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Sarit Slovak[a]; Yoram Cohen[a]
[a] The Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Tel Aviv, Israel

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In–out interactions of different guests with the hexameric capsule of resorcin[4]arene

Sarit Slovak and Yoram Cohen*

The Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Tel Aviv, Israel

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Hydrogen-bond molecular capsules of resorcin[4]arenes (**1**) and pyrogallol[4]arenes (**2**) attracted much interest in the last decade. It was found, for example, that resorcin[4]arenes form hexameric capsules in non-polar organic solvents that can accommodate both trialkylamines and tetraalkylammonium salts. In search for the bulkiest guest that can be accommodated in the cavity of such capsules we found, with the aid of diffusion NMR, that such guests can interact also with the external surface of the hexameric capsules. Interestingly, monitoring the effect of CD_3OD titration on the diffusion coefficients of the different components in such host–guest systems indicates that the interaction of such guests with the external surface of the hexameric capsule is significant and can be found also in case where guest's encapsulation occurs as in the case of trioctylamine (**3**) and tetraoctylammonium bromide (**6**). These CD_3OD titrations showed also that these interactions are disrupted before the hexamer is disrupted and that before observing the free guests one can observe apparently the formation of a 1:1 complex between **1** and the guests.

Keywords: supramolecular chemistry; resorcinarenes; capsules; NMR; diffusion NMR

Introduction

Molecular containers and capsules are an intriguing class of molecular species (*1*). Covalent molecular containers were first reported by Collet (*1a*) and Cram (*1b*) and have been subsequently used mostly as nanoreactors for stabilising reactive intermediates (*1c–e*). In addition, different kinds of molecular capsules have been developed on the basis of non-covalent interactions (*2*). These capsules were used, inter alia, for accelerating reactions (*3a*, *b*), for affecting product distributions (*3c*, *d*), for catalysis and as drug delivery systems (*3e*, *f*). Among the non-covalent interactions, hydrogen bonds have played a pivotal role in preparing molecular capsules, and they were studied both in the solid state (*4*) and in the solution (*5*, *6*), and recently also in the gas phase (*7*).

The rapid development in the field of supramolecular chemistry in general and molecular capsules in particular has underlined the need for additional analytical methods for characterising complex supramolecular systems in solution. Diffusion NMR has been found to be a useful tool for studying such systems in solution (*8*). Diffusion NMR studies revealed that resorcin[4]arenes **1** (*9*) and pyrogallol[4]arenes **2** (*10*) self-assemble spontaneously into hexameric capsules in organic solvents without the aid of any guest by encapsulating solvent molecules (*9a*, *10a*). For **1**, eight water molecules are needed for the construction of the hexameric capsule, but for **2**, no water molecules are required. It was also found that the solvent molecules within the capsules can be replaced by different guests (*9c*, *d*, *11*, *12*).

Results and discussion

In the quest for the bulkiest guest for these hexameric capsules, we suspected that some of these guests interact with the external faces of the hexameric capsule. Therefore, we decided to study the interactions between the hexameric capsules of resorcin[4]arene **1** and various guests without neglecting species that do not undergo encapsulation.

Figure 1 shows the ^{1}H NMR spectra of **1** in the presence of different long-chain trialkylamine guests such as trioctylamine (**3**), tridodecylamine (**4**) and trioctadecylamine (**5**) (Scheme 1). Addition of **3** to the 10 mM $CDCl_3$ solution of **1** afforded the ^{1}H NMR spectrum shown in Figure 1(a). In this ^{1}H NMR spectrum, new peaks of **3** in the high-field region are observed. These peaks were attributed to molecules of **3** encapsulated in the hexameric capsule of **1**. The spectrum was recorded about 15 min after the addition of guest **3** to the solution of **1**. The diffusion coefficient extracted for these high-field peaks was $0.26 \pm 0.01 \times 10^{-5}\,cm^2\,s^{-1}$ which was similar to that found for the hexameric capsule of **1** in the same solution. These results indicate that **3** is indeed encapsulated in the hexameric capsule of **1**. The next step was to add longer alkylamine guest such as **4** to the solution of **1**. Figure 1(b) and (c) shows the ^{1}H NMR spectra of 10 mM $CDCl_3$

*Corresponding author. Email: ycohen@post.tau.ac.il

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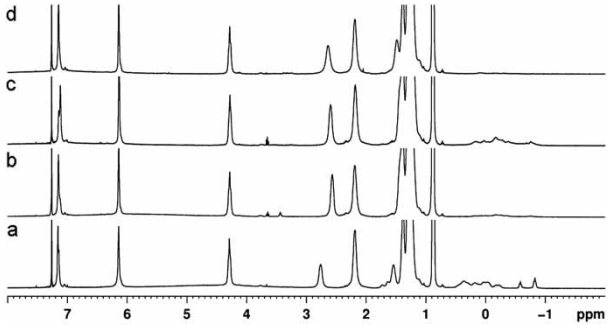


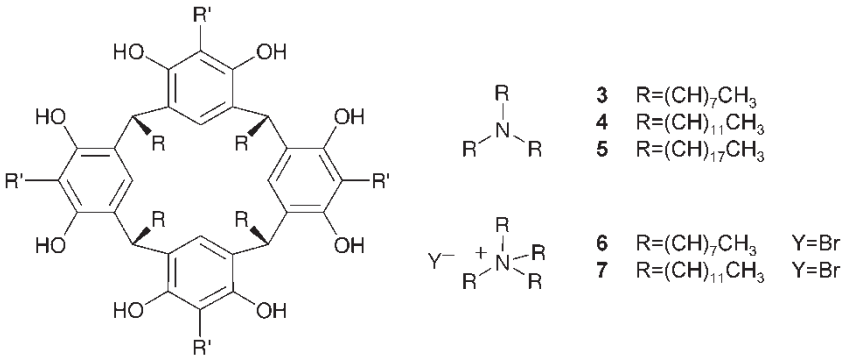
Figure 1. ^{1}H NMR spectra (400 MHz, 298 K) of 10 mM $CDCl_3$ solution of **1** in the presence of (a) **3** (8 mM), (b) **4** (8 mM) (1 h after the preparation), (c) **4** (8 mM) (1 month after the preparation) and (d) **5** (8 mM) (1 month after the preparation).

solution of **1** in the presence of **4**, 1 h and 1 month after the preparation of the solution, respectively. Figure 1(b) clearly shows that, 1 h after the preparation, no high-field peaks are observed in the ^{1}H NMR spectrum. After 1 month, high-field peaks are observed in the ^{1}H NMR spectrum (Figure 1(c)). A similar experiment was also carried out in $CHCl_3$ instead of $CDCl_3$. The ^{1}H NMR spectra of this sample performed immediately and 1 week after the preparation of the sample are shown in Figure S1(a) and (b), respectively (available online). At first, no high-field peaks of encapsulated **4** were observed and additional signals at 4.9–5.2 ppm, which are attributed to the encapsulated chloroform molecules, were observed. After 1 week, the peaks of the encapsulated chloroform molecules decrease and high-field peaks of encapsulated **4** appeared. These results show that the hexameric capsule **1** is capable of encapsulating long trialkylamine such as **4** but here the encapsulation process is time dependent. With time encapsulation of **4** occurs, concomitantly with expulsion of solvent molecules from the hexameric cavity of **1**. The ^{1}H NMR spectrum of the even larger guest **5**, 1 month after the preparation, showed no high-field peaks (Figure 1(d)). This result indicates that compound **5** is too large to be accommodated in the cavity of the hexameric capsule of **1**.

Although no guest encapsulation was observed for the solution of **1** in the presence of **5**, an external interaction between compound **5** and **1** was observed. Indeed, when we titrated the 10 mM solution of **1** in $CDCl_3$ with **5**, a small low-field shift was observed in the ^{1}H NMR spectrum for the peaks of compound **5** compared to the $CDCl_3$ solution of free **5** (Figure S2, available online). The diffusion coefficients of **1** and **5** for the 6:1 solution were $0.25 \pm 0.01 \times 10^{-5}$ and $0.36 \pm 0.01 \times 10^{-5}\,cm^2\,s^{-1}$, respectively. Interestingly, the diffusion coefficient of **5** was much lower than that found for free **5** in the same $CDCl_3$ solution ($0.55 \pm 0.01 \times 10^{-5}\,cm^2\,s^{-1}$) indicating that a certain population of **5** does interact with the external faces of **1**. Further addition of **5** to the same solution resulted in an increase in the diffusion coefficient of **5**, which means that the externally bound **5** and free **5** are in fast exchange on the NMR timescale (Figure 2).

To corroborate our findings, we performed a NOESY experiment on the $CDCl_3$ solution of **1** in the presence of **5** (Figure 3). The experiment clearly shows correlation peaks between the signals of **1** and the signals of **5**. These results indicate that **5** indeed interacts with the external surface of the hexamer of **1**.

To verify whether such interaction exists also in the case where the guest is encapsulated within the hexameric capsule of **1**, we repeated the titration of the solution of **1** with compound **3** (Figure S3, available online) and monitored the diffusion coefficients of all the components in the solution. We found that while the diffusion coefficient of the high-field peaks representing encapsulated molecules of **3** remained identical to the diffusion coefficient of the hexameric capsule of **1**, i.e. $0.25 \pm 0.01 \times 10^{-5}\,cm^2\,s^{-1}$, the diffusion coefficient of



Scheme 1. The structures of resorcin[4]arene **1**, pyrogallol[4]arene **2**, trioctylamine (**3**), tridodecylamine (**4**), trioctadecylamine (**5**), tetraoctylammonium bromide (**6**) and tetradodecylammonium bromide (**7**).

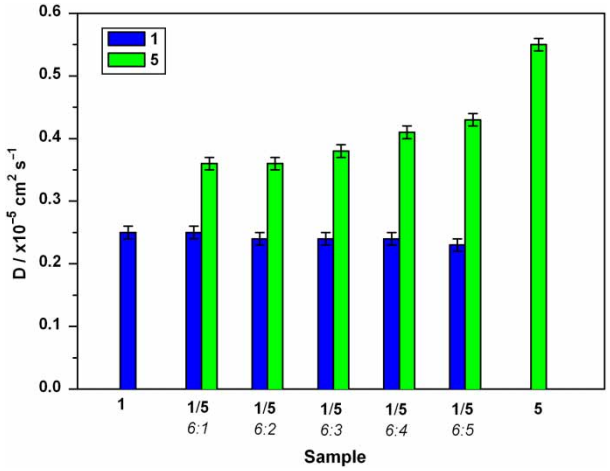


Figure 2. Diffusion coefficients (D) (298 K, $CDCl_3$) of **1**, **5** and of mixtures of **1** and **5** at the indicated ratios. The concentration of **1** was 10 mM in all samples.

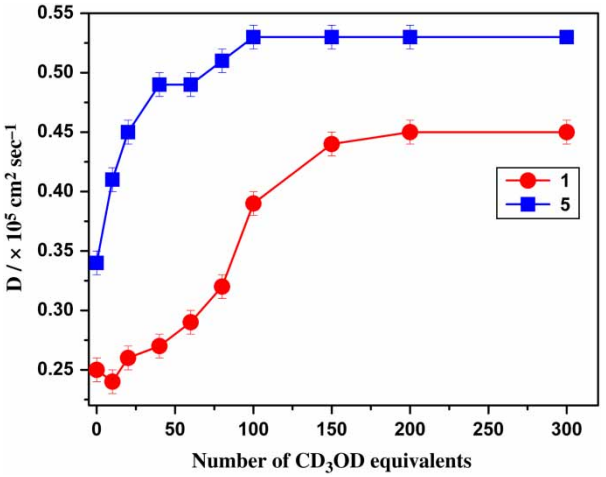


Figure 4. The effect of CD_3OD titration on the diffusion coefficient (D) of **1** and of **5** in the 6:2 $CDCl_3$ solution of **1** (10 mM) and **5** at 298 K.

the 'free' **3**, which in fact represents externally bound **3** molecules which are in fast exchange with free **3**, increased with the addition of **3** until it almost reached the diffusion coefficient of free **3** in $CDCl_3$ solution ($0.91 \pm 0.01 \times 10^{-5}\,cm^2\,s^{-1}$). This result shows that the interaction between **3** and the external faces of the hexamer of **1** prevails in the presence of encapsulated guest.

The next step was to determine if this interaction prevails when the hexamer is disrupted. For this purpose, we titrated the 6:2 solution of **1/5** with CD_3OD, a solvent which disrupts hydrogen bond. The graph showing the changes in the diffusion coefficients of **1** and of **5** upon the addition of CD_3OD is shown in Figure 4.

We found that the addition of the first 10 equivalents of CD_3OD resulted in an increase in the diffusion coefficient of **5** with no change in the diffusion coefficient of **1**. Addition of 40 equivalents of CD_3OD resulted in a sharp increase in the diffusion coefficient of **5** followed by less pronounced increase in the range of 40–100 equivalents until a plateau is reached when 100–150 equivalents of CD_3OD were added. For **1**, the diffusion coefficient, however, remained approximately constant upon the addition of 40 equivalents of CD_3OD and reached the plateau after the addition of 150–200 equivalents of CD_3OD. These results show that the interaction between **5** and **1** is easily disrupted even when a small amount of CD_3OD, which is not enough for the disruption of the hexameric capsule of **1**, is added. When the same titration was performed on the 6:2 $CDCl_3$ solution of **1/3** similar results were found (Figure S4, available online). Here again, we found that the first 10 equivalents of CD_3OD resulted in an increase in the diffusion coefficient of **3**. This sharp increase in the diffusion coefficient of **3** continued up to the addition of 40 equivalents of CD_3OD. Interestingly, the diffusion coefficient of the hexamer of **1** remained constant upon the addition of 40 equivalents of CD_3OD, while the diffusion coefficient of encapsulated **3** remained constant only when 20 equivalents of CD_3OD were added. After the addition of 40 equivalents of CD_3OD, a small increase in the diffusion coefficient of encapsulated **3** molecules was observed. Further CD_3OD addition to 80 equivalents resulted in a further small increase in the diffusion coefficient of the hexamer of **1** with nearly no effect on the diffusion coefficient of the non-encapsulated molecules of **3**. Only further increase in CD_3OD resulted in an increase in the diffusion coefficient

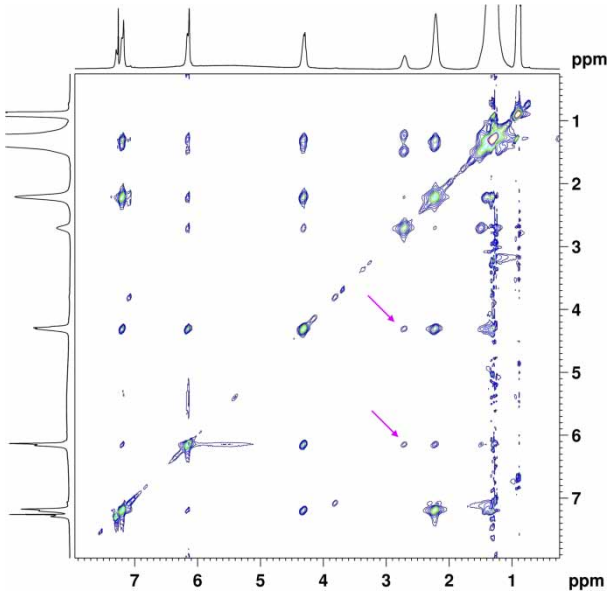
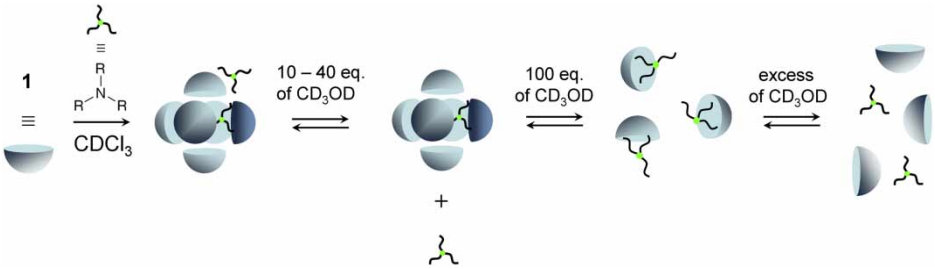


Figure 3. Sections of ^{1}H NMR 2D NOESY spectrum of **1** (10 mM, 298 K, $CDCl_3$) in the presence of **5** for the 6:2 mixture collected with a mixing time of 400 ms.



Scheme 2. The different interactions identified by monitoring the effect of CD_3OD titration on the diffusion coefficients of all the molecular species in the solution.

of **1** and **3** until plateaus are reached when 100–150 equivalents of CD_3OD are added to the solution. These results show that there is an interaction between the trialkylamine guests and the external faces of the hexamer of **1**. The interaction is not very strong and may be easily disrupted. Figures 4 and S4 show that first 40 equivalents of CD_3OD disrupts the interaction of the guests and the external surfaces of the hexamer of **1**, then there is a disaggregation of the hexamer concomitantly with the gradual formation of 1:1 complex between the monomer of **1** and the guest and finally free guests and monomeric host are obtained when about 150 equivalents of CD_3OD are added (Scheme 2).

Next, we examined the interaction of the hexamer of **1** with tetraalkylammonium salts such as tetraoctylammonium bromide (**6**) and tetradodecylammonium bromide (**7**). The ^{1}H NMR spectra of **1** in the presence of **6** or the presence of **7** are shown in Figure 5(a) and (b), respectively. For **6**, high-field peaks are observed in the ^{1}H NMR spectrum indicating the encapsulation of **6** within the hexameric capsule of **1**. Interestingly, for **7** no high-field peaks were observed even 1 month after the preparation, which means that **7** is too large to be accommodated in the hexameric capsule of **1**.

These results are to be expected since compound **7** is more bulky than **6** and thus cannot be accommodated in the cavity of **1**. The diffusion coefficients of **1** and **6** for the 6:1 solution of **1/6** were $0.26 \pm 0.01 \times 10^{-5}$ and $0.31 \pm 0.01 \times 10^{-5}\,cm^2\,s^{-1}$, respectively (Figure S5, available online). Further addition of **6** to the same solution resulted in an increase in the diffusion coefficient of **6**. The same trend was obtained for the solution of **1** in the presence of **7** (Figure S6, available online).

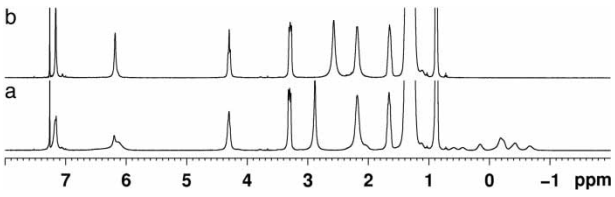


Figure 5. ^{1}H NMR spectra (400 MHz, 298 K) of 10 mM **1** in the presence of (a) **6** (8 mM) and (b) **7** (8 mM) in $CDCl_3$.

Conclusions

In conclusion, we have shown that trialkylamines and tetraalkylammonium salts, some of which can be encapsulated in the hexamer of **1**, interact with the external surface of the hexameric capsules of **1**. We found that the encapsulation of **4** within the hexameric capsule of **1** takes time, while no encapsulation occurs for too large guests such as **5** and **7**. Indeed, in addition to guest encapsulation, additional interaction was observed between the guests and the external surfaces of the hexameric capsule of **1**. The guest bound to the surface of the hexameric capsule is in the fast exchange with the free guest in the bulk. This interaction is easily disrupted by the addition of CD_3OD long before the hexamer is disrupted. We could also show that before obtaining 'free' guests and host one can apparently find indications for the formation of 1:1 complexes of **1** and the guests.

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Supporting Information

Experimental section and Figure S1 and S2 showing the ^{1}H NMR spectra of **1** in the presence of **4** and **5** and mixtures of **1/5** at different ratios; Figure S3 showing the diffusion coefficients of **1**, **3** and of mixtures of **1** and **3** and Figure S4 showing the effect of CD_3OD titration on the diffusion coefficient of **1** and **3**; Figure S5 and S6 showing the diffusion coefficients of **1**, **6**, **7** and of mixtures of **1** and **6** and of **1** and **7**, are all available to view online.

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