PERKIN 2

Tropylium cation capsule of hydrogen-bonded tetraurea calix[4]arene dimers

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Received (in Cambridge, UK) 5th September 2001, Accepted 22nd October 2001
First published as an Advance Article on the web 26th November 2001

The interaction between tropylium salts and tetraurea calix[4]arene derivatives (such as **1** and **2**) was studied in solution using 1D, 2D, diffusion, VT NMR and UV–visible spectroscopy. It was found that tropylium salts form charge transfer complexes with both the monomers and dimers of the tetraurea calix[4]arene derivatives depending on the experimental conditions. Compound **1** increases dramatically the solubility of tropylium salts in apolar solvents such as $C_2D_4Cl_2$, $CDCl_3$ and CD_2Cl_2 by forming the molecular capsule $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}$. In contrast to the benzene capsule of **1**, in $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}$ the hydrogen bonds in the equatorial region that hold together the two parts of the dimer change their directionality faster than the NMR time scale (at 400 MHz) at temperatures higher than 298 K. Interestingly, the free energy barrier for this dynamic process at 298 K ($\Delta G^{\ddagger}_{298}$), depends on the nature of the counter-anion. Free energies of activation of 14.3 ± 0.2 kcal mol^{-1} and 12.6 ± 0.2 kcal mol^{-1} were found by total lineshape analysis for the dimeric capsules of $C_7H_7^+PF_6^-$ and $C_7H_7^+BF_4^-$, respectively. The affinity of the tropylium cation toward the dimer's cavity is much higher than that of neutral organic guests. Although exact quantitative values are not available due to the low solubility of tropylium salts in apolar solvents, a rough estimation in CD_2Cl_2 shows that the tropylium cation affinity is several orders of magnitude higher than that of benzene, which is known to be a good guest. These results show that once the steric requirements are met, electronic effects may serve as an additional driving force for the formation of such molecular capsules demonstrating the importance of cation–π interactions in such systems.

Introduction

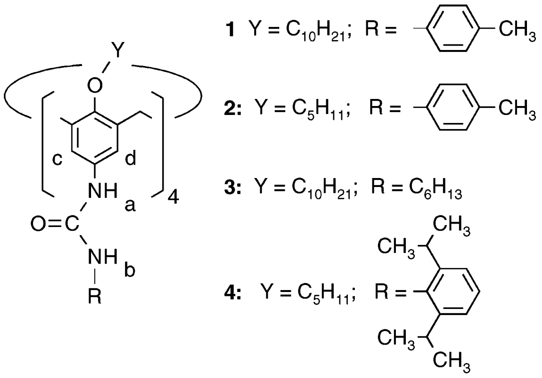
Molecular capsules in general[1] and those obtained by dimerization of tetraurea calix[4]arene derivatives in particular have attracted much interest in recent years.[2,3] These dimers, held together in non-polar solvents by a belt of hydrogen bonds between the urea functions, were studied in the solid state by X-ray crystallography[4] and in solution by 1D and 2D NMR.[2,3,5] With tetraalkylammonium cations as guests, electrospray mass spectrometry (ES-MS) could be also used to characterize the structure of such capsules.[6] Previously, we demonstrated that diffusion measurements using the pulsed gradient spin echo (PGSE) technique[7] provide a means of following molecular interactions in solutions.[8] Consequently, this technique was used to study the dimerization, encapsulation and the disruption of tetraurea calix[4]arene dimers in solutions.[8e]

Mostly steric effects such as size or shape were considered when discussing the relative affinity of various guests towards the cavity of the capsules. In the absence of stronger and more specific interactions such as hydrogen bonding or cation–π interactions a packing coefficient of 55%, as is found for many organic solvents, seems to be ideal for the inclusion of "molecules within molecules".[9] However, many exceptions in both directions have been found for dimers of tetraurea calix[4]arenes. Among neutral guests pyrazine (38%) and benzene (38%) are accepted as well as nopinone (71%) or myrtenol (76%).[6] The occupation of 78% of the capsule volume (if this is taken as 190 Å^3) by the tetraethylammonium cation may be due to its stronger interaction with the π-basic cavities.[10]

It was suggested that cation–π interactions play an important role in several biological systems.[11] Recently we were able to show that the formation of a dimeric capsule from resorcarene tetraesters could be induced by tropylium cations.[12a] Thus, we decided to study the molecular interaction between tetraurea calix[4]arenes and the tropylium cation which has the additional intrinsic advantage that the interaction with the calixarene host is also indicated in the UV spectrum by charge transfer bands, as in other cases.[12b,c]

Results and discussion

Addition of a tropylium salt to the colorless solution of tetraurea calix[4]arenes **1** (Scheme 1) results in a deep red solution



Scheme 1

DOI: 10.1039/b108043a

indicative of the formation of a charge transfer complex. This coloration occurs in apolar as well as in polar solvents.

NMR studies of tropylium complexation

In apolar solvents having the "wrong" shape or size,[9] such as CD_2Cl_2, tetraurea derivative **1** forms only ill defined aggregates as suggested by the broad signals in the ^1H NMR spectrum of **1** for example.[5] However, addition of small amounts of a suitable guest, such as benzene, induces the formation of a well defined species characterized by narrow signals in the ^1H NMR spectrum.[5] Similar observations were made for the addition of a tropylium salt (Fig. 1) where an even smaller amount is needed to induce the complete formation of a well-defined species in CD_2Cl_2. This suggests that the interaction between the tropylium cation and **1** is stronger than that between **1** and benzene.

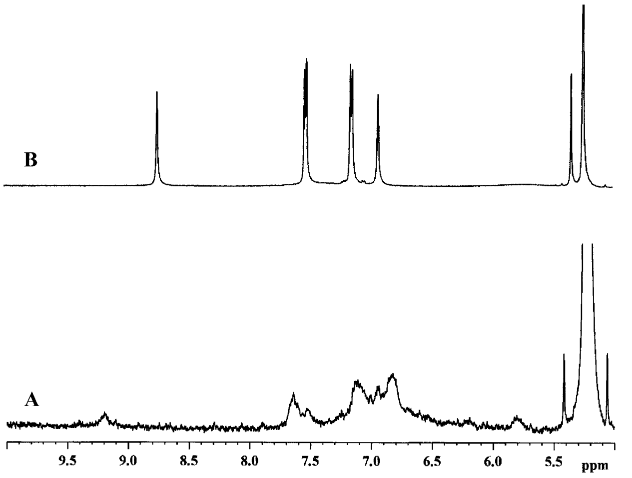


Fig. 1 The aromatic region of the ^1H NMR spectrum (500 MHz) of tetraurea calix[4]arene **1** in CD_2Cl_2 (at $C = 5 \times 10^{-3}$ M) at room temperature (A) and after saturation with tropylium hexafluorophosphate (B).

Additional support for the interaction between tetraurea calix[4]arenes **1** and tropylium cations is gained from the observation that a second set of signals appears in the ^1H NMR spectrum when small amounts of a tropylium salt are added to a solution of **1** in an organic solvent such as $C_2D_4Cl_2$ where tetraurea calix[4]arenes are known to form dimers. As one set of signals represents the dimer with an encapsulated solvent molecule (*i.e.* $C_2D_4Cl_2$) the second set of signals should be attributed to the species bound to tropylium, probably to the tropylium capsule (Fig. 2).

The fact that in apolar solvents the charge transfer complex of tropylium cation and **1** is a dimeric capsule was established by a combination of NMR measurements and by UV–visible spectroscopy. For $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}$ one should expect two doublets for $H_{e,f}$ (Scheme 1) and four additional signals in the aromatic region of the ^1H NMR spectrum; two singlets should represent the two NH groups ($H_{a,b}$, Scheme 1), and the two aromatic protons ($H_{c,d}$, Scheme 1) known to be chemically non-equivalent in capsules filled with benzene, chloroform *etc.* should show two *meta*-coupled doublets. The encapsulated tropylium cation should appear upfield shifted with respect to its usual position. However, only three and not five signals are found at 298 K in the aromatic region of the ^1H NMR spectrum of the complex formed between **1** and tropylium hexafluorophosphate in $C_2D_4Cl_2$ (Fig. 3) or CD_2Cl_2 (Fig. 1B) in addition to the AA′BB′ system attributed to $H_{e,f}$. Only when the ^1H NMR spectrum is recorded at lower temperatures is the expected pattern found and the two broad signals at 5.6 and at 7.4 ppm became clearly apparent (see below). Such changes in the ^1H NMR spectrum were observed in CD_2Cl_2, $CDCl_3$ and $C_2D_4Cl_2$ solutions of **1** and tropylium salts (Fig. 3).

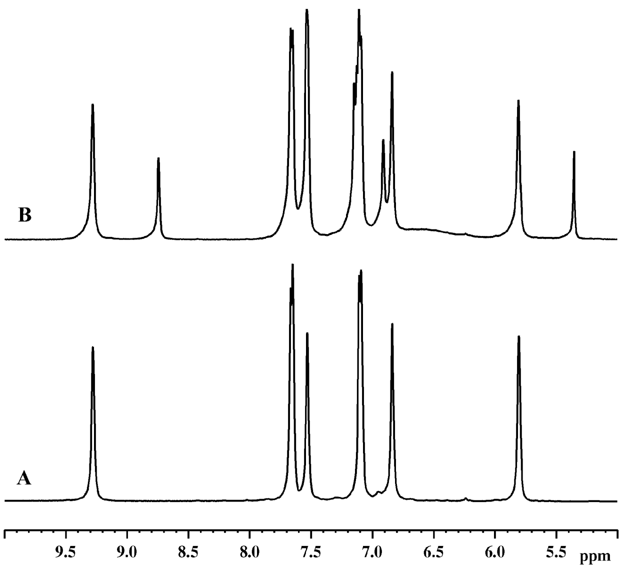


Fig. 2 The aromatic region of the 400 MHz ^1H NMR spectrum of tetraurea calix[4]arene **1** in $C_2D_4Cl_2$ at room temperature (A) in the absence, and (B) in the presence of a small amount of tropylium hexafluorophosphate.

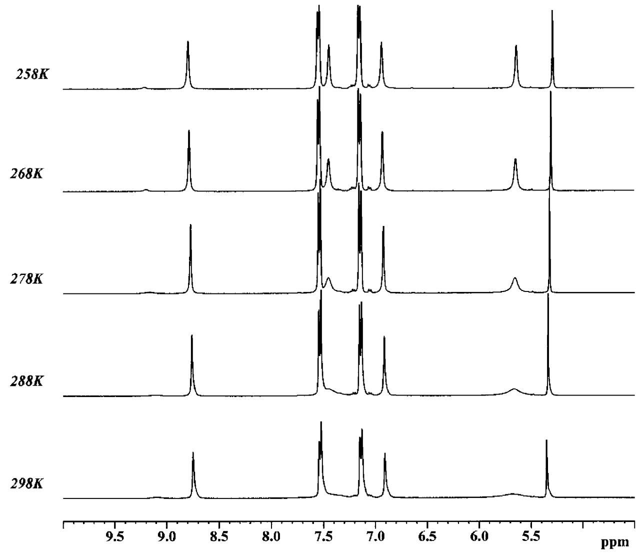


Fig. 3 The aromatic region of the 400 MHz ^1H NMR spectrum of $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}$ in $C_2D_4Cl_2$ (solution of **1** saturated with $C_7H_7^+$ PF_6^-) as a function of the temperature.

The assignment of the ^1H and ^{13}C NMR spectra of the dimeric capsule $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}$ in $C_2D_4Cl_2$ was obtained by a series of 2D NMR experiments performed at low temperature. First, the DQF-COSY ^1H NMR spectrum of this complex at 258 K showed a clear correlation only between the two signals at 5.6 ppm and 7.4 ppm suggesting that they belong to the two *meta*-coupled aromatic protons $H_{c,d}$. The HMQC spectrum revealed correlations between the protons at 5.6 and 7.4 ppm and the carbons at 126.0 and 126.7 ppm, respectively and a correlation between the proton at 5.4 ppm and the carbon at 160 ppm. No correlations could be found between the protons at 8.8 and 6.9 ppm and any carbon suggesting that these singlets represent the two protons of the NH groups (Scheme 1). Based on these observations we assigned the singlet at 5.4 ppm to the encapsulated tropylium cation. Indeed, a phase-sensitive NOESY experiment performed at 258 K on the $C_2D_4Cl_2$ solution of the complex revealed strong correlations between the two *meta*-coupled doublets and four out of the five signals, while the peak at 5.4 ppm showed only very weak correlations with the signals at 5.6 ppm and 7.4 ppm. This is to be expected since intramolecular NOEs are known to be much stronger than intermolecular NOEs. The large high field shift of 3.8 ppm thus observed for the complexed tropylium cation is in line with its encapsulation in the dimer **1·1**,[13] since a smaller shift would be expected for its inclusion in the monomeric **1**.[12a] For the encapsulated benzene in the dimer **1·1** a high field shift of 2.7 ppm was reported.[5]

Further evidence for the dimeric nature of this complex comes from diffusion measurements performed on the tropylium cation complex of **1** in $C_2D_4Cl_2$ solution at low temperatures. In this experiment we found that all the peaks at the aromatic region of the ^{1}H NMR spectrum, including the signal at 5.4 ppm, have the same diffusion coefficients within experimental errors (Fig. 4). This means that the tropylium cation and the tetraurea calix[4]arene **1** diffuse as one supramolecular entity. In addition, the diffusion coefficients of the signals of the tropylium cation complex of **1** and $\mathbf{1{\cdot}C_6D_6{\cdot}1}$ in C_6D_6 solutions[8e] were found to be equal, within experimental errors (0.30(±0.01) × 10^{-5} cm^2 s^{-1} and 0.32(±0.01) × 10^{-5} cm^2 s^{-1}, respectively.) (Fig. 5). These observations support the conclusion that the tropylium cation is included in a dimeric capsule like the benzene.

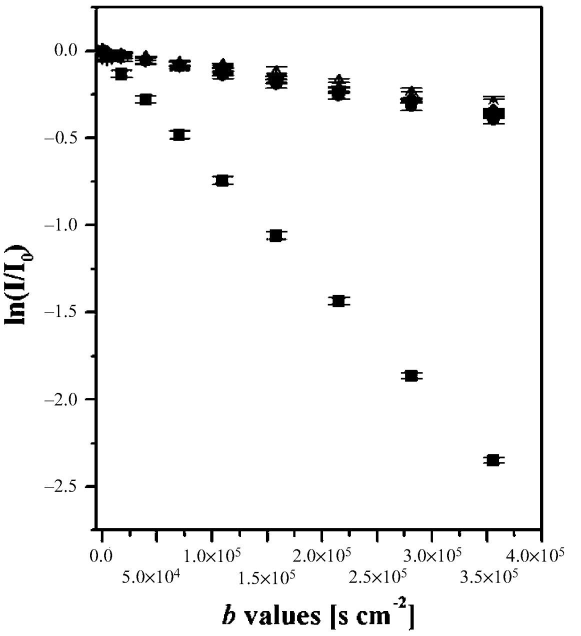


Fig. 4 The natural log of the normalized signal attenuation (ln I/I_0) as a function of the *b* values[19] for all the five signals observed in the aromatic region of the ^{1}H NMR spectrum of $\mathbf{1{\cdot}C_7H_7^+{\cdot}1}$ in $C_2D_4Cl_2$ at 258 K, including the singlet at 5.4 ppm attributed to encapsulated tropylium cation (●) and the peak of $C_2D_4Cl_2$ (■).

Finally, the formation of a dimeric capsule with included tropylium cation was proved, as in other cases, by the formation of heterodimers. The ^{1}H NMR spectrum of a mixture of two different tetraurea calix[4]arenes (**1** and **3**, Scheme 1) in the presence of tropylium hexafluorophosphate shows not only the signals found in the spectra obtained separately for each derivative, as expected for monomeric complexes with tropylium. It clearly reveals the presence of a third species with lower symmetry (Fig. 6). The only plausible explanation for these observations is the formation of a heterodimer $\mathbf{1{\cdot}C_7H_7^+{\cdot}3}$ in addition to the two homodimers $\mathbf{1{\cdot}C_7H_7^+{\cdot}1}$ and $\mathbf{3{\cdot}C_7H_7^+{\cdot}3}$.

Two *meta*-coupled doublets for the aromatic protons ($H_{c,d}$) are observed, if the directionality of the hydrogen bonded belt is "fixed on the NMR-time scale" (S_8-symmetry of the dimer); however, if the change in the directionality of the hydrogen bonds is rapid on the NMR time scale a single singlet (due to the D_{4d}-symmetry of the dimer) should be expected for those protons.[10] From the total lineshape analysis of the variable temperature ^{1}H NMR spectra as those reported in Fig. 3 we could extract for this rotation, at 298 K, an energy barrier of $\Delta G^\ddagger$ = 14.3 ± 0.2 kcal mol^{-1} and $\Delta G^\ddagger$ = 12.6 ± 0.2 kcal mol^{-1} for $\mathbf{1{\cdot}C_7H_7^+{\cdot}1}$ when the counter-anions were PF_6^- and BF_4^-, respectively.[14]

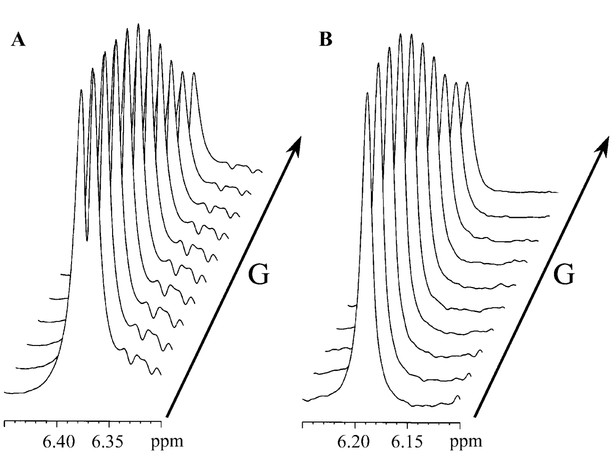


Fig. 5 ^{1}H NMR spectra of the Stejskal and Tanner diffusion experiment in C_6D_6 solution showing the signal intensity decay as a function of the pulsed gradient strength (*G*) of (A) $\mathbf{1{\cdot}C_6D_6{\cdot}1}$, and (B) $\mathbf{1{\cdot}C_7H_7^+{\cdot}1}$. For clarity only the signal decay of the peaks at 6.39 and 6.19 ppm of $\mathbf{1{\cdot}C_6D_6{\cdot}1}$ and $\mathbf{1{\cdot}C_7H_7^+{\cdot}1}$, respectively are shown.

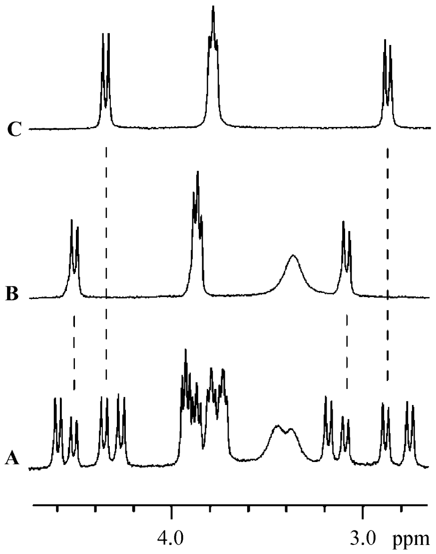


Fig. 6 Sections of the 400 MHz ^{1}H NMR spectra of tetraureacalix[4]arene derivatives in the presence of tropylium hexafluorophosphate in CD_2Cl_2 at 298 K, (A) a mixture of **3** and **1**, (B) **3**, and (C) **1**.

For steric reasons it can be excluded that the anions (PF_6^- or BF_4^-) are also encapsulated by the dimer,[15] while it is not clear if these anions interact with the molecular capsule from the outside. To get some insights concerning the interaction of PF_6^- and BF_4^- with $\mathbf{1{\cdot}C_7H_7^+{\cdot}1}$ in the solution, we have measured the ^{19}F NMR of these tropylium salts in $C_2D_4Cl_2$ in the presence and in the absence of **1**. Interestingly, we found no changes in the chemical shifts and the lineshape of the ^{19}F NMR in the case of $C_7H_7^+PF_6^-$ upon addition of **1**; however, a pronounced lineshape change was observed for the $C_7H_7^+BF_4^-$ case. These results may suggest that BF_4^- interacts more significantly than PF_6^- with the tropylium encapsulated dimer and may explain the larger assistance of BF_4^-, which results in a lower energetic barrier for the rotation of the hydrogen bond belt of $\mathbf{1{\cdot}C_7H_7^+{\cdot}1}$. In addition, we have measured the diffusion coefficient of PF_6^- using ^{31}P diffusion NMR spectroscopy on a more concentrated solution of **1** and $C_7H_7^+PF_6^-$ in $C_2D_4Cl_2$. The diffusion coefficient of PF_6^- was found to be much higher than that of the encapsulated tropylium (0.73(±0.09) × 10^{-5}

$cm^2\ s^{-1}$ and 0.21(±0.01) × $10^{-5}\ cm^2\ s^{-1}$, respectively). Due to the relatively low solubility of $C_7H_7^+PF_6^-$ in $C_2D_4Cl_2$ we could not measure the diffusion coefficient of PF_6^- in the absence of **1**. However, the large difference between the diffusion coefficients of the dimer and the PF_6^- suggests that there is very little, if any, interaction between the two species under these experimental conditions. Basically the $C_7H_7^+PF_6^-$ ion pair behaves as a solvent separated ion-pair in $C_2D_4Cl_2$ in the presence of **1**. Assuming a spherical shape for the dimer and the PF_6^- the ratio between their diffusion coefficients should be inversely proportional to the cubic root of their molecular weights ratio. Therefore one should expect a ratio of 2.8 between the diffusion coefficients of PF_6^- and **1**, while experimentally a ratio of 3.5 was found.

From the results presented so far it is clear that tropylium cations have a much stronger tendency to induce the formation of dimeric capsules, than neutral organic templates. Unfortunately, we could not characterize this "tendency" in a more quantitative way by giving template ratios.[16] Many of the solutions of $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}\ PF_6^-$ and other competing neutral guests in apolar solvents were unstable over a period of 1–4 weeks. During this time precipitate is formed and one (in CD_2Cl_2) or two (in $CDCl_3$, see below) additional sets of signals are observed. The relative integral intensities of all signals continuously change and we could never reach quantitatively the same situation starting either from the complex $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}$ adding a neutral guest or from separate components (**1**, $C_7H_7^+PF_6^-$, neutral guest and non-competing solvent), which of course would be the best proof that the thermodynamic equilibrium is reached.

The addition of ~10% DMSO-d_6 to a solution of $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}$ in an apolar solvent disrupts the capsule as shown by the ^1H NMR spectrum, *e.g.* by the disappearance of the singlet at 5.4 ppm attributed to the encapsulated tropylium cation. A concentration dependent peak between 7.0 and 9.0 ppm for $C_7H_7^+$ shifted to high field for increasing [**1**] and to low field for increasing $[C_7H_7^+]$ is characteristic for a time-averaged situation for free $C_7H_7^+$ (9.2 ppm in $C_2D_4Cl_2$ with 10% DMSO-d_6) and its complex with monomeric **1**. Consequently, the downfield shift of this peak is accompanied by a gradual increase in the extracted diffusion coefficient. The red colour of $C_2D_4Cl_2$ solutions of $C_7H_7^+$ and tetraurea **4**, which for steric reasons cannot form dimers, is an additional indication of the interaction of the tropylium cation with the monomeric tetraureas.

UV–vis studies of tropylium complexation

The complex $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}\ PF_6^-$, prepared in dichloromethane by extraction of $C_7H_7^+\cdot PF_6^-$ into the solution of **1**, filtration from excess salt and subsequent evaporation, can be easily dissolved in a range of apolar solvents like dichloromethane, 1,2-dichloroethane and chloroform forming red solutions. The spectra recorded in dichloromethane and dichloroethane are very similar with two very broad bands at about 344 and 491 nm, indicating a charge transfer interaction between the included tropylium cation and benzene rings of the calixarene dimer. Similar UV–vis spectra with two very broad bands (at λ 339.3 and 415.5 nm in acetonitrile) have been observed for the tropylium complex with dibenzo-24-crown-8.[12b] The red shift especially for the second band reflects a smaller energy gap for the charge transfer process for the $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}\ PF_6^-$ complex due to, most probably, a stronger interaction between the tropylium cation and the dimeric capsule of **1**. All absorption bands follow the Lambert–Beer law in the concentration range of 1.0–0.02 mM, which proves that no detectable dissociation occurs.

The spectra recorded in chloroform show an additional shoulder at 405.5 nm (Fig. 7). This might be caused by the presence of a complex of monomeric **1** with tropylium cation (see below) under these conditions. In fact, the ^1H NMR spectrum of the complex $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}\ PF_6^-$ dissolved in $CDCl_3$ (Fig. 8), clearly reveals two additional sets of calixarene signals. The first is due to the complex $\mathbf{1}\cdot CDCl_3\cdot\mathbf{1}$ and the second most probably due to the complex $\mathbf{1}\cdot C_7H_7^+\cdot PF_6^-$, which is in fast exchange with the monomer of **1**. This would explain why, under these conditions, signals for the free tropylium are not observed. A small amount of a white precipitate is attributed to the tropylium salt $C_7H_7^+\cdot PF_6^-$.

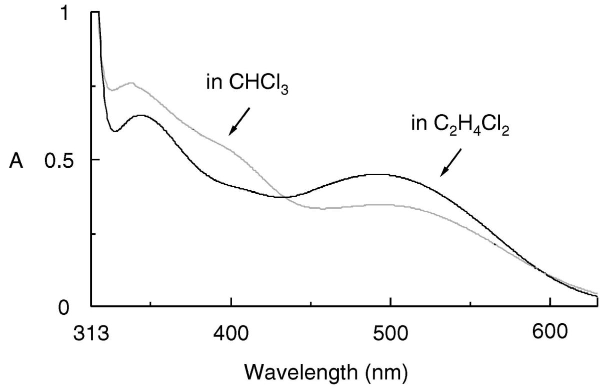


Fig. 7 The UV–vis spectra of the $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}\ PF_6^-$ complex recorded in two different solvents at 2.71 × 10^{-4} M concentration.

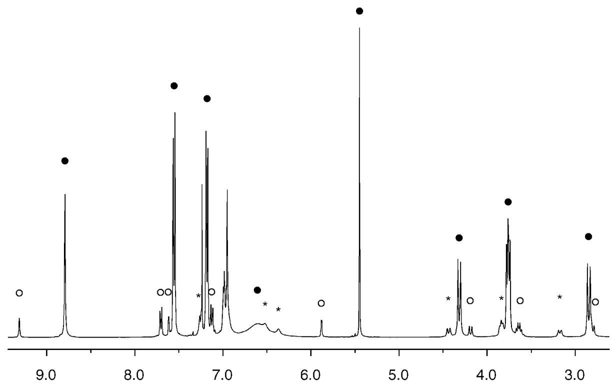


Fig. 8 The ^1H NMR spectrum of the complex $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}\ PF_6^-$ dissolved in $CDCl_3$ ($c \approx$ 7 mM). In addition to the signals of the $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}\ PF_6^-$ (●), signals for $\mathbf{1}\cdot CDCl_3\cdot\mathbf{1}$ (○) and a third species (*) can be distinguished.

If increasing amounts of DMSO are added to the 1,2-dichloroethane solution of the complex first a decrease of the absorption at 344 and 491.5 nm and a simultaneous increase at ~400 nm is observed (Fig. 9). For DMSO contents of more

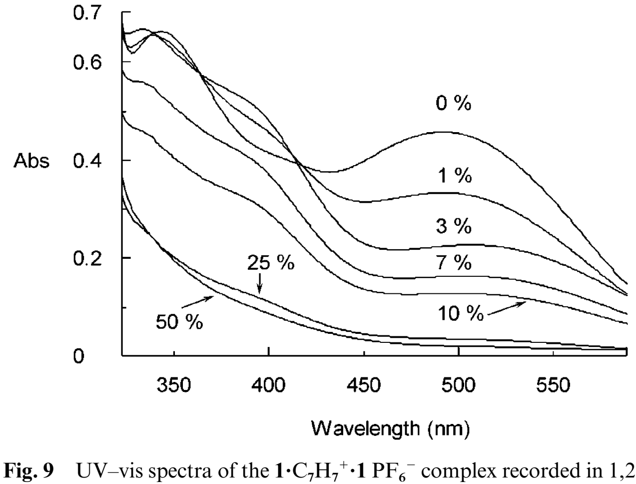


Fig. 9 UV–vis spectra of the $\mathbf{1}\cdot C_7H_7^+\cdot\mathbf{1}\ PF_6^-$ complex recorded in 1,2-dichloroethane at 2.42 × 10^{-4} M concentration with different amounts of DMSO.

than 3% a general decrease of the absorption in the whole 320–500 nm range is observed. This can be reasonably explained by a dissociation of the 2 : 1 complex *via* the 1 : 1 complex into the monomeric urea and the tropylium cation with increasing polarity of the solvent mixture. A Job plot in 1,2-dichloroethane (Fig. 10a) unequivocally proves the 2 : 1 (host : guest) stoichiometry of the complex under these conditions, which is in line with the NMR data. For the mixture of 1,2-dichloroethane with 25% of DMSO the maximum in the Job plot is observed at 1 : 1 (**1**: $C_7H_7^+PF_6^-$, Fig. 10b) ratio, in agreement with a complete dissociation of the dimer and the formation of a tropylium complex with the monomeric tetraurea calix[4]arene. These results are completely in line with the ^{1}H NMR results, which were discussed previously and were depicted in Figs. 1 and 2.

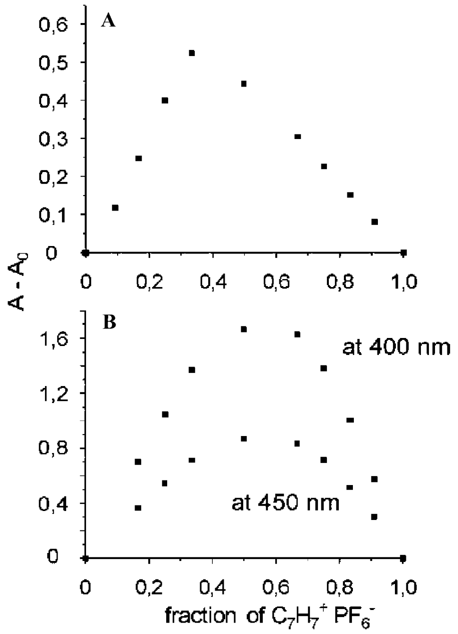


Fig. 10 Job plots obtained for the urea **1** and $C_7H_7^+PF_6^-$ in (A) 1,2-dichloroethane (at $c = 7.84 \times 10^{-4}$ M) and (B) in 1,2-dichloroethane with 25% of DMSO (at $c = 5.70 \times 10^{-3}$ M).

While the complex **1**·$C_7H_7^+$·**1** PF_6^-, is not sufficiently soluble in cyclohexane it dissolves in solvents like benzene and isopropanol, however the initial red color disappears almost immediately. Most probably this is due to the complete substitution of the included tropylium cation by benzene in the first case and to the complete dissociation of the dimeric capsules in the latter case.[17] In tetrachloromethane the color disappears within 20–30 minutes[18] which offers the possibility of following kinetically the exchange of the included tropylium cation by the solvent molecules. First experiments show, however, that the rate law is obviously not of the expected pseudo-first order.

Conclusion

We have demonstrated that tetraurea calix[4]arenes form molecular capsules in apolar solvents with the tropylium cation included in the cavity formed by this dimerization. The relative affinity of the tropylium cation towards the tetraurea calix[4]arene cavity **1** is at least several orders of magnitude larger than that of benzene which has a similar size. The directionality of the belt of hydrogen bonded urea groups holding the two parts of the dimer changes relatively fast at 400 MHz above room temperature. The energy barrier for this dynamic process was found to be anion dependent. These results prove that electronic effects play a decisive role in determining the relative affinity of $C_7H_7^+$ toward the capsule cavity. UV and NMR data demonstrate that tropylium cations interact also with **1** in its monomeric form.

In summary these results suggest that once the steric requirements are met electronic interactions can be used to drive the formation of such molecular capsules. These data provide an additional example for the importance of cation–π interactions in such systems.

Experimental

Materials

All the deuterated solvents were supplied by Aldrich (USA) and used as is. The tetraurea calix[4]arene derivatives were prepared according to the procedure published in references 2*c*, *d*.

Complexation

Since tropylium salts are poorly soluble in most organic solvents, solutions of tropylium capsules in various solvents were prepared by treating the tetraurea calix[4]arene and a slight excess of the tropylium salt with dichloromethane or 1,2-dichloroethane, followed by filtration, evaporation and addition of the desired deuterated solvent.

^{1}H NMR of 1·$C_7H_7^+$·1 PF_6^- (400 MHz, 298 K, $C_2D_4Cl_2$). δ = 8.75 (s, 8H), 7.53 (d, J = 7.9 Hz, 16H), 7.4 (broad, 8H), 7.14 (d, J = 7.9 Hz, 16H), 6.91 (s, 8H), 5.6 (broad, 8H), 5.35 (s, 7H), 4.28 (d, J = 12 Hz, 8H), 3.71 (m, 16H), 2.82 (d, J = 12 Hz, 8H), 2.21 (s, 24H), 1.89 (m, 16H), 1.24 (m, 112H), 0.82 (t, J = 6.2 Hz, 24H).

^{1}H NMR of 1·$C_7H_7^+$·1 PF_6^- (400 MHz, 258 K, $C_2D_4Cl_2$). δ = 8.80 (s, 8H), 7.55 (d, J = 7.9 Hz, 16H), 7.45 (s, 8H), 7.15 (d, J = 7.9 Hz, 16H), 6.94 (s, 8H), 5.64 (s, 8H), 5.29 (s, 7H), 4.25 (d, J = 12 Hz, 8H), 3.68 (m, 16H), 2.83 (d, J = 12 Hz, 8H), 2.23 (s, 24H), 1.91 (m, 16H), 1.23 (m, 112H), 0.83 (t, J = 6.2 Hz, 24H).

NMR measurements

NMR spectra were recorded on 500 MHz ARX and 400 MHz Avance Bruker NMR spectrometers (Karlshruhe, Germany). The solvents were used as internal lock and internal references (^{1}H NMR: C_6D_6 7.15 ppm, CD_2Cl_2 5.3 ppm, $C_2D_4Cl_2$ 3.65 ppm, $CDCl_3$ 7.26 ppm; ^{13}C NMR: C_6D_6 128.7 ppm, $C_2D_4Cl_2$ 51.7 ppm, $CDCl_3$ 77.0 ppm). Diffusion experiments were carried out on the 500 MHz NMR spectrometer equipped with a B-AFPA 10 pulsed gradient unit capable of producing Z-gradient of about 50 G cm^{-1} or on the 400 MHz NMR spectrometer equipped with a Great 1/10 pulse gradient unit capable of producing Z-gradient of about 50 G cm^{-1}. All experiments were carried out in a 5 mm inverse probe using a 4 mm NMR tube inserted in a 5 mm NMR tube. All ^{1}H diffusion measurements were performed with a PGSE pulse sequence[7] with pulse gradient duration of 2 ms and a pulsed gradient separation of 62 ms. The pulsed gradients were incremented from 0 to 46.8G cm^{-1} (in the 500 MHz instrument) or to 40.2G cm^{-1} (in the 400 MHz instrument) in ten steps. The diffusion experiments were preformed at least three times and in the ^{1}H NMR diffusion experiment only data for which the correlation coefficient was higher than 0.999 were included. In the ^{31}P NMR diffusion experiments due to the lower signal to noise the correlation coefficients were only 0.995.

UV–vis studies

All spectra were measured with a Jasco V-530 instrument at 22 °C using 1 cm cuvettes.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft (BO 523/14-1) and the Israel Science Foundation (ISF) is gratefully acknowledged.

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16 The template ratios K_r which are usually defined as the ratio of the stability constants K of the (self-assembled) complexes. **2**1 + G $\leftrightarrows$ **1**·G·**1** with $K = [\mathbf{1}\cdot\mathrm{G}\cdot\mathbf{1}]/([\mathrm{G}][\mathbf{1}]^2)$ and $K_r = K_1/K_2 = ([\mathbf{1}\cdot\mathrm{G}_1\cdot\mathbf{1}]\,[\mathrm{G}_2])/([\mathrm{G}_1]\,[\mathbf{1}\cdot\mathrm{G}_2\cdot\mathbf{1}])$. This new constant K_r can be understood also as the equilibrium constant for the exchange reaction: $[\mathrm{G}_1] + [\mathbf{1}\cdot\mathrm{G}_2\cdot\mathbf{1}] \leftrightarrows [\mathrm{G}_2] + [\mathbf{1}\cdot\mathrm{G}_1\cdot\mathbf{1}]$ To determine K_r the ratio $[\mathbf{1}\cdot\mathrm{G}_1\cdot\mathbf{1}]/[\mathbf{1}\cdot\mathrm{G}_2\cdot\mathbf{1}]$, which follows from the integration of analogous peaks of the two complexes, and the ratio $[\mathrm{G}_1]/[\mathrm{G}_2]$, both usually applied in excess to **1**, must be known. In the present case the situation is further complicated by the low solubility of tropylium salts in apolar solvents and at the moment we can only give an estimate for the lower limit for K_r. If C_6D_6 (= G_2) is added to a 1.87 mM solution of $\mathbf{1}\cdot\mathrm{C_7H_7}^+\cdot\mathbf{1}$ in CD_2Cl_2 (a solvent which does not induce the dimerization) up to $[C_6D_6] = 3.66$ M the NMR spectrum showed only small changes in the chemical shifts, but signals for $\mathbf{1}\cdot\mathrm{C_6D_6}$ **1**·could not be detected. (The solution shows no changes within several days, while a precipitate occurs after weeks). Thus, the ratio $[\mathbf{1}\cdot\mathrm{G}_2\cdot\mathbf{1}]/[\mathbf{1}\cdot\mathrm{C_7H_7}^+\cdot\mathbf{1}]$ should be lower than 0.1 (under the surely not too optimistic assumption that 10% of an additional dimer would be detected), and for the same reason the actual ratio $[\mathrm{C_7H_7}^+]/[\mathrm{C_6D_6}]$ should be less than $(0.1 \times 1.87 \times 10^{-3})/3.66)$. Therefore, under these experimental conditions $K_r > 2 \times 10^5$.

17 In these cases the tropylium salt precipitated from the solution what was observed by appearance of turbidity of the solutions with following formation of a white crystalline powder.

18 A similar behavior is observed for toluene solutions.

19 The diffusion coefficients were determined by the PGSE technique according to which the ratio between the echo intensity in the presence (I) and in the absence of pulsed gradient (I_0) is given by eqn. (1)[7] in which γ is the gyromagnetic ratio, g is the pulsed

$$\ln (I/I_0) = -\gamma^2 g^2 \delta^2 (\Delta - \delta/3) D = -bD \qquad (1)$$

gradients strength, Δ and δ are the time separation between the pulsed-gradients and their duration, respectively and D is the diffusion coefficient. For an isotropic solution, a plot of $\ln(I/I_0)$ *vs.* b should give a straight line which slope is equal to $-D$.[7]