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Vibrational spectroscopy of a tetraureidocalix[4]arene based molecular capsule†

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Structural models for self-assembled dimers composed of two urea calix[4]arenes which entrap benzene or cyclohexane are developed using Fourier transform infrared (FTIR) spectroscopy. Based on the host–guest ratio determined by ^{1}H NMR spectroscopy in solution, and confirmed for the solid state by a thermogravimetric analysis, it is possible to prove by a comparison of the FTIR data of host, guest, complex and model compounds, that the capsule is held together by a cyclic array of weak and strong hydrogen bonds between the urea units attached at the wide rim of the calixarenes. The dimerization of the two urea units leads to a loss of symmetry, and an averaged C_4 symmetrical arrangement is probable. Guest molecules, such as benzene or cyclohexane, are enclosed inside the container rotating fast on the IR timescale around a longitudinal axis of the guest. From the observed splitting of absorption bands upon dimerization and inclusion it follows that either two crystallographically independent types of capsules exist in the crystal lattice or that the guests are occupying two major orientations in the capsule. As indicated by a higher complexation induced shift for cyclohexane, this guest exhibits a tighter interaction with the host molecules compared to benzene.

Introduction

Molecular capsules based on calixarenes[1–3] or resorcinarenes can be formed by metal–ligand interactions[4,5] or by hydrogen bonds. Calix[4]arenes substituted by four urea functions at the wide rim represent an especially interesting example.[6–9] In apolar solvents they form dimeric capsules held together by a seam of hydrogen bonds between the interlocking urea moieties (Fig. 1). A guest molecule—often the solvent—is included in a cavity of about 200 Å^3 and serves as a template for the capsule formation. Kinetically stable capsules in apolar solvents (*e.g.* benzene) were accessible using sterically demanding urea residues.[8] The kinetic stability is in general drastically increased in cyclohexane[10] in comparison to benzene, and in a special example it is observed also in DMSO.[11] Such (weak) molecular assemblies can be studied by single crystal structure determination in the solid state,[7,9] NMR spectroscopy in solution,[6,8,12,13] or mass spectrometry in the gas phase.[14]

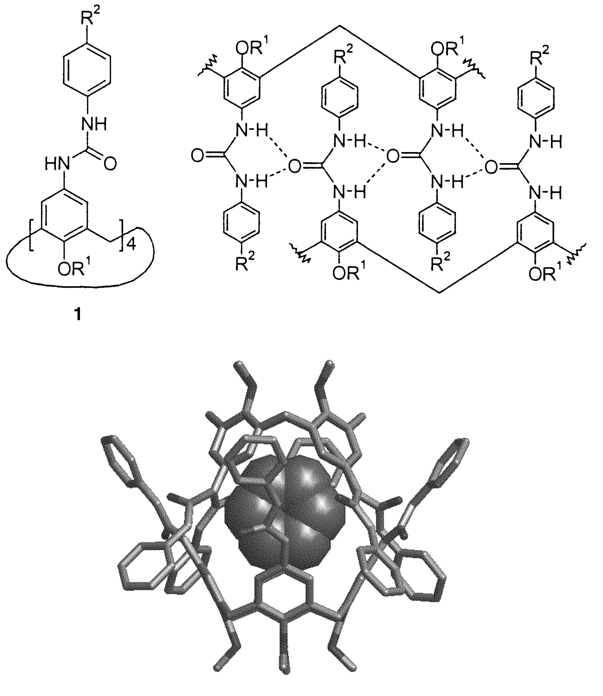

Fig. 1 Tetraureido calix[4]arene **1** ($R^1 = C_5H_{11}$, R^2 = Me), Top right: schematic representation of the hydrogen bonds keeping the capsule together. Bottom: calculated structure for the dimer of tetraureido calix[4]arene **1** with included benzene (R^1 and R^2 are omitted for clarity).

We are interested in the development of alternative methods to determine structural models of calix[*n*]arene–guest complexes for those cases where a single crystal structure determination is not accessible.[15–17] Capsules based on tetra-urea calixarenes are interesting candidates for the use of a thorough Fourier transform infrared (FTIR) spectroscopic analysis. To gain a deeper insight into the solid state structure we have chosen for a first study dimeric capsules formed from calix[4]arene **1** with enclosed benzene or cyclohexane, respectively. Results gained by a FTIR spectroscopic analysis have already proved to give structural information for calixarene complexes in solution,[18–23] hydrogen bonded,[24–27] or surface-bound systems,[28,29] and structures in the solid state, which are comparable with results obtained by X-ray structure determination.[16,30]

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† Electronic supplementary information (ESI) available: three tables containing fully assigned IR data of tetraureido calix[4]arene **1**, its complex with cyclohexane and benzene, and the corresponding model substances **2**–**5** as well as ^{1}H NMR spectra of the capsules $\mathbf{1}\cdot C_6H_6\cdot\mathbf{1}$ and $\mathbf{1}\cdot C_6H_{12}\cdot\mathbf{1}$ in solution. See http://www.rsc.org/suppdata/p2/b1/b108055p/

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Results and discussion

Materials

The two complexes $\mathbf{1}\cdot C_6H_6\cdot\mathbf{1}$ and $\mathbf{1}\cdot C_6H_{12}\cdot\mathbf{1}$ were prepared as colourless powders by dissolving **1** in benzene or cyclohexane, respectively, evaporating the clear solution and drying the residue at 100 °C at <1 Torr. Monomeric **1** was obtained by recrystallisation of **1** from chloroform–methanol. From ^{1}H NMR spectra of $\mathbf{1}\cdot$guest$\cdot\mathbf{1}$ measured in C_6D_{12}, where these capsules show a high kinetic stability,[10] it could be concluded that the samples did not contain free guest (C_6H_6 or C_6H_{12}), and that one guest molecule (δ = 3.87 for benzene; δ = −1.44 for cyclohexane) is included per dimeric capsule.

This host–guest ratio was confirmed by thermogravimetric analysis.[15] From the loss of weight during heating of the crystalline samples (Fig. 2) host–guest ratios of 2 : 0.82 for cyclohexane and 2 : 0.86 for benzene as guest molecule, respectively, can be deduced. This is in reasonable agreement with the data obtained by ^{1}H NMR spectroscopy in solution. Most guest molecules leave the crystal lattice when the samples are heated *ca.* 110–120 K above the boiling point of the free solvent (ΔT_{bp}). Similar ΔT_{bp} values can be found for *p-tert*-butylcalix[4]arene clathrates with THF (121 K), chloroform (121 K), or benzene (110 K) as guest molecules.[15]

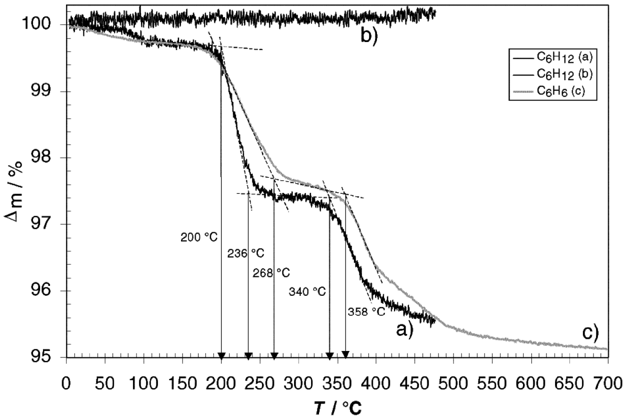


Fig. 2 Thermogravimetric analysis of calixarene-based capsules $\mathbf{1}\cdot C_6H_{12}\cdot\mathbf{1}$ (a and b) and $\mathbf{1}\cdot C_6H_6\cdot\mathbf{1}$ (c) (heating rate 10 K min^{-1} under nitrogen, curve b) was obtained by heating $\mathbf{1}\cdot C_6H_{12}\cdot\mathbf{1}$ up to 450 °C (a), cooling to room temperature and heating again to 470 °C.

At *ca.* 200 °C the interdigitating hydrogen bonds start to break and the entrapped guest molecules leave the interior of the capsule irrespective of their nature. Cooling the sample back to room temperature and re-heating up to 400 °C did not show any loss of weight, indicating that all guest molecules have left the capsule during the first heating cycle. The temperature interval ΔT in which the solvent is completely lost is somewhat broader for $\mathbf{1}\cdot C_6H_6\cdot\mathbf{1}$ (83 K) compared to $\mathbf{1}\cdot C_6H_{12}\cdot\mathbf{1}$ (36 K) and *p-tert*-butylcalix[4]arene·benzene (32 K). As expected, the loss of the entrapped molecule is endothermic (ΔH = 3.2 J g^{-1} was determined by differential scanning calorimetry for $\mathbf{1}\cdot C_6H_{12}\cdot\mathbf{1}$).

General procedure for the vibrational analysis of calixarene-based molecular capsules

To gain a deeper insight into the structural properties of the urea-based capsules, FTIR spectra of monomer **1**, the capsules $\mathbf{1}\cdot$guest$\cdot\mathbf{1}$, and free guest were recorded both at room and at low temperature (80 K). The measurements at low temperature show better resolution of individual absorption bands because the molecular motion is decreased significantly at 80 K. After full assignment of all absorptions observed, structural information can be deduced by comparing the obtained spectra. Information about symmetry and interaction with the surrounding capsule of the included guests are accessible when the data of the free guest and signals observable for the guest in the dimers ($\mathbf{1}\cdot$guest$\cdot\mathbf{1}$) are compared (Tables 1 and 2). From the line width of significant absorptions conclusions for the dynamic behaviour of the guests can be drawn. In case the capsule itself comes into focus, a comparison of the signals observed for the calixarene monomer **1** and dimer $\mathbf{1}\cdot$guest$\cdot\mathbf{1}$

Table 1 IR data (ν/cm^{-1}) and assignment of the *N′*-tolylureido capsule $\mathbf{1}\cdot C_6H_6\cdot\mathbf{1}$ and benzene (sh = shoulder, w = weak)

T = 293 K	T = 80 K	Int.[a]	C_6H_6	Assignment[33]
—	3075	[b]	3090	$\nu_2 + \nu_{13} + \nu_{18}\ E_{1u}$
—	3054	[b]	3070	$\nu_{13} + \nu_{16}\ A_{2u} + E_{1u}$
3027 sh	3024	[b]	3035	$\nu_{12}\ E_{1u}$
—	1954	[b]	1960	$\nu_7 + \nu_{19}\ E_{1u}$
1477	1479	[b, c, d]	1478	$\nu_{13}\ E_{1u}$
	1471 sh			
1387 sh	1386	[c, d, f]	1385	$\nu_2 + \nu_{20}\ E_{2u}$
	1378 sh			
—	1285 sh		1308	$\nu_9\ B_{2u}$
1244 sh	1243	[b, c, d, f]	1245	$\nu_{11} + \nu_{20}\ E_{1u}$
1244	1224 sh			
—	1171		1177	$\nu_{17}\ E_{2g}$
1138 sh	1141 sh		1147	$\nu_{10}\ B_{2u}$
—	1086	[e]	1097 sh	$\nu_4 + \nu_{20}\ E_{2g}$
1044	1043 sh	[b, c e]	1035	$\nu_{14}\ E_{1u}$
	1031			
1008 sh	1007 sh	[e]	1008	$\nu_6\ B_{1u}$ or $\nu_7\ B_{2g}$
850	857, 849 sh	[b, c, d, e]	849	$\nu_{11}\ E_{1g}$
—	793		793	$\nu_{17} - \nu_{20}\ A_{2u}$
673	679 sh, 671	[c, e]	668	$\nu_4\ A_{2u}$
—	592	[e]	608 w	$\nu_{18}\ E_{2g}$

[a] Interpretation of band splitting. [b] Superposition of guest and host bands. [c] Different orientations of the guest molecule in the crystal lattice/dimer. [d] Lifting of degeneracy. [e] Forbidden band becoming active. [f] Several components possible and/or combination tones with a degenerated component.

Table 2 IR data (ν/cm^{-1}) and assignment of the *N′*-tolylureido capsule $\mathbf{1}\cdot C_6H_{12}\cdot\mathbf{1}$ and cyclohexane[31] (sh = shoulder, w = weak)

T = 293 K	T = 80 K	Int.[a]	C_6H_{12}	Assignment
3131	3130		3155	$\nu_3 + \nu_{19} + \nu_{32}\ E_u$[b] $2\nu_{19} + \nu_{32}\ E_u$
3071	3075		3094	$\nu_5 + \nu_{19} + \nu_{31}\ E_u$[b]
2925	2919		2952	$\nu_{12}\ A_{2u}$[b]
—			2898	$\nu_{25}\ E_u/\nu_1\ A_{1g}$
—	2881		2898	$\nu_{25}\ E_u/\nu_1\ A_{1g}$[b]
—	2846		2847	$\nu_{26}\ E_u/\nu_2\ A_{1g}$[b]
2661	2662		2660	$\nu_{21} + \nu_{28}\ E_u$
2476	2476		2477	$\nu_{14} + \nu_{22}\ E_u/2\nu_{21}\ A_{1g} + E_g$
—	2365		2366	$\nu_3 + \nu_{30}\ E_u/\nu_{19} + \nu_{30}\ E_u$
—	2128		2136	$\nu_{21} + \nu_{31}\ E_u$
1446	1444	[c, d]	1450	$\nu_{14}\ A_{2u}/\nu_{27}\ E_u$[b]
1429	1429			
1386	1389	[c, d, f]	1350	$\nu_4 + \nu_{32}\ E_u$[b]
	1374			
1243	1243	[c, d]	1257	$\nu_{29}\ E_u$
1225	1226			
1047	1050		1039	$\nu_5 + \nu_{32}\ E_u$[b]
1012	1015	[c, e]	1014	$\nu_{23} + \nu_{32}\ A_{2u} + E_u$[b]
933	936	[c, e]	941	$\nu_{15}\ A_{2g}$
	928			
903	906	[c, d]	904	$\nu_{30}\ E_u$
	898			
866	867	[c, d]	862	$\nu_{31}\ E_u$
845	846			
—	802		821	$\nu_5\ A_{1g}$[b]
781	785		806	$\nu_{23}\ E_g$
524	522		524	$\nu_{16}\ A_{2u}\ \nu_{25}\ E_u/\nu_1\ A_{1g}$[b]

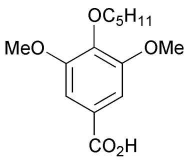
[a] Interpretation of band splitting. [b] Superposition of guest and host bands. [c] Different orientations of the guest molecule in the crystal lattice/dimer. [d] Lifting of degeneracy. [e] Forbidden band becoming active. [f] Several components possible and/or combination tones with a degenerated component.

Table 3 Selected IR data (ν/cm^{-1}) and assignment of the urea monomer **1**, urea dimer **1**·C_6H_6·**1**, and urea dimer **1**·C_6H_{12}·**1** [I_{rel}: estimated relative intensities of the members of a cluster (%-transmission)[30]]

1		**1**·C_6H_6·**1**		**1**·C_6H_{12}·**1**		
T = 293 K	I_{rel}	T = 80 K	I_{rel}	T = 80 K	I_{rel}	Assignment‡
3599		3599		3590		ν(NH)
3479	30	3482	30	3482	30	
3339	100	3408	70	3408	70	
3309	100	3354	100	3350	100	
3221	70	3290	100	3283	80	
3138		3203	70	3258	70	
		3134		3226	65	
				3196	60	
				3134		
3076		3081		3081		ν_2; $\nu_{20a'}$(CH)
3030	100	3025	100	3025	100	ν_{20a}; ν_{20b} (CH)
3002	20	2998	20	2998	20	ν_{7b}, ν_{20b}; ν_{20a} (CH)
2952		2952		2952		ν_{as} (CH_3)
2926		2927		2927		ν_s (CH_3)ν_{as} (CH_2)
2869	100	2869	100	2869	100	ν_s (CH_3)
2857	95	2859	95	2857	95	
2760	50	2763	50	2763	50	$\nu_{13} + \nu_{17}$
2730	100	2733	100	2731	100	
1889		1889		1893		$\nu_7 + \nu_{19}$
1705 sh		1705	40	1705 sh	24	ν (CO)
		1682	65			
1658		1666	100	1665	100	
		1648	70			
1602		1616	80	sh	80	β (NH), ν_{8a}; ν_{8a}
		1604	100	1608	100	β (NH)
		1584	80	sh	80	β (NH)
1553	100	1554	100	1558	100	β (NH)
1516	80	1512	80	1514	80	ν_{19a}

instructs about type, strength and symmetry of intermolecular forces involved in the formation process of the capsule. Observed band splittings, changes of intensities and shifts of absorption are important experimental data for this purpose (Table 3).

Because it is not possible to rule out any hydrogen bonding between the urea units in the calixarene monomer **1** itself, a reference system based on model compounds **2**–**5** (Fig. 3) can be used to obtain complexation induced shifts (CIS) and estimate the strength of such hydrogen bonds in the monomer as well as in the dimer **1**·guest·**1** (Table 4). The chosen model substances **2**–**5** reflect important parts of the calix[4]arene **1** concerning bond strength and substitution pattern. In the latter case, the weight of the substituents must reflect the real situation rather than their actual chemical structure. Further details about the general procedure used for the vibrational analysis have been published earlier.[30]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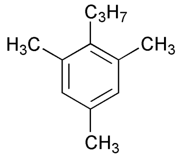
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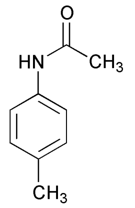
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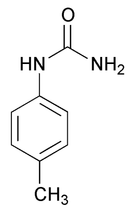
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Fig. 3 Model compounds **2**–**5** used for the vibrational analysis of the empty cavitand and molecular capsules.

According to the NMR data in solution,[8] the dimers posses S_8-symmetry while the X-ray structure of a comparable urea capsule[9] reveals C_4 symmetry. In case of deviation from this symmetry, C_2 or C_1 must be considered as the corresponding point groups. According to the vibrational spectroscopic analysis of cyclohexane,[31] this guest belongs to the point group D_{3d} or has lower symmetry when the structure deviates from the chair conformation; benzene belongs to the point group D_{6h}. Hence it follows for included cyclohexane or benzene, respectively, that all vibrations are IR- and Raman active and all degeneracies are lifted.

Vibrational analysis of 1·C_6H_6·1

The FTIR spectra (KBr disks) obtained for **1**·C_6H_6·**1** are shown in Fig. 4 and the results of the analysis of these data are summarised in Tables 1 and 3.

Apart from the lifting of degeneracy, the splitting of several absorptions (*e.g.* 1245 ⟶ 1244, 1224 cm^{-1}, *cf.* Table 1) of included benzene is clearly observed.

Because benzene molecules are found only inside the capsules, there are two possible explanations for this observation. Either there are two independent orientations of the capsule in the crystal lattice or included benzene has two major orientations inside the cavity. Because the line width of the included benzene is similar to that of pure benzene and interactions between encapsulated benzene molecules are unlikely due to size-limitations, the band width is presumably a result of fast rotation of the guest molecules around their longitudinal axes at the two main orientations.

Most frequencies of benzene are shifted downwards (*e.g.* 3090 ⟶ 3075). Large effects up to 16 cm^{-1} for the C–H and 23 cm^{-1} for the C=C valence vibrations are observed, while the average shift for all absorptions is about 11 cm^{-1}. Few frequencies are shifted to higher values with shifts up to 9 cm^{-1}. This can be explained as complexation-induced shift (CIS) by

Table 4 IR data (ν/cm^{-1}) and assignment of the empty urea derivative **1** and its dimer **1**·C$_6$H$_6$·**1** for the calculation of interactions

1 (T = 293 K)	**1**·C$_6$H$_6$·**1** (T = 80 K)	BS[a] |Δ|/cm^{-1}	CIS[b] |Δ|/cm^{-1}	Assignment
3599	3599	19–99[c]	9–69	ν (NH)
3479	3482			
3339	3408			
3309	3354			
3221	3290			
3138	3203			
	3134			
1658	1705	58	8–65	ν (CO)
	1682			
	1666			
	1648			
1602	1616	62	11–21 2	β (NH)
	1604			β (NH)
	1584		2	β (NH)
1553	1554			β (NH)
1418	1431	29	8–21	ν (C–N)
1402	1418			
	1402			
640	638	—	2	γ (NH)
	sh			
619	619	—	5	
	sh			
601	601	37	4–33	γ (CO)
593	594			
585	586			
578	576		2	
	564			
553	553	—		

[a] BS: band splitting. [b] CIS = complexation induced shift; Δ = ν(**1**·C$_6$H$_6$·**1**) − ν(model substance). [c] 3221, 3309, 3339 are split into two components, *e.g.* 3221 into 3203 and 3290.

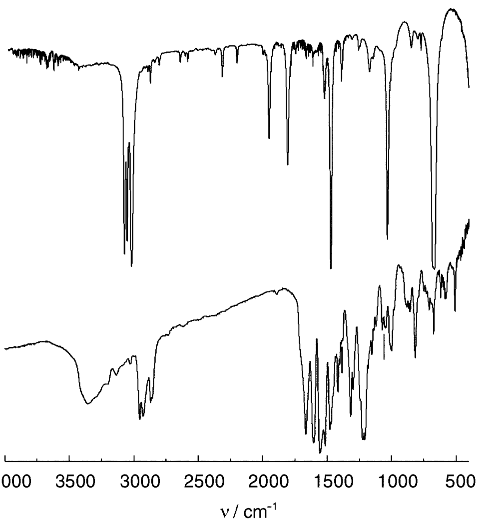

Fig. 4 IR spectra of benzene and **1**·C$_6$H$_6$·**1** (bottom) (T = 293 K, KBr disks).

CH–π interactions[32] of the benzene molecules in the inner cavity. For the 1 : 1 complex of *p-tert*-butylcalix[4]arene with benzene a similar averaged CIS is observable (12 cm^{-1}).[16]

However, in this case a maximum shift of 26 cm^{-1}for the C–H and 30 cm^{-1} for the C=C valence vibration, respectively, is observable indicating a somewhat stronger contact of benzene in the cavity of *p-tert*-butylcalix[4]arene. This difference can be rationalized by additional CH–π interactions of the *tert*-butyl groups of the *p-tert*-butylcalix[4]arene skeleton towards the included guest which increase the binding strength. Such an additional binding force is not possible for the urea–calixarene **1**, because the urea moieties are involved in hydrogen bonds which hold the capsule together.

Comparison of IR data of the monomer and the dimers (Table 3) clearly reveals some significant shifts of the frequencies. As expected, the shift of the amide bands in the monomer is up to 69 cm^{-1} and in the dimer up to 99 cm^{-1}, compared to model compounds.

Due to dimerization there is a splitting of some bands of the calixarene **1** into two components, *e.g.* the methyl group vibrations of the *N*-tolyl-ureido group and the vibrations of the pentyloxy group (*e.g.* 2926 ⟶ 2927 and 2869 cm^{-1}). The ratio of the split components is 1 : 1. Because the splitting is mainly observed for molecular regions on the outside of the capsule, influences of the guest molecule are not likely. Therefore, the splitting is probably due to a C_4 symmetrical arrangement in which both calixarenes are not exactly twisted by 45° as required for a S_8 symmetrical arrangement. This is in accordance with the crystal structure of urea calixarene **1** (R^1 = CH$_2$CO$_2$Et) in which a twist of 43° was observed.[9] This observation is diagnostic irrespective of whether a dimer or monomer is present.

For the calixarene monomer **1** two types of NH groups are present, *i.e.* a calixaryl-NH and a tolyl-NH. Because one expects symmetrical [ν_s (NH)] and anti-symmetrical [ν_{as} (NH)] vibrations for both types of amide band, involving these NH-groups in identical hydrogen bonds would lead to a signal set consisting of four components. However, each of these bands is split again into two, partly overlapping, components: one is shifted downwards (up to 19 cm^{-1}, 3309 ⟶ 3290 cm^{-1}), one upwards (up to 99 cm^{-1}, 3309 ⟶ 3408 cm^{-1}). This must be caused by the arrangement of the dimer and gives evidence for a weak and a strong hydrogen bond.

The included benzene has no further influence on the conformation and geometry of the dimer.

In summary, the observed complexation induced shifts and shifts derived from the comparison with model compounds **2**–**5** give evidence for two types of hydrogen bonds between the urea monomers as well as CH–π interactions between included benzene and the aromatic rings of the host molecule.

Vibrational analysis of 1·C$_6$H$_{12}$·1

The line width of the included cyclohexane is similar to that of benzene. Therefore, a similar dynamic behaviour (rotation) can be assumed.

Most frequencies of cyclohexane are shifted up to 33 cm^{-1} down, with an average shift of about 14 cm^{-1}; few frequencies are shifted to higher values by up to 39 cm^{-1} with an average shift of 13 cm^{-1}. This can be explained as complexation induced shift, which is clearly stronger compared to the inclusion of benzene. This may be due to the *ca.* 20% higher molecular volume of cyclohexane compared to benzene which results in a tighter fit of this guest inside the capsule. The different spatial fit of the two different guests inside the cavity is also reflected in solution. However, in the latter case a higher CIS could be detected for benzene (−3.38ppm) compared to cyclohexane (−2.88 ppm) by ^{1}H NMR spectroscopy.[10] This is not a contradiction because the complexation-induced shift observed by NMR spectroscopy is mainly based on the fact that a guest molecule is located in the anisotropic cone of the phenyl rings, whereas CIS obtained by FTIR spectroscopy depends on the anisotropic fields induced by all surrounding functional groups.

Comparison of the monomer and the dimer shows, that there are some significant shifts in the frequencies. The shift of the amide bands is up to 99 cm^{-1}, the other shifts are up to 16 cm^{-1}.

All amide bands of the dimer are split into four components. These components are again split caused by the arrangement of the dimer (*cf.* **1**·C$_6$H$_6$·**1**). Because the C=O stretching mode of both capsules (1666 for C$_6$H$_6$ and 1665 cm^{-1} for C$_6$H$_{12}$) is very similar but significantly different from the monomer (1658 cm^{-1}), one can assume that the hydrogen bonding towards this oxygen atom is of comparable strength in both dimeric systems. The included cyclohexane has no further influence on the conformation and geometry of the dimer. The splitting of the signals for both benzene and cyclohexane is therefore due to two different arrangements of the guest molecules in the cavity of the capsule or by two types of crystallographically independent capsules. On the basis of the experimental data available up to now, it is not possible to distinguish between the two explanations.

Again, due to the dimerization some bands are split into two components, and the complexation induced shifts obtained as before give evidence for two types of hydrogen bond between the calixarene monomers and CH–π interactions of the included cyclohexane to the aromatic rings of the calixarenes.

Some low lying vibrations which cannot be assigned to any of the modes of the subunits have to be characterised as specific for the calixarene capsule *in toto*. They are denoted as "calixarene ring mode".

Conclusion

By the use of FTIR spectroscopy, the complexes **1**·C_6H_6·**1** and **1**·C_6H_{12}·**1** could be characterised. The capsules are held together by two types of hydrogen-bond bridges from two types of different urea NH groups, one showing strong and the other less favourable interactions as indicated by the splitting of the amide bands. The structures of the monomers and corresponding subunits in the dimer are nearly identical; the included guest molecules have little influence on the overall geometry of the surrounding non-covalently assembled container molecule. The mobility of benzene and cyclohexane, respectively, is similar taking the half-width of the corresponding absorption into consideration. Compared with **1**·C_6H_6·**1**, the IR data of the capsule **1**·C_6H_{12}·**1** exhibit larger shifts, which suggests stronger interactions. Because the overall geometry of the capsule is nearly independent from the guest, which is rotating fast on the IR timescale, the splitting observed for the included solvent molecule is likely to be due to two main orientations of the guests inside the capsule. However, on the basis of the current experimental data, it remains unclear whether the guest molecules are located at two different sites in the capsule or two different types of capsules are existing in the crystal.

Three tables containing fully assinged IR data of tetraureido calix [4] arene **1**, their clathrates with cyclohexane and benzene and e the corresponding model substances 2–5 as well as ^{1}H NMR spectra of the capsule **1**·C_6H_{12}·**1** in solution.

Experimental

The preparation of the calixarene **1** and the capsules have been described earlier.[8,10,34] Infrared spectra were recorded on a FTIR spectrophotometer IFS 113v (Bruker) using KBr windows and a DGTS detector, with a resolution of approximately 0.5 cm^{-1}. Raman spectra were recorded with the Raman-Laser spectrophotometer Dilor XY (multi- and single-channel detector, resolution 1 cm^{-1}) using an Ar-Laser (Coherent, exciting line 514.53 nm). The temperature of the samples was 293 K and 80 K, respectively. Host–guest ratios of the samples used for the IR analysis were determined by NMR spectroscopy[10] and thermogravimetric analysis as described earlier.[15]

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