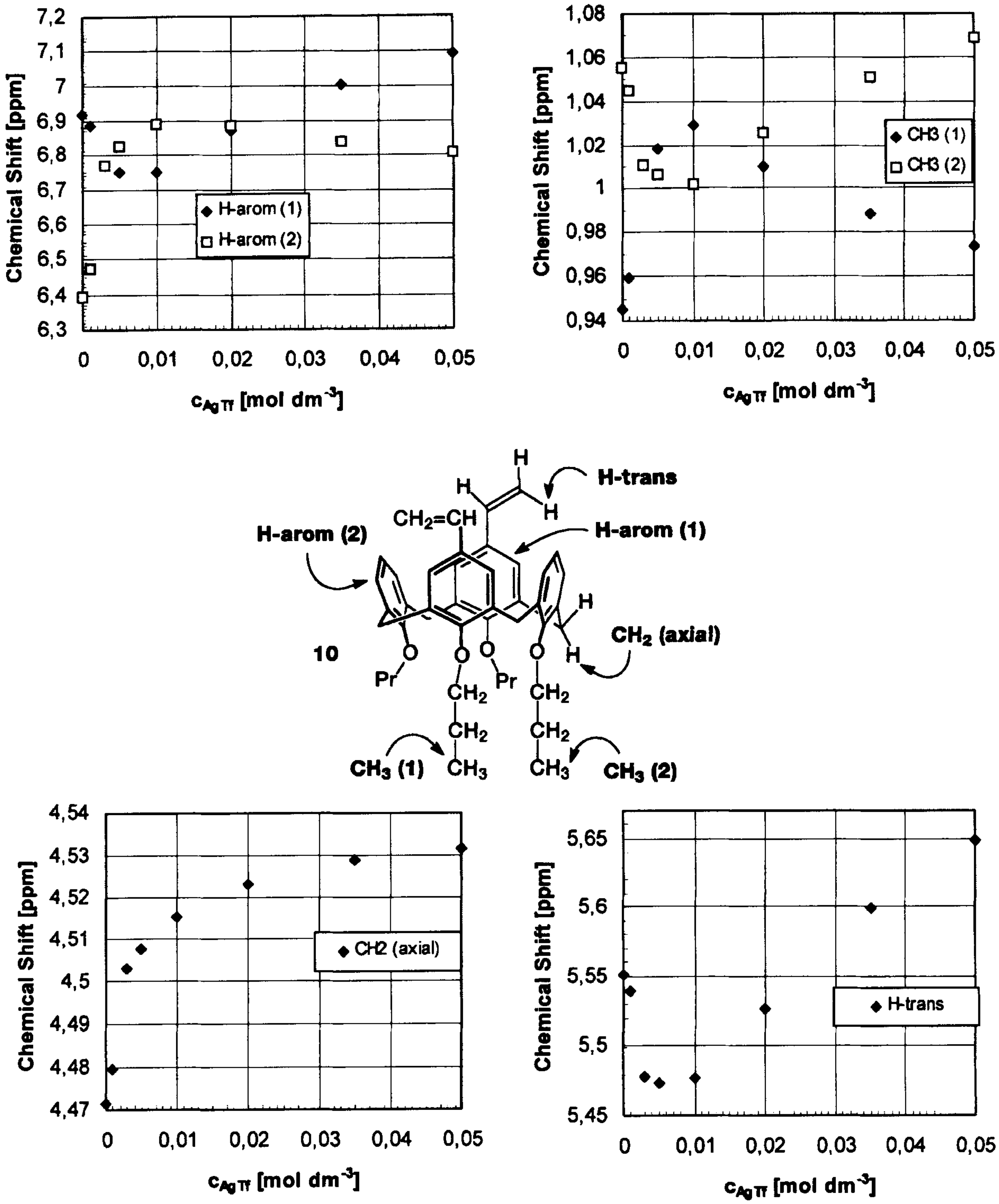

FIGURE 7 Titration curves of **10** (c = 5 mmol dm^{-3}) with AgTf ($CDCl_3$:CD_3OD = 4:1 v/v at 25°C, 250 MHz).

TABLE I Complexation constants (mol^{-1} dm^3) of calix[4]arene derivatives towards AgTf, CD_3OD-$CDCl_3$ = 1:4 v/v, 298 K

Derivatives	8	2b	14	9	15	10	13
Without double bonds	15.8 ± 1.8		1150 ± 120		1110 ± 145		1852 ± 200
With double bonds		36.2 ± 1.5		1730 ± 180		8000[a]	

[a]Approximation from first five points of the titration curve of aromatic protons assuming 1:1 comples formation.

than 1:1 stoichiometry that is not stable enough to be confirmed by mass spectrometry. Such a complex is enabled by additional interactions of silver cation with vinyl groups on the upper rim.

We have also studied the behavior of calixarenes **10**, **13**, and **15** in the presence of 1-methylpyridinium iodide (**1-MP**), which is known to be attracted by calixarene cavities due to cation-π interactions.[6f,14] Figure 9 shows such a typical binding curve obtained by plotting N-CH_3 chemical shifts against the reciprocal concentration of guest molecule.[15] Because of the self-association of 1-methylpyridinium iodide (upper curve in Figure 9 is concentration dependent) the correction has been taken into account and the difference between two curves was taken as an input to the calculation. We have used the same curve fitting the program mentioned above, assuming 1:1 complex stoichiometry. The enhancement of the complexation constant after introduction of the double bonds is clearly seen from Table II. One can conclude that the additional double bonds can stabilize the pyridinium cation inside the cavity (Figure 10) and this phenomenon even prevails the increased sterical hindrance caused by the substitution of smaller hydrogen atoms

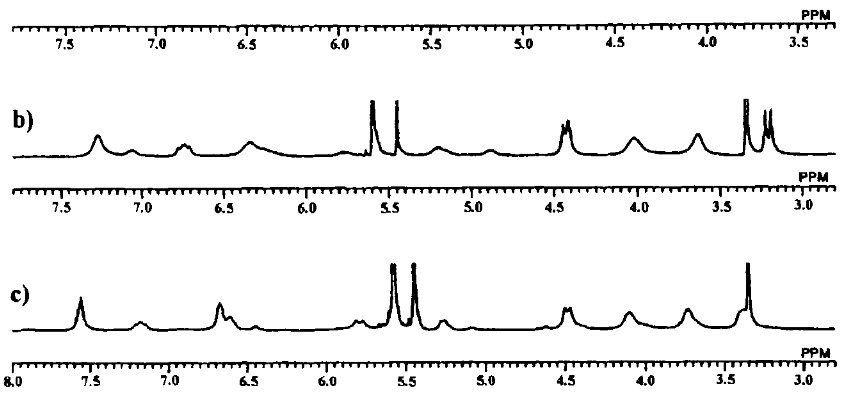

FIGURE 8 The partial ^1H NMR spectra of **10** (c = 5 mmol dm^{-3}, CD_2Cl_2:CD_3OD = 4:1 v/v, −85°C, 400 MHz); (a) in the absence of Ag^+; (b) in the presence of 0.4 equiv. of Ag^+; (c) in the presence of 10 equivs. of Ag^+.

TABLE II Complexation constants (mol^{-1} dm^3) of 1-methylpyridinium iodide (**1-MP**) ($CDCl_3$:CD_3CN = 4:1 v/v, 298 K, 250 MHz)

Dervatives	**10**	**13**	**15**
K [mol^{-1}dm^3]	18.4	4.2	4.0

with bulkier CH = CH_2 groups. Derivative **13** does not show any significant enhancement of K_C because of impossibility to create similar stabilization effect.

In summary, we have reported here very novel, straight, and simple procedure for the preparation of calix[4]arene derivatives bearing double bonds at the upper rim. Such vinyl substituents can contribute to the binding of suitable guest cations) by additional cation-π interactions. Calix[4]arenes with styrene subunits could also serve as monomers for the preparation of calix[4]arene-based polymers. Further exploitation of these compounds is currently in progress.

EXPERIMENTAL

Melting points were determined on a Micro Melting Point Apparatus Yanaco MP-500D and are uncorrected. ^{1}H NMR spectra were measured on a Bruker AC-250P and JEOL-GSX 400 spectrometers in $CDCl_3$ at 25°C with TMS as an internal standard. Mass spectra were recorded with a Hitachi M-2500 spectrometer using positive secondary ions mass spectrometry (SIMS) method with m-nitrobenzyl alcohol as a matrix. IR spectra were obtained with a Jasco A-100 spectrophotometer. Preparative thin layer chromatography was performed on glass plates (20 x 20 cm) coated by *Silica gel* GF_{254} (Merck). All reactions were carried out under a nitrogen atmosphere.

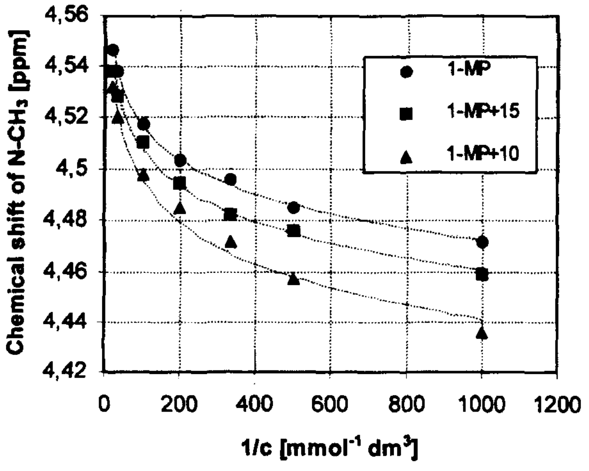

FIGURE 9 Titration curves of **10** and **15** with 1-methylpyridinium iodide (**1-MP**) ($CDCl_3$:CD_3CN = 4:1v/v, 25°C, 250 MHz).

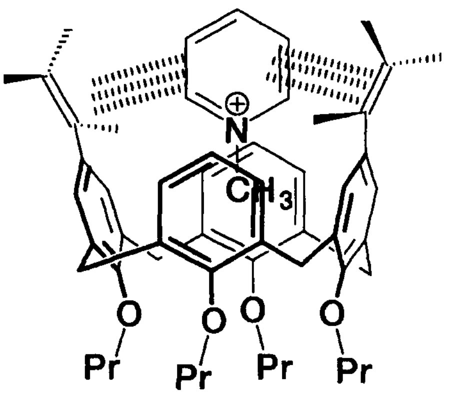

FIGURE 10 Proposed structure of calix[4]arene-**1-MP** complex.

Materials

The preparation of following compounds has been already described: **1**,[16] **3**,[17] **8**,[18] **11**,[19] **14**,[6d] and **15**.[20]

5,17-Diethenyl-26,28-dipropoxycalix[4]arene (2b)

A mixture of **1** (1.50 g, 2.66 x 10^{-3} mol), malonic acid (1.66 g, 15.94 x 10^{-3} mol), and 0.5 ml piperidine (5.06 x 10^{-3} mol) in 30 ml of pyridine was stirred under reflux for 50 h. Reaction mixture was then cooled to room temperature, neutralized by 1N HCl, resulted precipitate was collected by a suction, and dried at 80°C in a drying oven.

Pure product was obtained by column chromatography on *silica gel* ($CHCl_3$)-0.60 g of **2b** (40%), m.p. 245.5–247°C. ^1H NMR spectrum (250 MHz, $CDCl_3$): δ 1.30 (t, 6H, J = 7.4 Hz, $O\text{-}CH_2CH_2\underline{CH_3}$); 2.05 (m, 4H, $O\text{-}CH_2\underline{CH_2}CH_3$); 3.37 (d, 4H, J = 12.9 Hz, $Ar\text{-}CH_2\text{-}Ar$, eq); 3.98 (t, 4H, J = 6.3 Hz, $O\text{-}\underline{CH_2}CH_2CH_3$); 4.40 (d, 4H, J = 12.9 Hz, $Ar\text{-}CH_2\text{-}Ar$, ax); 5.04 (d, 2H, J_{cis} = 10.9 Hz, $Ar\text{-}CH{=}\underline{CH_2}$); 5.56 (d, 2H, J_{trans} = 17.5 Hz, $Ar\text{-}CH{=}\underline{CH_2}$); 6.59 (dd, 2H, J_{cis} = 10.8 Hz, J_{trans} = 17.5 Hz, $Ar\text{-}\underline{CH}{=}CH_2$); 6.74 (t, 2H, J = 7.8 Hz, H-para); 6.92 (d, 4H, J = 7.5 Hz, H-meta); 7.21 (s, 4H, H-arom); 8.29 (s, 2H, OH). IR (nujol) ν (cm^{-1}): 1620, 1600, 1580 (C=C), 3200 (O-H). EA calcd. for $C_{38}H_{40}O_4$: C, 81.38; H, 7.20%. Found C, 80.96; H, 7.05%.

5,11,17,23-Tetrakis(2-hydroxycarbonylethenyl)-25,26,27,28-tetrapropoxycalix[4]arene (4)

This compound was prepared according to the same procedure described above for **2b**, using **3** as a starting compound. Product was isolated by reprecipitation from $CHCl_3$-DMF-MeOH mixture-98.5% yield, m.p. > 350 °C. ^1H NMR spectrum (250 MHz, DMSO-d_6): δ 1.10 (t, 12H, J = 7.4 Hz, $O\text{-}CH_2CH_2\underline{CH_3}$); 2.00 (m, 8H, $O\text{-}CH_2\underline{CH_2}CH_3$); 3.38 (d, 4H, J = 13.4 Hz, $Ar\text{-}CH_2\text{-}Ar$, eq); 3.96 (t, 8H, J = 7.2 Hz, $O\text{-}\underline{CH_2}CH_2CH_3$); 4.45 (d, 4H, J = 12.7 Hz, $Ar\text{-}CH_2\text{-}Ar$, ax); 6.24 (d, 4H, J_{trans} = 15.9 Hz, $Ar\text{-}CH{=}\underline{CH}\text{-}COOH$); 7.19 (s, 8H, H-arom); 7.37 (d, 4H, J_{trans} = 15.8 Hz, $Ar\text{-}\underline{CH}{=}CH_2\text{-}COOH$). EA calcd. for $C_{52}H_{56}O_{12}$: C, 71.53; H, 6.48%. Found C, 71.08; H, 6.64%.

Reaction of model compounds: 4-Hydroxystyrene (7)

This compound was prepared in 10% yield by the same procedure as mentioned above for **2b** from 4-hydroxy-bezaldehyde **5b**, m.p. 70–71°C (petroleum ether) (Lit.[11] m.p. 72–73.5°C). ^1H NMR spectrum (250 MHz, $CDCl_3$): δ 4.78 (s, 1H, OH); 5.12 (d, 1H, J_{cis} = 11.0 Hz, $Ar\text{-}CH{=}\underline{CH_2}$); 5.60 (d, 1H, J_{trans} = 17.5 Hz, $Ar\text{-}CH{=}\underline{CH_2}$); 6.35 (dd, 1H, J_{cis} = 10.8 Hz, J_{trans} = 17.6 Hz, $Ar\text{-}\underline{CH}{=}CH_2$); 6.79 (d, 2H, J = 8.5 Hz, H-arom); 7.28 (d, 2H, J = 8.6 Hz, H-arom).

The same reaction of 4-ethoxybenzaldehyde **5a** yielded 99% of ***trans*-4-ethoxycinnamic acid (6)**, m.p. 192–195°C (ethanol) (Lit.[21] m.p. 191–192°C). ^1H NMR spectrum (250 MHz, $CDCl_3$): δ 1.43 (t, 3H, J = 7.0 Hz, $O\text{-}CH_2\underline{CH_3}$); 4.07 (q, 2H, J = 6.9 Hz, $O\text{-}\underline{CH_2}CH_3$); 6.31 (d, 1H, J_{trans} = 15.9 Hz, $Ar\text{-}CH{=}\underline{CH}\text{-}COOH$); 6.90 (d, 2H, J = 8.6 Hz, H-arom); 7.49 (d, 2H, J = 8.7 Hz, H-arom); 7.74 (d, 1H, J_{trans} = 16.0 Hz, $Ar\text{-}\underline{CH}{=}CH\text{-}COOH$).

5,17-Diethenyl-25,26,27,28-tetrapropoxycalix[4]arene/1,3-alternate/(9)

A mixture of **2b** (0.30 g, 0.54 × 10^{-3} mol), Cs_2CO_3 (3.49 g, 10.7 × 10^{-3} mol), and 0.52 ml of propyl iodide (5.35 × 10^{-3} mol) in 100 ml of dry acetone was stirred under reflux for 18 h. The reaction mixture was acidified with 1N HCl, and the product extracted into $CHCl_3$. Chloroform extract was washed with water, dried over $MgSO_4$, and evaporated on vacuum evaporator. The residue was purified by column chromatography on *silica gel* (hexane:AcOEt = 5:1) to give 0.280 g of product (81%), m.p. 190.5–192 °C ($CHCl_3$-MeOH). ^1H NMR spectrum (250 MHz, $CDCl_3$): δ 0.89 (m, 12H, $O\text{-}CH_2CH_2\underline{CH_3}$); 1.58 (m, 8H, $O\text{-}CH_2\underline{CH_2}CH_3$); 3.51 (m, 8H, $O\text{-}\underline{CH_2}CH_2CH_3$); 3.63 (s, 8H, $Ar\text{-}CH_2\text{-}Ar$); 5.04 (d, 2H, J_{cis} = 11.0 Hz, $Ar\text{-}CH{=}\underline{CH_2}$); 5.50 (d, 2H, J_{trans} = 17.4 Hz, $Ar\text{-}CH{=}\underline{CH_2}$); 6.53 (dd, 2H, J_{cis} = 10.7 Hz, J_{trans} = 17.5 Hz, $Ar\text{-}\underline{CH}{=}CH_2$); 6.70 (t, 2H, J = 7.4 Hz, H-para); 6.99 (d, 4H, J = 7.5 Hz, H-meta); 7.05 (s, 4H, H-arom). IR (nujol) ν (cm^{-1}): 1620, 1580 (C=C). EA calcd. for $C_{44}H_{52}O_4$: C, 81.93; H, 8.14%. Found C, 81.76; H, 8.06%.

5,17-Diethenyl-25,26,27,28-tetrapropoxycalix[4]arene/cone/(10)

To a solution of **2b** (0.2 g, 0.357 × 10^{-3} mol) in 10 ml of THF:DMF (5:1) mixture was added 0.06 g of NaH (60% oil disp., 1.43 × 10^{-3} mol) at -15°C. The contents were stirred for 30 min at the same temperature, after which 0.35 g of propyl iodide was introduced. The reaction was continued at -15°C for 2 h and then 2 days at room temperature. The reaction mixture was decomposed by 1N HCl, and the product was extracted into chloroform. The extract was washed with water, dried over $MgSO_4$ and evaporated on a reduced pressure. The residue was chromatographed over *silica gel* using hexane-$CHCl_3$ = 5:2 mixture as an eluent to give 0.186 g of product (82%), m.p. 214.5–216°C ($CHCl_3$-MeOH). ^{1}H NMR spectrum (250 MHz, $CDCl_3$): δ 0.92 (t, 6H, J = 7.4 Hz, $\mathrm{O\text{-}CH_2CH_2\underline{CH_3}}$); 1.04 (t, 6H, J = 7.3 Hz, $\mathrm{O\text{-}CH_2CH_2\underline{CH_3}}$); 1.90 (m, 8H, $\mathrm{O\text{-}CH_2\underline{CH_2}CH_3}$); 3.13 (d, 4H, J = 13.4 Hz, Ar-CH_2-Ar, eq); 3.74 (t, 4H, J = 7.0 Hz, $\mathrm{O\text{-}\underline{CH_2}CH_2CH_3}$); 3.93 (t, 4H, J = 7.7 Hz, $\mathrm{O\text{-}\underline{CH_2}CH_2CH_3}$); 4.43 (d, 4H, J = 13.3 Hz, Ar-CH_2-Ar, ax); 5.03 (d, 2H, J_{cis} = 10.8 Hz, $\mathrm{Ar\text{-}CH{=}\underline{CH_2}}$); 5.51 (d, 2H, J_{trans} = 17.4 Hz, $\mathrm{Ar\text{-}CH{=}\underline{CH_2}}$); 6.37 (brs, 6H, H-meta,para); 6.54 (dd, 2H, J_{cis} = 10.6 Hz, J_{trans} = 17.4 Hz, $\mathrm{Ar\text{-}\underline{CH}{=}CH_2}$); 6.92 (s, 4H, H-arom). IR (nujol) v (cm^{-1}): 1620, 1600 (C=C). Mass spectrum (positive SIMS) m/z 753 (M + Ag^+). EA calcd. for $C_{44}H_{52}O_4$: C, 81.93; H, 8.14%. Found C, 81.66; H, 8.12%.

5,17-Diacetyl-25,26,27,28-tetrapropoxy-calix[4]arene/cone/(12)

A solution of **11** (1.64 g, 2.77 × 10^{-3} mol) in 30 ml of DMF was treated with 0.221 g of NaH (60% oil disp., 5.53 × 10^{-3} mol) at -15 °C and reaction mixture was stirred for 1 h at the same temperature. Then 0.65 ml of propyl iodide (6.64 × 10^{-3} mol) was added during 2 h at -15 °C, the temperature was allowed to rise up to room temperature during additional 1.5 h, and reaction was continued for 12 h at room temp. Mixture was quenched with 1N HCl, extracted with chloroform, organic layer was washed with water, and dried over $MgSO_4$. After evaporation of solvent the crude product was isolated with the help of column chromatography (SiO_2, hexane-EtOAc = 4:1) to yield 0.61 g of **12** (33%), m.p. 177–178 °C ($CHCl_3$-MeOH). ^{1}H NMR spectrum (250 MHz, $CDCl_3$): δ 1.00 (m, 12H, $\mathrm{O\text{-}CH_2CH_2\underline{CH_3}}$); 1.92 (m, 8H, $\mathrm{O\text{-}CH_2\underline{CH_2}CH_3}$); 2.28 (s, 6H, -CO-$CH_3$); 3.21 (d, 4H, J = 13.5 Hz, Ar-CH_2-Ar, eq); 3.88 (m, 8H, $\mathrm{O\text{-}\underline{CH_2}CH_2CH_3}$); 4.46 (d, 4H, J = 13.5 Hz, Ar-CH_2-Ar, ax); 6.67 (m, 6H, H-para, meta); 7.19 (s, 4H, H-arom). IR (nujol) n (cm^{-1}): 1670 (C=O), 1590 (C=C). EA calcd. for $C_{44}H_{52}O_6$: C, 78.06; H, 7.76%. Found C, 77.88; H, 8.00%.

5,17-Diethyl-25,26,27,28-tetrapropoxy-calix[4]arene/cone/(13)

(From 12) The mixture of starting calixarene **12** (100 mg, 1.48 × 10^{-4} mol) and Et_3SiH (0.17 g, 1.48 × 10^{-3} mol) in 3 ml of CF_3COOH has been stirred at room temp. for 15 h, then poured into water and extracted with chloroform. The extract was dried over $MgSO_4$, evaporated, and the crude product purified by preparative TLC on *silica gel* using hexane: $CHCl_3$ (3:1) mixture as an eluent to yield 79 mg of **13** (82% yield), m.p. 212–214°C (acetone). ^{1}H NMR spectrum (250 MHz, $CDCl_3$): δ 0.95 (t, 6H, J = 7.2 Hz, $\mathrm{O\text{-}CH_2CH_2\underline{CH_3}}$); 1.03 (t, 6H, J = 7.4 Hz, $\mathrm{O\text{-}CH_2CH_2\underline{CH_3}}$); 1.09 (t, 6H, J = 7.9 Hz, $\mathrm{\text{-}CH_2\underline{CH_3}}$); 1.92 (m, 8H, $\mathrm{O\text{-}CH_2\underline{CH_2}CH_3}$); 2.39 (q, 4H, J = 7.6 Hz, $\mathrm{\text{-}\underline{CH_2}CH_3}$); 3.10 (d, 4H, J = 13.3 Hz, Ar-CH_2-Ar, eq); 3.80 (m, 8H, $\mathrm{O\text{-}\underline{CH_2}CH_2CH_3}$); 4.43 (d, 4H, J = 13.0 Hz, Ar-CH_2-Ar, ax); 6.46 (s, 6H, H-para, meta); 6.59 (s, 4H, H-arom). EA calcd. for $C_{44}H_{56}O_4$: C, 81.42; H, 8.71%. Found C, 81.16; H, 8.52%.

(From 10) Calix[4]arene **10** (50 mg, 0.74 × 10^{-4} mol) in 20 ml of THF was hydrogenated at room temperature in the presence of 10 mg of Pd/C (5%) for 12 h. Catalyst was then removed by filtration, the filtrate was evaporated and residue crystallized from acetone to yield 42.2 mg of product (82%), identical with that obtained from previous reaction.

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[12] The induced shift is a linear function of complexation, therefore we can write the equations:

$$\alpha = \frac{c_{\text{complex}}}{c_0} \qquad \alpha = \frac{\delta_i - \delta_0}{\delta\text{sat} - \delta_0}$$

where c_0 is initial concentration of calixarene, complex is concentration of complexed species, d_i, d_0, and d_{sat} are chemical shifts of measured sample, pure calixarene and saturated sample (100% complexation), respectively.

[13] Complexation constant for **7** has been computed using only first 5 experimental points from the titration curves of aromatic hydrogens. The authors are aware of likely uncorrect stoichiometric model for this calculation (Ag: 7 = 1:1).

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