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Selective dimerisation of tetraurea calix[4]arenes†

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The formation of hydrogen-bonded dimeric capsules from tetraurea calix[4]arenes is controlled by loops, connecting adjacent urea functions, and more or less bulky substituents. The dimerisation is only possible if loops are not overlapping and if the respective residues can pass the loops. A sorting scheme based on small and bulky residues and one to four loops allows reducing the number of possible dimers from 35 to 6 in a stoichiometric mixture of 11 ureas. With three different loop sizes (O—$(CH_2)_n$—O chains with $n = 10$, 14, 20 connecting adjacent phenylurea functions via their *meta* positions), it is possible to distinguish four urea residues of different sizes (small, medium, bulky and giant) ranging from tolyl to 4-[tris-(4-*t*-butylphenyl)methyl]-phenyl. While the smallest residue can pass all loops, the largest is excluded by all loops.

Keywords: calixarene; dimerisation; hydrogen bonds; self-assembly

Introduction

About 15 years ago, J. Rebek Jr described hydrogen-bonded capsules in which two calix[4]arenes in the cone conformation are held together by a seam of hydrogen bonds between the interlocking urea functions which simultaneously act as hydrogen bond donor (—NH) and acceptor (O═C) (*1*). The inclusion of a suitable guest is necessary for this dimerisation, which could be confirmed shortly afterwards by the formation of heterodimers in addition to the two homodimers in a mixture of two tetraureas (*2*), and by a first crystal structure (*3*). However, this statistical (homo- and hetero-) dimerisation is not the rule. A stoichiometric (1:1) mixture of tetraaryl (**1**, Figure 1) and tetratosyl urea (**2**) contains exclusively the heterodimer (*4*), while a homodimer is only observed if one of the tetraureas is present in excess. If, on the other hand, a tetraurea derived from tetraalkyl ether (**1**) is mixed with a tetraurea of a biscrown[3] derivative (**3**), not a heterodimer but only two homodimers are formed. Due to the two short crown[3] loops, the calix[4]arene skeleton of **3** is conformationally rigidified. Thus, in the latter case, an explanation is readily given by the loss of entropy connected with the formation of the (rigid) heterodimer (*5*). In the first case, the energetically unfavourable conformation of one of the two tetratosyl ureas in the homodimer of **2** is the most probable explanation (*6*, *7*).

Early examples for selective assemblies

Two tetraurea calix[4]arenes may be covalently connected via their narrow rim. In apolar solvents, under conditions where the dimerisation occurs, these molecules will form linear hydrogen-bonded polymers. The exclusive formation of heterodimers between tetratolyl and tetratosyl ureas was used to create some regularity in their structure. A stoichiometric mixture of a bis-tetratolyl urea **4** (T–T) and a bis-tetratosylurea **5** (S–S) thus leads to the alternating polymer $\sim[\mathbf{4}\cdot\mathbf{5}]_n\sim$ with alternating bis-tetraurea units, and the dimerisation of the mixed bis-calixarene **6** (T–S) leads to the formation of the regular polymeric assembly $\sim[\mathbf{6}\cdot\mathbf{6}]_n\sim$ with alternating tetraurea units (Figure 2) (*8*, *9*).

If three or four tolyl urea units are covalently connected via their narrow rim, the exclusive hetero-dimerisation with tetratosyl urea **2** allows the selective formation of three-fold **7** (*8b*) and four-fold **8** (*10*) tetraurea dimers.

Finally, in combination with other independent and selective dimerisations, e.g. between triureas derived from triphenylmethanes (*11*), this selective formation of heterodimers was also used to form well-defined dendrimers via self-assembly (*12*, *13*). In the course of these studies, the search for further selectivities controlling the dimerisation of tetraurea calix[4]arenes started.

Steric restrictions of the dimerisation

The substituent attached to the urea group(s) can be easily varied, using different isocyanates or activated urethanes for the introduction of the urea groups. In the first attempts, we thus tried to steer/control the dimerisation by bulky residues R attached to the urea function (—NH—CO—NHR). However, even the tetraurea **1d** (Figure 3) bearing four 4-[tris-(4-*t*-butylphenyl)methyl]-phenyl

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†Dedicated to the memory of Dmitry Rudkevich.

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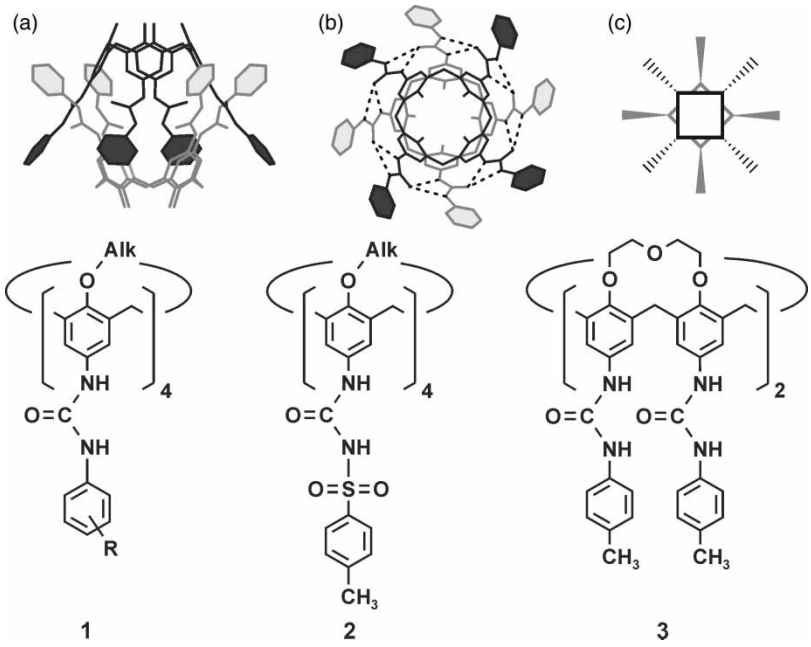

Figure 1. Top: Dimeric capsule of a tetraaryl tetraurea calix[4]arene **1**: (a) side view, (b) top view, hydrogen bonds are indicated by dashed lines, and (c) graphical representation of the dimer. Bottom: Structural formulae of tetraurea calix[4]arenes **1**–**3**.

residues readily forms a dimer, confirmed even by a crystal structure (*14*). Therefore, steering or controlling of the dimerisation by bulky urea residues *alone* obviously is not a reasonable possibility. However, the covalent connection of adjacent urea residues into a loop turned out to offer an alternative!

Tetraurea calix[4]arenes with two different urea residues ABBB (e.g. compound **9**) or AABB (e.g. compound **10**) usually form two regioisomeric homodimers, as illustrated in Figure 4. Both homodimers are chiral, and exist as a pair of enantiomers. A tetraurea of the type ABAB (e.g. compound **11**), with alternating sequence of the urea residues, forms only one pair of enantiomeric dimers.

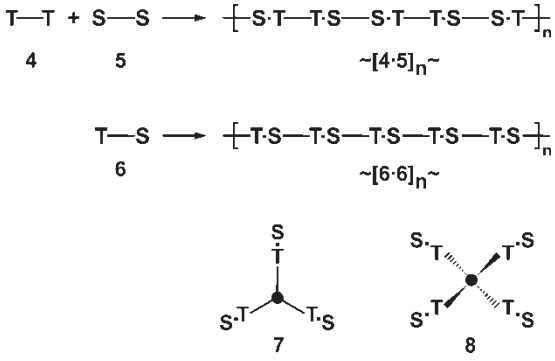

Figure 2. Formation of polymers with regular sequence ($\sim[\mathbf{4\cdot5}]_n\sim$, $\sim[\mathbf{6\cdot6}]_n\sim$) and of well-defined oligomers (**7**, **8**) using the selective heterodimerisation between tetratolyl ureas (T) and tetratosyl ureas (S).

If, in a compound of AABB type, two identical residues are covalently connected by a flexible, aliphatic chain which does not hinder the dimerisation, e.g. by distortion (compound **13**), only one homodimer is observed (Figure 5). The only reasonable explanation for this observation is that the dimer with overlapping loops cannot be formed.

In addition, we found that for tetraureas of the type AABB, with one loop covalently connecting the residues A and two bulky residues B (e.g. compound **15**), no dimerisation occurs if either the loop is too small or the bulky residues are too large. Consequently, if the residues A are covalently connected with an aliphatic chain, and B and C represent urea groups with a bulky (B) and a small (C) substituent (e.g. compound **16**), only *one* pair of enantiomeric homodimers is formed (*15*). As illustrated in Figure 5, it consists (necessarily) of the same enantiomer, and therefore it is chiral itself.

Covalent connection of the two 'small' residues in the dimer of type **16**·**16**, which can be achieved, for instance, by olefin metathesis between ω-alkenyl groups attached to the urea functions, leads to a 'fixed' dimeric molecule with unique topology (*15*).

Synthetic remarks

Before we discuss more complicated cases involving the potential (hetero)dimerisation of various tetraurea calix[4]arenes, it seems reasonable to insert a short section about the synthesis of these compounds. Starting with *t*-butyl calix[4]arenes fixed in the cone conformation by four sufficiently large ether residues (e.g. *n*-propyl or

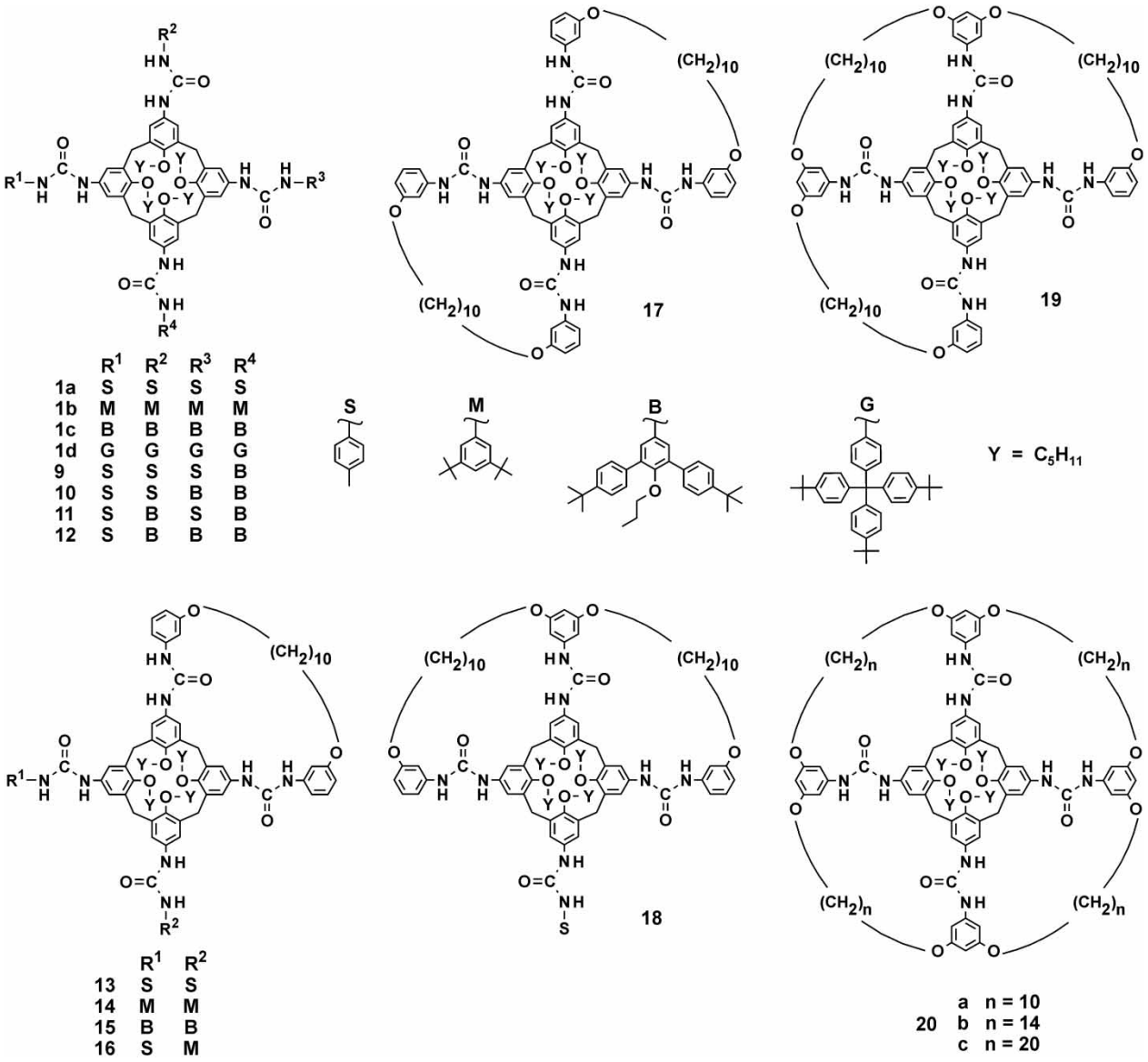

Figure 3. Formulae survey. The urea residues are abbreviated as S (= small), M (= medium), B (= bulky) and G (= giant).

larger), four amino functions are introduced by ipso-nitration followed by catalytic hydrogenation (*16*). Urea residues were generally attached by acylation with the respective isocyanates (*16*) or activated urethanes (*17*). Here, the protection of one, two adjacent or three amino groups by the Boc-group (*18*) or of two opposite amino functions by the trityl group (*19*) was extremely helpful.

In principle, the creation of loops connecting two adjacent amino functions can be achieved in a similar way, using the appropriate activated bisurethane as the reagent (*20*). In general, however, loops were formed by olefin metathesis between ω-alkenyloxy residues attached to the *m*-position(s) of phenylurea groups, followed by hydrogenation of the double bond. To avoid cross-cavity bridging by the reaction between opposite alkenyl groups, the coupling was done using the heterodimer of the alkenyloxy-substituted tetraureas with tetratosyl urea calix[4]arene **2**. The synthetic principle is summarised in Figure 6.

After metathesis and subsequent hydrogenation, the heterodimer was split under hydrogen-bond-breaking conditions, and the bisloop compounds **17** (*21*) and **18** (*22*), the trisloop compound **19** (*22*) or the tetraloop compound **20** (*23–25*) were isolated by column chromatography in yields of up to 90% (*26*).

Remarkably good yields (>70%) were found even for the trisloop compounds, although, in this case, a side

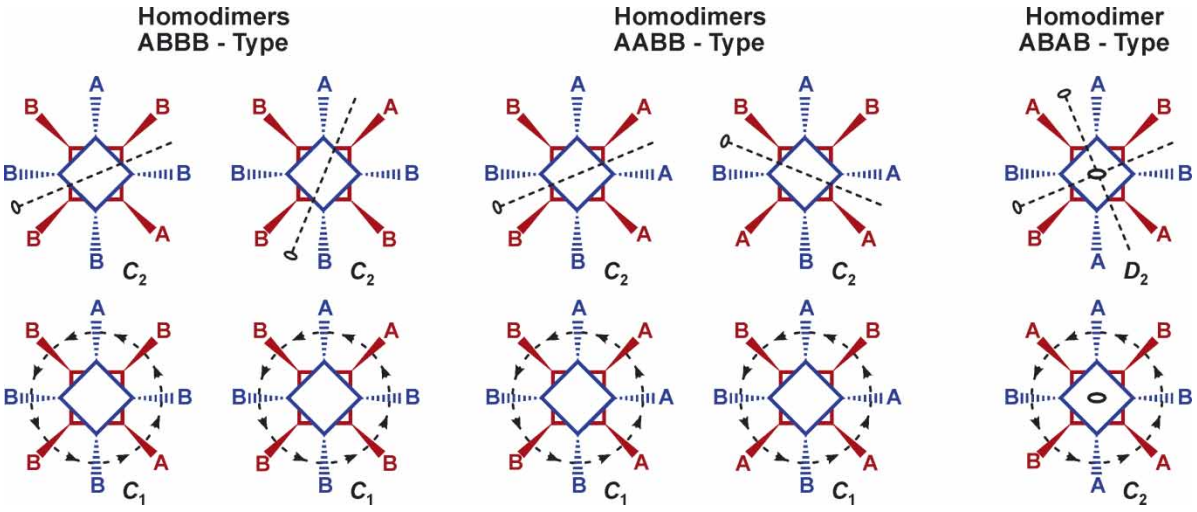

Figure 4. Symmetry properties of homodimers of tetraurea calix[4]arenes. Symmetry classes (point group symmetry) and symmetry elements are shown. The directionality of the hydrogen bonds is indicated by a cycle of arrows.

reaction leading to a bisloop compound with two isolated vinyl groups is (at least) possible. Only for very short loops, containing six or eight methylene groups, a splitting of the formed tetraloop tetraurea from the tetratosyl urea used as the template was impossible. Thus, the resulting products are fourfold [2]rotaxanes (*27*).

Mixtures of tetraureas

The ^{1}H NMR spectrum of a tetraloop tetraurea in a solvent such as $CDCl_3$ or C_6D_6 is broad and unresolved (Figure 7(a)), indicating an ill-defined mixture of hydrogen-bonded species, but obviously not a well-defined dimer. (The same holds true for tris- and bisloop compounds.) Under the same conditions, the ^{1}H NMR spectrum of an open-chain tetraurea is characteristic for its homodimeric capsule (Figure 7(c)). If both solutions are mixed in the molar ratio of 1:1, a well-defined ^{1}H NMR spectrum develops in a short time, which is in full agreement with the ^{1}H NMR spectrum expected for the heterodimer of both compounds, while the signals of the homodimer disappear completely what is best seen for

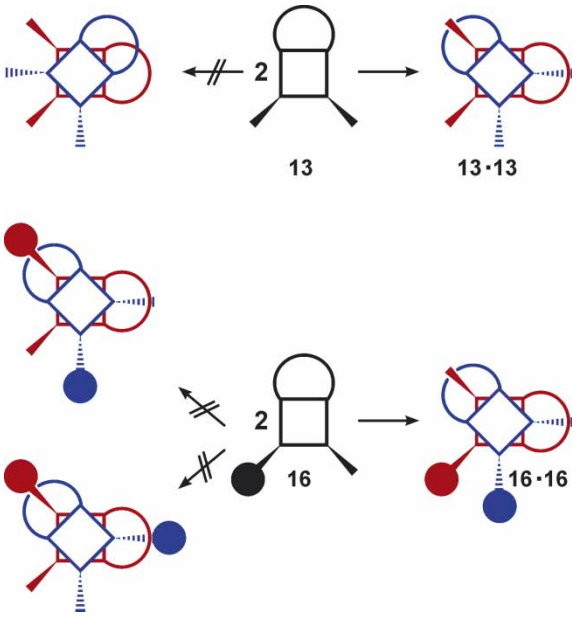

Figure 5. Schematic representation of the dimerisation of monoloop tetraureas.

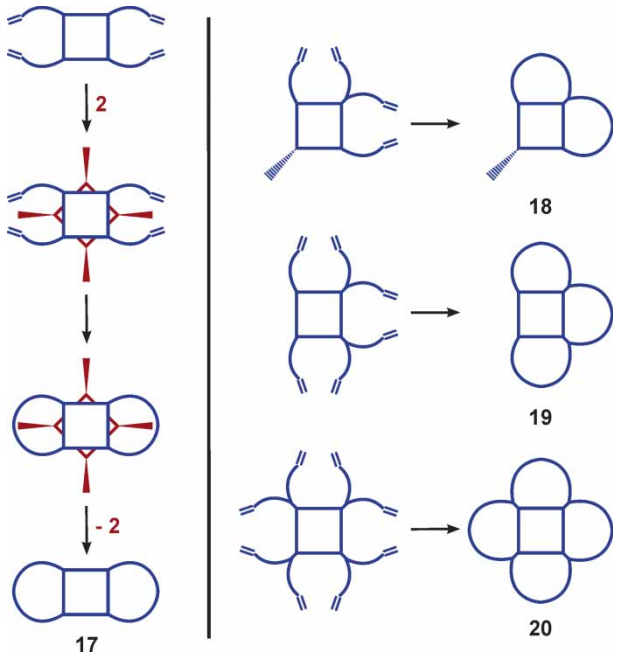

Figure 6. Syntheses (schematic) of bis-, tris- and tetraloop calix[4]arenes by olefin metathesis.

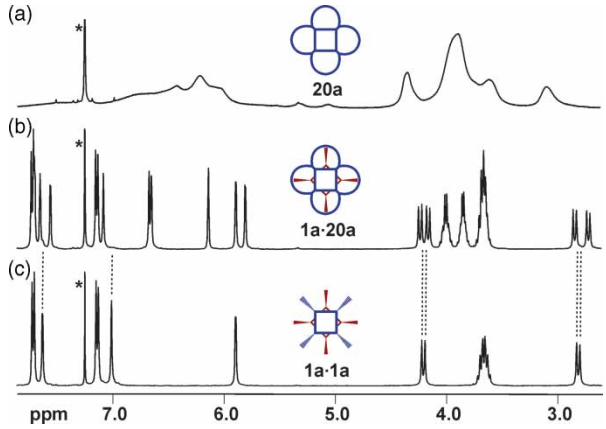

Figure 7. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25°C) of (a) tetraloop calix[4]arene **20a**, (b) heterodimer **1a·20a** and (c) homodimer **1a·1a**. The solvent signal is marked by an asterisk.

the signal at ~7.0 ppm (Figure 7(b)). Obviously, the complete formation of the heterodimer is the only possibility, where *all* tetraurea molecules can form a dimer.

Another more sophisticated example (*22*) is shown in Figure 8. Again, in the apolar solvent $CDCl_3$, the ^{1}H NMR spectrum of the trisloop compound **19** is broad and unresolved, since a homodimer cannot be formed, although a more or less irregular interaction via hydrogen bonds certainly takes place. The spectrum of **9** (Figure 8(b)) is also

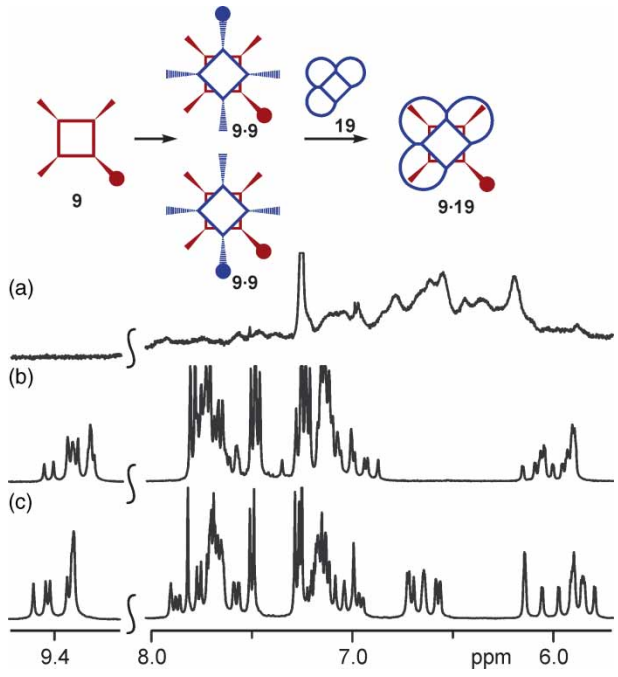

Figure 8. Sections of the ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25°C) of: (a) trisloop derivative **19**, (b) tetraurea **9** (mixture of two regioisomeric homodimers) and (c) stoichiometric mixture of **9** and **19** (heterodimer).

complicated, since two regioisomeric dimers exist in this case, but in contrast to the spectrum of **19** (Figure 8(a)), it is in agreement with well-defined species, kinetically stable on the NMR time scale. The spectrum of the stoichiometric mixture shown in Figure 8(c) is sharp, but completely different from Figure 8(b) and in agreement with the quantitative formation of the heterodimer **9·19**.

Rules for the dimerisation

As shown by the examples above, in mixtures of tetraurea calix[4]arenes, a regrouping may take place until all tetraurea calix[4]arenes are combined to dimers. This regrouping is controlled by the following two rules:

(1) Only those dimers that do not require an overlap of loops are formed.
(2) The urea groups that have to pass through the loops of the partner must be small enough.

For selected examples, these rules have been checked and also confirmed by mass spectrometry, using the tetraethylammonium cation as a charged guest (Figure 9) (*28*). Two open chain tetraureas **1a** and **1b**, which differ by the size of their urea residues (tolyl and 3,5-di-*t*-butylphenyl, respectively) and two tetraloop tetraureas **20a** and **20c** with different ring sizes (10 and 20 methylene units, respectively), were used for the two series shown in Figure 9. The (equimolar) mixture of the first two calix[4]arenes **1a** and **1b** contains the two homodimers **1a·1a** and **1b·1b** and the heterodimer **1a·1b**.[1] Addition of the tetraloop compound **20a** to this mixture leads to the formation of the heterodimer **1a·20a**, which is complete when **1a·1a** and **1a·1b** are consumed. Consequently, no further change is observed after the addition of one equivalent **20a** (with respect to **1a**) and the mixture now contains the two dimers **1a·20a** and **1b·1b**. (The excess of **20a** cannot form dimers, and is not detected by ESI-MS.) The larger tetraloop compound **20c** forms dimers with both **1a** and **1b**. Therefore, the addition of only one equivalent of **20c** to the above-mentioned mixture leads to the formation of all five possible dimers (because **20c** is not able to distinguish between **1a** and **1b**) and two equivalents of **20c** are required to obtain the mixture containing just the heterodimers **1a·20c** and **1b·20c**.

A general sorting scheme

Based on the rules explained above, a sorting scheme for a mixture of 11 tetraurea calix[4]arenes can be established (see Figure 10). The mixture consists of six 'open chain' derivatives covering all possible combinations of 'bulky' and 'small' residues within the tetraurea molecule[2] and all five possible loop-containing compounds (mono-, two bis-, tris- and tetraloop). Statistically, a mixture of *N* different

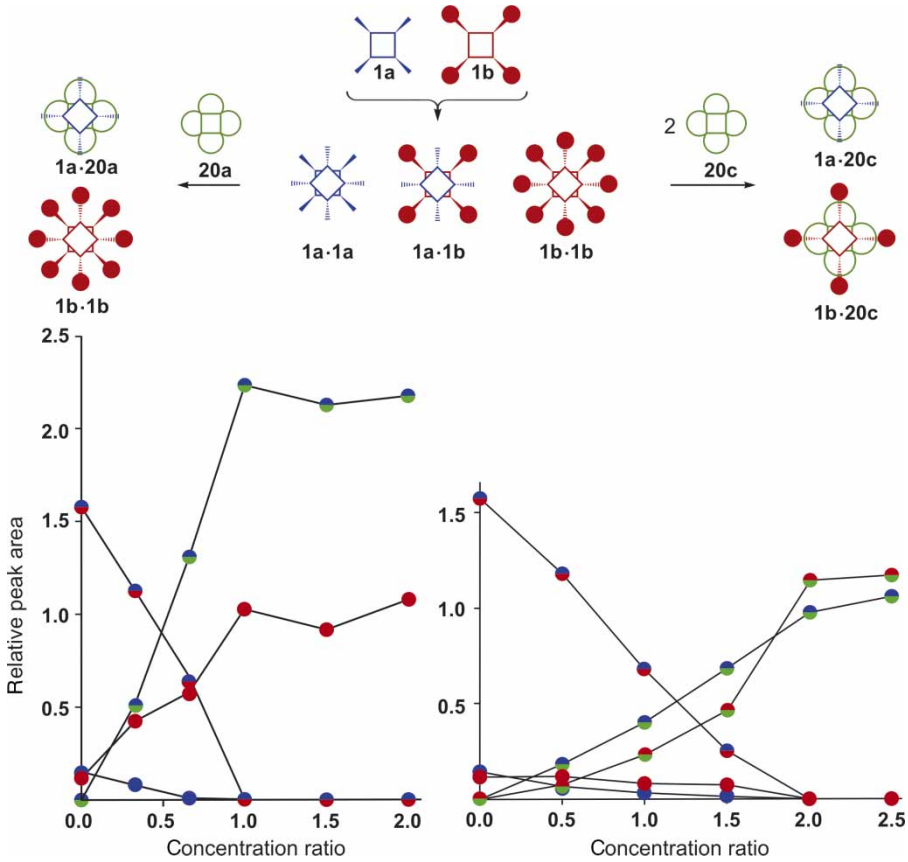

Figure 9. Self-sorting and ESI-MS titration of an equimolar mixture of **1a** and **1b** by tetraurea **20a** with small loops (left) and **20c** with large loops (right).

objects can combine to $0.5 \times N \times (N + 1)$ dimers (66 dimers for $N = 11$). Due to the first rule, 13 combinations are impossible, while 18 additional combinations are excluded by the second rule. From the remaining 35 possibilities, only *six* are finally realised under (pairwise) stoichiometric conditions (*29*). The 'driving force' for this sorting process is obviously the strong tendency to form hydrogen-bonded dimers in an apolar solvent, which is possible for all tetraureas only in this manner.

The tetraloop compound **20a** can only form heterodimers with tetraurea **1a**, which is consumed in this way. The tetraurea **9** is consumed analogously by the trisloop derivative **19**, the tetraurea **10** by **18** and so on. Thus, all open-chain tetraureas are combined by loop-containing compounds, with the exception of **1c**. Its four bulky residues prevent a dimerisation with any loop compound, but not the formation of its homodimer.

Variation of loops and residues

The sorting scheme described so far is based on a certain loop, a chain of 10 methylene groups (—O—$(CH_2)_{10}$—O—) connecting adjacent arylurea functions and two urea residues of different size (small and medium). However, even a further differentiation was possible, using three loops with different chain lengths ($n = 10$, 14 and 20) in combination with four substituents with different sizes (see Figure 3):

small (S) = tolyl (compound **1a**)
medium (M) = 3,5-di-*t*-butylphenyl (**1b**)
bulky (B) = 3,5-di-(4-*t*-butylphenyl)-4-propyloxy-phenyl (**1c**)
giant (G) = 4-[tris-(4-*t*-butylphenyl)methyl]-phenyl (**1d**).

It could be shown (*30*) that the tetraurea with the smallest loop **20a** ($n = 10$) forms dimers only with **1a**, the tetraurea bearing the smallest urea residues. For the tetraurea with four medium-sized rings **20b** ($n = 14$), a dimerisation is possible also with **1b**, and for large rings **20c** ($n = 20$) additionally with **1c**. The tetraurea **1d** does not form heterodimers with any of the tetraloop compounds studied, but it combines easily to homodimers. These results are summarised in Table 1. Figure 11 shows a section of the ^{1}H NMR spectra of the three heterodimers **1a·20a**, **1b·20b** and **1c·20c** and of their mixture

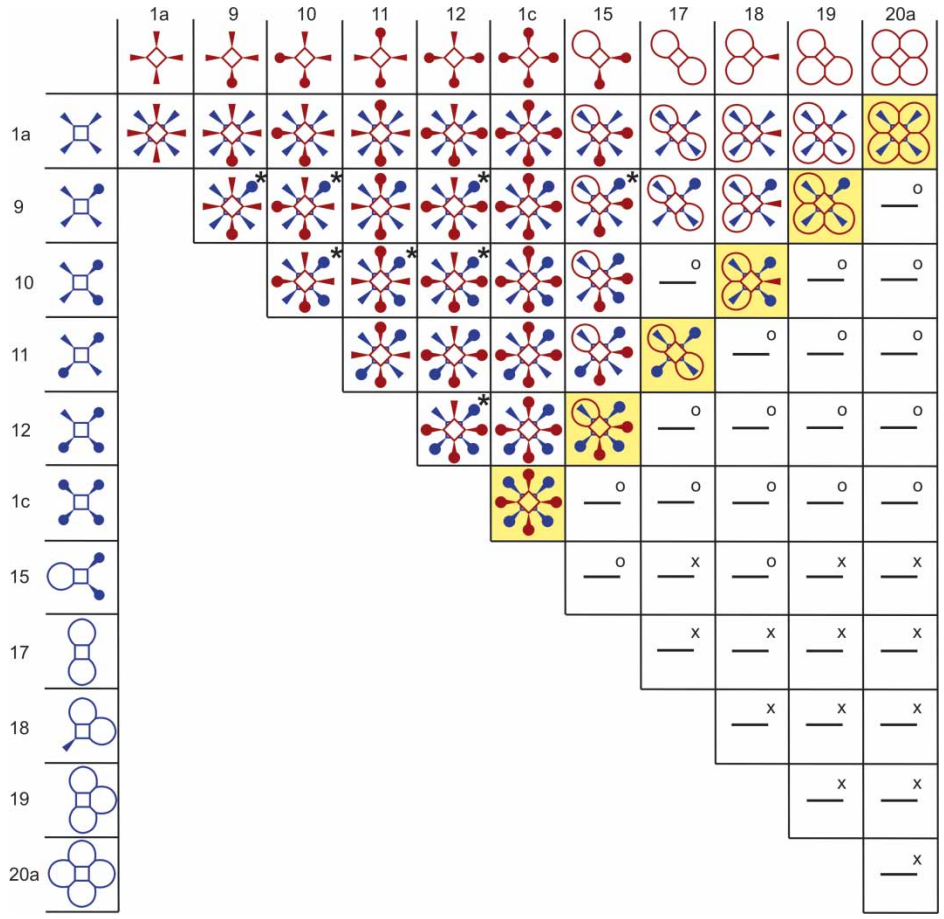

Figure 10. Schematic representation of the self-sorting process in the mixture of 11 tetraurea calix[4]arene derivatives. Dimeric combinations marked by 'x' are impossible due to overlapping loops (the first rule), while 'o' indicates the impossibility of bulky residues to penetrate these loops (the second rule). For dimers marked by '*' two or three regioisomers are possible.

(Figure 11(d)). Only signals characteristic of these heterodimers are found in Figure 11(d). The spectrum of the homodimer **1d·1d**, shown in Figure 11(e), suggests that even some of its signals can be distinguished in a mixture of all four dimers.

Limits

The principles outlined above offer numerous possibilities to construct larger, well-defined structures in a controlled and predictable way, using building blocks in which two (or more) tetraurea units are covalently connected via their narrow rim. They may be used also in combination with similar motifs of self-assembly, e.g. the dimers formed by triurea triphenylmethanes (*31*) or the tetrameric assembly formed by triurea monoacetamide of calix[4]arenes (*32*). However, in doing this, one should not stress this idea to the very end, since we are always dealing with more or less flexible molecules and not with rigid building blocks. This will be illustrated by two examples.

Table 1. Dimerisation of tetraureas **1a**–**d**, bearing urea groups of different sizes with tetraloop tetraureas with different loop sizes **20a**–**c**.

Compound	**1a**	**1b**	**1c**	**1d**
20a ($n = 10$)	+	−	−	−
20b ($n = 14$)	+	+	−	−
20c ($n = 20$)	+	+	+	−

A monoloop derivative with two bulky residues should not form homodimers. Definitely, this is true for compound **15** with the smallest loop ($n = 10$) in combination with the largest residue. However, for the monoloop derivative **14** ($n = 10$, R = 3,5-di-*t*-butylphenyl), the originally broad and unresolved ^{1}H NMR spectrum is developed into a sharp, well-resolved spectrum (Figure 12) characteristic of the homodimer **14·14** after several days. This means that the homodimerisation is kinetically slow but not entirely impossible for this combination of loop size and bulky residue.

The tetraloop compound **20a** does not form heterodimers with **1b** and the same should be true for the bisloop compound **17** if the residues of **1b** really could not pass

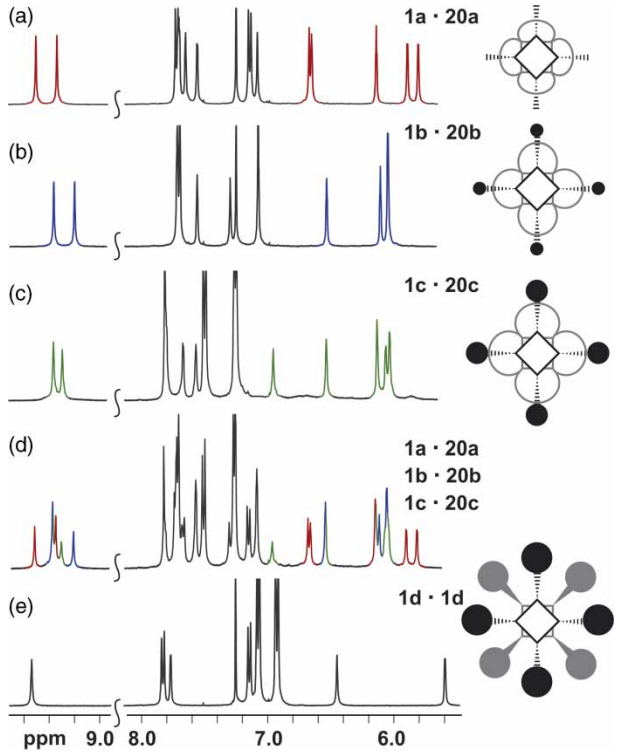

Figure 11. Sections of the ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25°C) of (a) heterodimer **1a·20a**, (b) heterodimer **1b·20b**, (c) heterodimer **1c·20c**, (d) mixture of the three heterodimers **1a·20a**, **1b·20b** and **1c·20c** and (e) homodimer **1d·1d**.

loops of this size. However, after several weeks, the homodimer **1b·1b** is completely replaced by the heterodimer **1b·17** in a mixture of **1b** and **17**. The fact that the urea residues of **1b** can penetrate the two loops of **17** but not the four loops of **20a** may be due to the higher flexibility of the bisloop compound in comparison to the tetraloop compound, and by a 'pinched' cone conformation (*33*) of **1b** which allows its combination with the bisloop, but not with the tetraloop compound.

Conclusions/outlook

The covalent connection of adjacent urea functions of tetraurea calix[4]arenes by aliphatic loops leads to restrictions and additional selectivities for their dimerisation. Up to now, there is no example known for the formation of dimers with overlapping loops, although this might not be entirely impossible, e.g. by using even longer and entirely aliphatic chains to connect adjacent urea groups. Restrictions are observed, however, for the size of residues in relation to the loop size for tetraphenyl ureas connected by aliphatic (ether) chains. These selectivities could be adjusted/fine-tuned for four residues of different sizes in combination with three loops with different lengths. The possibilities of obtaining larger structures via self-assembly are drastically increased in this way.

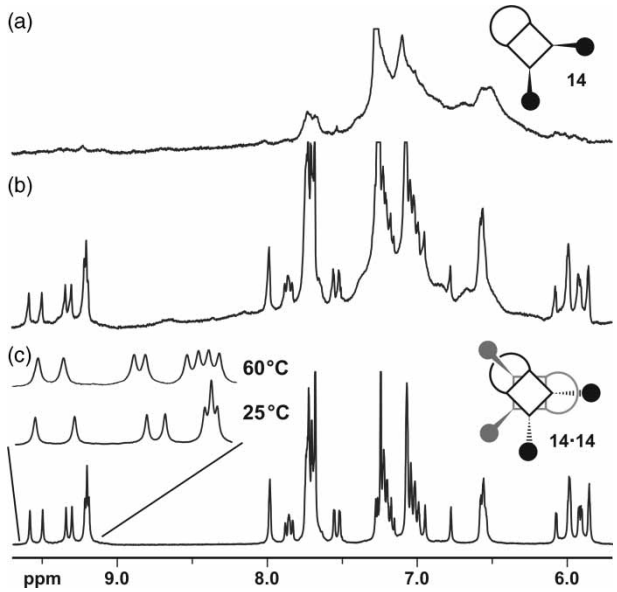

Figure 12. Sections of the ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25°C) of **14** (a) immediately after mixing, (b) after one day and (c) after three days.

Acknowledgement

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Notes

1. Their peak area does not correspond to their quantity. The advantage of ESI-MS in comparison to ^{1}H NMR is that several (charged!) species can be detected simultaneously, although their response is not proportional to their concentration. Disadvantages are the slow formation of complexes with tetraethylammonium (in principle, a good guest) and a low 'working concentration' at the limits of 'quantitative' formation of dimers.
2. The sorting scheme was realised with the following residues: 'bulky' = 3,5-di-(4-*tert*-butylphenyl)-4-propoxyphenyl; 'small' = *p*-tolyl. For the loops, adjacent phenylurea residues were connected by —O—$(CH_2)_{10}$—O— chains between their *m*-positions.

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