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Phototransformation of Stilbene in van der Waals Nanocapsules

Gennady S. Ananchenko,*[a] Konstantin A. Udachin,[a] John A. Ripmeester,[a] Thomas Perrier,[b] and Anthony W. Coleman[b]

Abstract: We have utilized *para*-hexanoylcalix[4]arene nanocapsules as hosts to carry out phototransformations of *cis*- and *trans*-stilbene. Single-crystal X-ray diffraction studies were performed to define precisely the location of encapsulated stilbenes inside the capsule and to analyze possible pathways of phototransformation. *cis*-Stilbene stacks as a π–π dimer located at the center of the capsule, whereas *trans*-stilbene does not form such a dimer. Irradiation of the crystalline inclusion complexes of each isomer of stilbene in the solid state leads to the appearance of the second isomer, and after prolonged photolysis, photodimerization also occurs. *syn*-Tetraphenylcyclobutane is formed as the major product of dimerization and its yield depends on the time and intensity of irradiation. In most cases, the single crystals of the complexes remain intact during irradiation; hence, the nanocapsules have the potential to serve as robust nanoreactors in the solid state. The confinement in the nanocapsules is sufficient to keep the reacting molecules together, although this is less restrictive than for *trans*-stilbene crystals, in which the molecules cannot achieve a favorable orientation for dimerization.

Keywords: calixarenes · isomerization · nanocapsules · photochemistry · supramolecular chemistry

Introduction

The rational design of host–guest structures, with particular attention given to the robustness of the materials, enables one, in principle, to achieve not only unique physical properties, such as controlled capture and release of guest materials, but also the controlled chemical transformations of captured guest molecules within the host.[1–5] To carry out chemical reactions in such environments, the construction of large capsules that can accommodate two or more substrates in the cavity is particularly important. The frameworks can be constructed by using covalent or metal–ligand bonds,[2–9] hydrogen bonds,[9–13] or even van der Waals interactions.[14–16] The last case is particularly interesting, as even these weak interactions collectively can potentially create relatively stable structures that also display considerable flexibility. We have shown recently that amphiphilic *para*-hexanoylcalix[4]arene (Figure 1) forms container-type[17] or capsule-type[16] inclusion complexes, depending on whether they crystallize from highly or weakly polar solvents in the presence of an excess of guest material. The essential feature of such nanocapsules is a hydrophobic nanoenvironment constructed from only weak van der Waals interactions. As a result, the calixarene crystal structures exhibit well-defined cavities of near-constant size and shape that can be occupied by a variety of organic guest molecules, and are, thus, utilizable as robust hydrophobic microvessels for thermal as well as photochemical reactions.

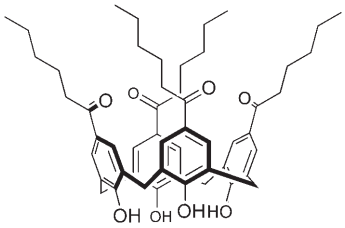

Figure 1. *para*-Hexanoylcalix[4]arene C6OH.

In this context, we have examined the influence of hydrophobic nanocapsules based on amphiphilic *para*-hexanoylca-

[a] Dr. G. S. Ananchenko, Dr. K. A. Udachin, Dr. J. A. Ripmeester
Steacie Institute for Molecular Sciences
National Research Council Canada
100 Sussex Drive, Ottawa, Ontario, K1A 0R6 (Canada)
Fax: (+1) 613-998-7833
E-mail: Gennady.Ananchenko@nrc-crnc.gc.ca

[b] T. Perrier, Dr. A. W. Coleman
Institut de Chimie et Biologie des Proteins
7 Passage du Vercors, 69367 Lyon Cedex 07 (France)

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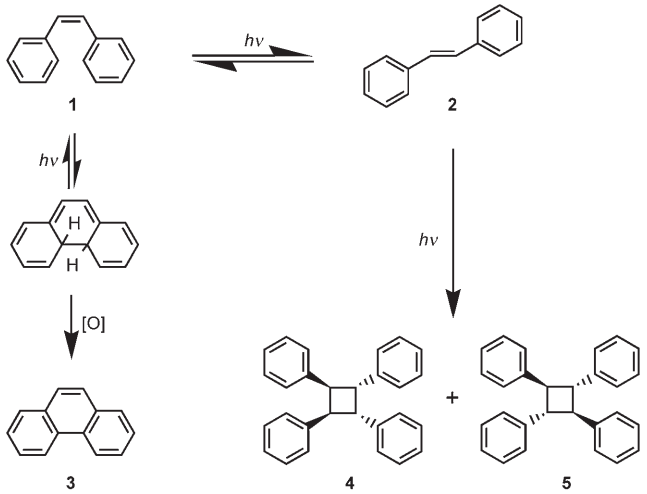
lix[4]arene (Figure 1) on the photoreactions of stilbenes. Stilbenes exhibit diverse photochemical behavior in solution,[18] for example, reversible *cis*/*trans* isomerization,[19] cyclization of *cis*-stilbene[20] **1** to dihydrophenanthrene and further oxidation to phenanthrene **3**, and dimerization[21,22] of *trans*-stilbene to yield tetraphenylcyclobutane products **4** and **5** (Scheme 1). Hence, they are good candidates for demonstrating the modulation of photochemical reactivity by solid-state host–guest interactions. So far, stilbenes have been utilized to study their phototransformation on flat surfaces,[23a] in zeolites,[23b] cyclodextrins[24–27] in solution and in the solid state, as well as in micelles in aqueous solutions.[25] The essential feature of unsubstituted stilbenes is that neither liquid *cis*- nor crystalline *trans*-isomers undergo photodimerization.[18] Here, inclusion complexes of *cis*- and *trans*-stilbene with *para*-hexanoylcalix[4]arene were prepared and characterized by single-crystal X-ray diffraction, and these were irradiated by using steady-state techniques to explore their phototransformation pathways.



Scheme 1.

Results and Discussion

***cis*-Stilbene/*para*-hexanoylcalix[4]arene inclusion complexes**: Slow evaporation of chloroform from a solution of the calixarene in chloroform/*cis*-stilbene at 80 °C results in the crystallization of *para*-hexanoylcalix[4]arene (C6OH) (Figure 1) in large, square, colorless crystals of up to 3 × 3 mm in size. NMR analysis of the solution of the complex in $CDCl_3$ shows host/guest ratios from 2/1.6 to 2/1.9 for different batches. Single-crystal X-ray diffraction reveals that the calixarene molecules are arranged in tail-to-tail pairs to form a hydrophobic capsular complex with a cavity approximately 8 Å wide and 16 Å long, and with two molecules of *cis*-stilbene within the capsule (Figure 2). The inclusion complex (complex **A**) has tetragonal *P*4/*nnc* symmetry with unit-cell parameters 15.52; 15.52; 22.71 Å and is quite similar to the structure of the complex of C6OH with chloroform.[16] Two molecules of *cis*-stilbene are located in the center of the capsule, and these are intermeshed in an attempt to achieve π–π interactions of the benzene rings. The shortest distance between benzene-ring planes is around 3.3 Å, which is somewhat less than the sum of the van der Waals radii of carbon atoms (ca. 3.4 Å), and also less than the typical distance of benzene rings that interact through π–π stacking (3.5–4.2 Å).[28–30] As a result, the repulsion between rings may well exceed possible stabilizing interactions.[28–30] The torsion angle along the ethylenic double bond is 20.9°, which is larger than the optimum for *cis*-stilbene obtained from ab initio calculations[31] or gas-phase electron diffraction experiments[32] (6 and 5°, respectively). On the other hand, the average phenyl rotation angle of approximately 29° out-of-plane is smaller than those given in the literature (40 and 43°, respectively),[31,32] and this is probably due to the molecule's attempt to achieve a more planar conformation for π–π stacking with a neighbor. The entire "dimer" appears to be a compromise between π-electron stabilization of a single *cis*-stilbene molecule and π–π interaction of the two molecules. Notably, our attempts to fix the aforementioned angles according to literature values[31,32] did not improve the quality of refinement of the structure.

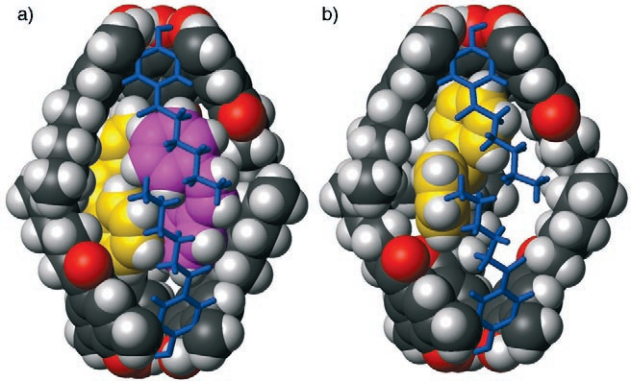


Figure 2. Cut-away view of C6OH capsules entrapping a) two molecules of **1** (complex **A**); b) one molecule of **1** (complex **B**). The two molecules of *cis*-stilbene in complex **A** are marked in different colors. For simplicity, only one of several disordered positions of each alkyl arm of the calixarene is shown.

The inclusion complex **A** is not expected to be stable at elevated temperatures and it would probably prefer to eject a molecule of *cis*-stilbene. Indeed, the thermogravimetric analysis (TGA) trace (Figure 3) clearly shows that one *cis*-stilbene molecule leaves the capsule within the temperature interval 60–120 °C. We monitored the release of **1** within the range 25–100 °C by hyperpolarized (HP)-^{129}Xe NMR spectroscopy, which provides an in situ probe of the temperature-dependent access to the guest sites in the complex.[33,34] Figure 4 shows a set of ^{129}Xe NMR spectra for complex **A** in

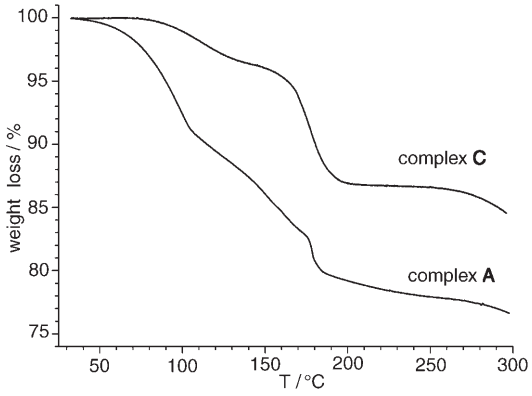


Figure 3. TGA traces of complexes **A** and **C**.

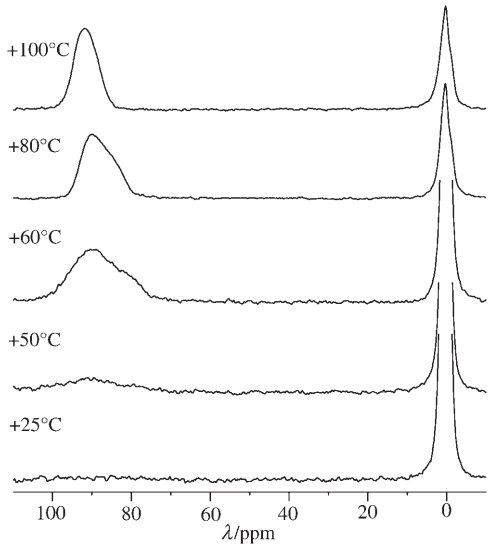


Figure 4. In situ study of the transformation (from bottom to top) of complex **A** to complex **B** by exposing it to a Xe/He/N_2 gas mixture at elevated temperatures, as monitored by continuous-flow HP-^{129}Xe NMR spectroscopy.

contact with a flowing gas mixture (98% He, 1% N_2, 1% Xe) containing HP Xe (partial pressure of 7 Torr) as a function of temperature under static conditions. The room-temperature spectrum shows a resonance at 0 ppm only, which can be assigned to free xenon gas. In the spectrum recorded at 50°C, another line appears as a very broad signal at around 90 ppm and this can be attributed to xenon interacting with host cavities.[15,35] The relatively high chemical shift reflects only the start of the interaction with the solid before Xe actually enters the deep cavity. As the temperature increases, the line becomes sharper and a small signal (seen as a right shoulder) appears, indicating that Xe starts to displace stilbene in the capsule, and, hence, more space for the gas becomes available in the cavity. At around 100°C, Xe finally occupies a position deep within the capsule, and a relatively sharp line at 92 ppm indicates fast exchange between the gas interacting with the outside surface, and that interacting with the host cavities.

After the complex has been purged by Xe at 100°C, it contains just a single molecule of *cis*-stilbene per capsule (complex **B**), as confirmed by results of solution NMR studies and TGA. The single crystal of complex **A** survives the thermal treatment of three hours at 120°C, therefore, XRD analysis of the resulting complex **B** was performed. The unit-cell parameters obtained are almost the same as those of complex **A**, that is, tetragonal *P*4/*nnc* symmetry with 15.52; 15.52; 22.32 Å. Figure 2b shows the structure of complex **B**. One can see that *cis*-stilbene has moved deeper into the cavity. The electron-density map in XRD data for encapsulated guests was very complicated because it contained residual densities from π–π-stacked *cis*-stilbene molecules from the original complex, as well as those from *cis*-stilbene in complex **B**. Hence, we were unable to obtain precise data for bond lengths and angles in the stilbene molecule. However, it is clear that, because π–π stacking with the partner stilbene is not possible, the remaining guest now can interact through π–π interactions with the benzene rings of the calixarene rim, analogous with other calixarene-based systems.[14–16] The approximate distances between host and guest aromatic carbon atoms are approximately 3.7–4.0 Å.

Comparison of the ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR spectrum of complex **A** with the spectrum of liquid *cis*-stilbene recorded in the CP-MAS probe without spinning reveals an upfield shift of approximately 1 ppm of all signals of the encapsulated stilbene (Figure 5). It has been reported[16] that the extra shielding of

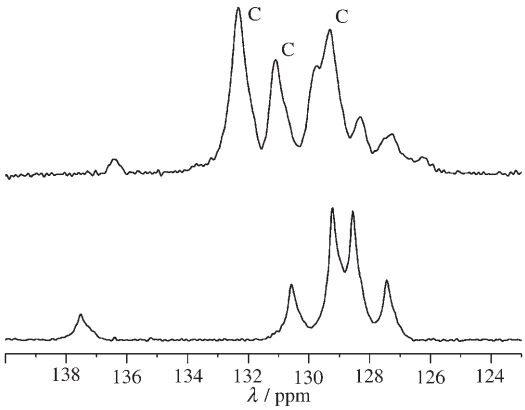


Figure 5. Comparison of the ^{13}C CP-MAS NMR spectra of complex **A** (top) and pure *cis*-stilbene (bottom). Signals of calixarene are marked by "c".

guests in *para*-hexanoylcalixarene nanocapsules is not very high and that 1 ppm represents a typical difference between the carbon chemical shifts of free and encapsulated guests. This is contrary to other inclusion complexes within capsules formed by covalent or hydrogen bonds,[11,36–38] but is characteristic of dynamic systems, as moieties that are fixed deep inside the cavity can experience shifts as large as 5–6 ppm. The C6OH-capsule provides sufficient freedom for the guest

within it to move and, therefore, for the large deshielding to be modified by chemical-shift averaging.

***trans*-Stilbene/*para*-hexanoylcalix[4]arene inclusion complex**: The inclusion complex of the calixarene with *trans*-stilbene (complex **C**) was prepared by recrystallization from an ethanol solution containing the components in an approximately 1/5 ratio of calixarene/stilbene, upon very slow cooling (ca. 5 °C per day). Although the material was of excellent quality for XRD, we were unable to collect larger amounts of the pure complex for HP-^{129}Xe or for solid-state NMR experiments. ^{1}H NMR analysis of the solution of the crystals in acetone revealed the ratio of components to be 2-(C6OH)/0.65(EtOH)/1.3(**2**). The crystals appeared under the microscope to be uniform, so one can conclude that two types of complex are present: in the first, the capsule contains one molecule of **2** and one molecule of ethanol; in the second, the capsule captured two molecules of **2** with probably a small amount of ethanol. This generally agrees with TGA traces obtained for this complex (Figure 3), in which the first weight loss of around 4 % at 70–130 °C corresponds to the release of ethanol and *trans*-stilbene to form a complex with only one molecule of **2** per capsule, and the second loss reflects ejection of the remaining guest. Attempts to isolate the pure complex with two molecules of **2** per capsule by increasing the concentration of **2** in the solution yielded the simultaneous precipitation of complex **C** and pure *trans*-stilbene. Therefore, the precise control of the composition of complex **C** was not possible.

The unit-cell parameters of complex **C** derived from single-crystal X-ray diffraction experiments proved to be different from those for complexes **A** and **B**: monoclinic $P2_1/n$ symmetry with unit-cell parameters 15.58; 22.14; 15.96 Å; and angles 90.0; 91.0; 90.0°. The two cups of the calixarene (Figure 6) in the capsule are almost aligned, but are not twisted, as for the tetragonal *P*4/*nnc* complexes **A** and **B**, that is, the benzene rings of the lower cup lie almost exactly below those of the upper cup. The entire capsule appears to be more open to the environment and the cups are slightly shifted along the equatorial plane. Considering that this complex was obtained from ethanol, in which no capsules are formed in the absence of appropriate guests,[17] one can regard this structure as a transition from the capsule-type to an open-container[17] or self-inclusion complex.[17,39]

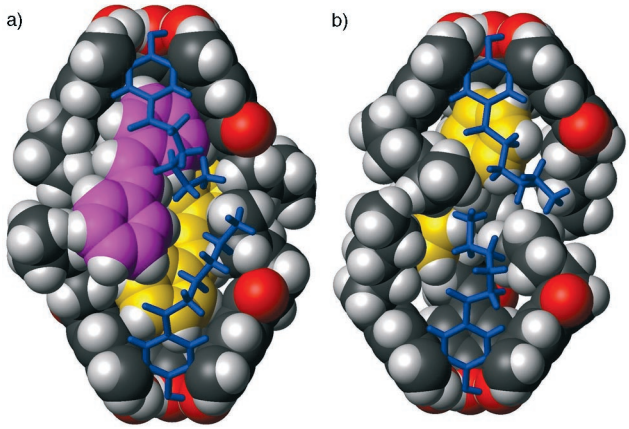


Figure 6. Cut-away view of complexes **C** with a) two molecules of *trans*-stilbene; b) one molecule of *trans*-stilbene. For simplicity, only one of several disordered positions of each alkyl arm of the calixarene is shown.

trans-Stilbene is disordered over six symmetry-independent positions in the unit cell. This probably reflects capsules containing one and two molecules of **2** each. Only three relative orientations of two *trans*-stilbene molecules are possible (Figure 7): edge-to-edge (ee), edge-to-plane (ep), and plane-to-plane (pp). By analogy with complexes **A** and **B**, and by minimizing the van der Waals repulsion between two guests, we can expect the structures of the capsules containing one and two molecules of **2**, shown in Figure 6 (for simplicity, ethanol was not taken into account). The position of *trans*-stilbene in the capsule with one molecule of **2** (Figure 6b) resembles that of **1** in complex **B**, that is, π–π interactions between guest and host benzene rings. In the capsule with two *trans*-stilbene molecules (Figure 6a), we expected π–π interactions between guests to be more preferable. The smallest distance between two molecules is approximately 3.7 Å between the benzene rings and approximately 4.4 Å between the olefinic carbons. Because the molecules are shifted with respect to each other, they cannot yield a good π–π stack, though local stabilization remains possible. Therefore, the entire structure is a compromise between π-electron interaction of a *trans*-stilbene molecule with the host and π–π interactions of the two *trans*-stilbene molecules. Notably, ep configuration of two stilbene molecules (Figure 7) in the capsule cannot be ruled out completely, due to the expected favorable edge-to-plane interaction of benzene rings.[40] However, such configuration seems to be less probable because of restricted space in the cavity.

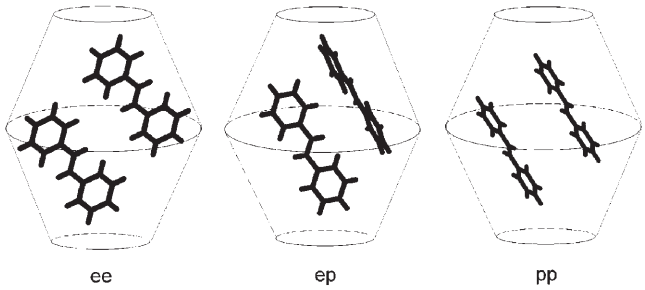


Figure 7. Possible orientations of two *trans*-stilbene molecules within the capsule.

Photolysis: The solid inclusion complexes of C6OH with *cis*-stilbene (complexes **A** and **B**) and *trans*-stilbene (complex **C**) were irradiated by UV light (320–390 nm, either 500 or 2500 mW cm^{-2}) at 0 °C. Single crystals or powders of the complexes were used. After a variable duration of photolysis, the samples were dissolved in deuterated acetone and analyzed by ^{1}H NMR spectroscopy. The results indicated the

presence of at least one of the following products (Scheme 1): *cis*-stilbene **1** (olefinic protons at 6.65 ppm), *trans*-stilbene **2** (*p*- and *m*-aromatic protons at 7.62 and 7.38 ppm, respectively), phenanthrene **3** (H-9,10 at 8.82 ppm), and the two photodimers of 1,2,3,4-tetraphenylcyclobutane, **4** and **5** (cyclobutane protons at 4.60 and 3.71 ppm,[27,41] respectively).

All three photochemical reactions depicted in Scheme 1 occurred upon irradiation of complex **A** (Figure 8). The *cis*/*trans* isomerization is the fastest process with the highest

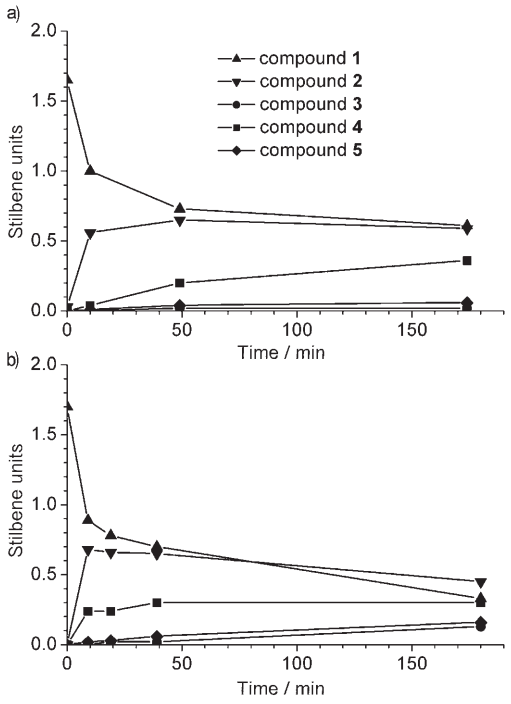


Figure 8. Kinetic traces of the photolysis of complex **A** at light intensities a) 500 mW cm^{-2} and b) 2500 mW cm^{-2}.

quantum yield,[18] and this agrees with literature data for the photolysis of stilbenes in solution[18–22] and in some organized media.[23–27] In addition, slow accumulation of the dimeric products is observed after longer periods of photolysis. An increase in light intensity (Figure 8b) increases dimer formation, although the quality of the material worsens and the solid turns brown. Because all reaction pathways originate from the excited-singlet state of stilbene as the common precursor,[18,42] the predominance of the photoisomerization[43] is due solely to its rapid rate relative to that of the diffusion-limited photodimerization. After fast equilibration, the concentration of **2** reaches its photostationary value, so the isomer ratio [**1**]/[**2**] at equilibrium can be estimated from Figure 8 to be almost 1/1. Because the *cis*/*trans* ratio upon equilibrium is very close to that published for sensitized photolysis of stilbenes in solution[44] in the presence of aromatic ketones and at about the same wavelength, one can conclude that the capsule, acylphenol, serves, at least partly, as a scavenger of the excited stilbene providing rapid sensitization and, therefore, isomerization.

At higher concentrations of *trans*-stilbene, at which two molecules of **2** are present in one capsule of the photolyzed complex **A**, photodimerization becomes possible. This removes **2** irreversibly from the mixture at this wavelength, however, the fast isomerization of **1** maintains the overall concentration of **2** as relatively constant. The stilbene photodimer, yield about 15% (Figure 8), was detected after 3 hr of photolysis, and significant *syn*-stereoselectivity (ca. 5/1) is achieved. An increase in light intensity affects the stereoselectivity, so that the ratio of the dimers becomes about 2/1 again in favor of the *syn*-dimer **4**. It is expected that in the photolyzed complex **A**, most of the *trans*-stilbene molecules are positioned in close proximity and in fixed orientations to each other and, thus, can readily dimerize upon photoexcitation. If the orientations of two molecules of **2** in the capsule after photolysis of complex **A** are about the same as those in complex **C**, that is, plane-to-plane (Figure 7), then the probability of dimerization should be sufficient, because the distance between olefinic double bonds is already close to the required 4.2 Å,[45] and only a small sliding of the molecules is needed to give overlapping orbitals. However, due to fast *cis*/*trans* isomerization, the probability that at a given moment two molecules of *trans*-stilbene are present in one capsule and are located at an appropriate distance is not so high. This can explain why the yield of tetraphenylcyclobutanes **4** and **5** is low even after a reasonable reaction time. We tried to check the positions of the products in the photolyzed complex **A** and to compare this with complex **C**. A single crystal of complex **A** remains intact following irradiation for 20 min (Figure 8). X-ray diffraction data were easily obtained after photolysis of the same crystal that was used for the structural study before irradiation. The quality of the crystal was satisfactory; however, because the material already contains capsules with both isomers of stilbene that are highly disordered, it was not possible to localize each compound precisely. Nevertheless, the unit-cell parameters proved to be accurate and equal to those obtained for the parent complex **A**, that is, tetragonal and not monoclinic.

The possibility of obtaining large encapsulated molecules, such as **4** and **5**, by the photolysis of stilbene is very interesting and promising. Our attempts to co-crystallize C6OH with the independently synthesized *syn*-dimer **4** failed, and both components precipitated separately from ethanol solution. Thus, the photolysis of encapsulated "building blocks" can be a potential source of larger encapsulated molecules.[38]

The photolysis of complex **B** (Figure 9a) leads to the accumulation of *trans*-stilbene and to slow cyclization of **1** to phenanthrene **3**. An increase in light intensity affects only the proportion of **3**, which doubles after the same duration of photolysis. The quantum yield of reversible formation of the intermediate dihydrophenanthrene (Scheme 1) is around 3.5-times smaller then that of isomerization (at 313 nm[18]), so the low yield of product **3** is not surprising. The absence of dimeric products **4** and **5** is confirmation that the capsule

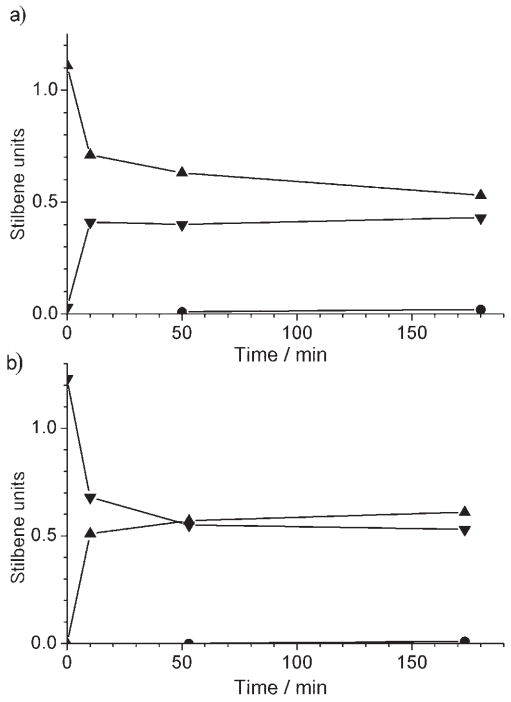


Figure 9. Kinetic traces of the photolysis of a) complex **B** and b) complex **C** at 500 mW cm^{-2}.

contains only one molecule of the guest. One can see from Figure 9a that the isomerization rate and the [**1**]/[**2**] ratio at the photostationary state are very similar to those during the photolysis of complex **A** and, hence, the position of the guest inside the capsule has no influence. Moreover, we can conclude that the possible self-quenching[44] of excited stilbene by neighboring ground-state stilbene in one capsule of complex **A** is insignificant.

The same products were detected following photolysis of complex **C** (Figure 9b). The ratio of stilbene isomers [**1**]/[**2**] reaches its photostationary value of around 55/45 after a similar period of photolysis, so there is no distinct dependence of product ratio on the structure of the complexes, that is, tetragonal vs monoclinic. Only traces of dimers **4** and **5** were detected, which unambiguously confirms that primarily one molecule of *trans*-stilbene occupies the capsule.

Conclusion

The photolysis of stilbenes encapsulated in van der Waals nanocapsules in the solid state enabled us to gain a deeper understanding of the features of host–guest interactions in hydrophobic nanocapsules. The nanocapsule constructed of amphiphilic calixarenes is sufficiently robust to keep reagents close to each other and to prevent the easy escape of the two components. It allows reagents to interact closely and to form some kind of sub-complexes, as in the example of two *cis*-stilbene molecules π–π stacked inside complex **A**. On the other hand, the capsule allows the reagents to reorient relatively freely within it. This gives these nanocapsules some advantages over micelles,[25] for which escaping guests must always be accounted for. The nanocapsule can be considered as a solvent cage isolated in the solid state. In almost all our experiments, single crystals of the complexes remained intact after irradiation and, hence, were suitable for single-crystal XRD. This unambiguously confirms the stability of this supramolecular structure during various chemical transformations. Notably, amphiphilic calixarenes can easily form solid lipid nanoparticles[35,46] that can serve as prospective carrier systems. The combination of controlled release of encapsulated guest with the possibility of phototransformations during transportation of biologically active guests provides the opportunity to fine tune the properties of encapsulated species according to biological targets.

Experimental Section

All chemicals were obtained from Aldrich and were used as received. *para*-Hexanoylcalix[4]arene was synthesized as described in ref. [47]. *cis,trans,cis*-1,2,3,4-Tetraphenylcyclobutane **4** was prepared by photolysis of *trans*-stilbene in benzene.[48] Thermogravimetric analysis was performed by using a TA Instruments device with a temperature ramp of 3 °C min^{-1}. Solid-state and HP-^{129}Xe NMR spectra were recorded by using Bruker AMX 300 and DSX 400 spectrometers, respectively. The experimental setup for obtaining HP Xe was described in ref. [33].

Photolysis was performed by using a Novacure 2100 spot curing system within a UV range of 320–390 nm. 10 mg of powders of complexes were distributed equally over an area of approximately 3 cm^2 in the bottom of a vial. The vial was placed in an ice/water mixture to avoid overheating of samples during UV irradiation. The distance between the edge of the light guide and the samples was 5 cm. Two light intensities, 500 and 2500 mW cm^{-2}, were applied.

Crystals of complex **A**: The calixarene (500 mg) was dissolved in chloroform (3 mL) and *cis*-stilbene (2 g) was added. The solution was placed in a furnace preheated to 80 °C. After 5 d, large (up to 5×5 mm), colorless, square crystals were isolated. Crystals of complex **B** were obtained from complex **A** by heating the latter in a furnace at 120 °C for 3 hr.

Complex **C**: *trans*-Stilbene (90 mg) was dissolved in ethanol (20 mL) with some heating. *para*-Hexanoylcalix[4]arene (100 mg) and ethanol (10 mL) were then added and the mixture was stirred under slow boiling until the calixarene had dissolved completely. The hot solution was placed in a furnace that was preheated to 80 °C and programmed to decrease in temperature by 5 °C every 12 hr. The solvent was allowed to evaporate slowly. After the volume of the solution had returned to its original 20 mL, the flask was closed tightly and cooling continued without evaporation until RT was reached. The crystals were isolated by filtration and rinsed with cold methanol.

The single-crystal structure studies of complexes **A**, **B**, and **C** were performed by using a Bruker SMART diffractometer with $Mo_{K\alpha}$ radiation, up to $2\theta = 56°$. The structures were solved by direct methods and refined by full-matrix least-squares analysis (SHELXL-97). All non-hydrogen atoms (except guest molecules in complex **C**) were refined anisotropically, whereas all hydrogen atoms were placed at their idealized positions. Benzene rings in guest molecules were set as planar and their bond lengths were fixed, so that only internal rotation around double and single bonds of the olefinic part of *cis*-stilbene was allowed during refinement.

The site occupancies were found to be 0.25(3) for guest in complex **A**, 0.050(5) and 0.10(1) for old and new positions of guests, respectively, in complex **B**, and 0.07(1), 0.12(1), 0.17(2), 0.21(2), 0.21(2), and 0.22(2) for six positions of *trans*-stilbene in complex **C**.

Errors were measured by variations in fixed isotropic thermal parameters from 0.1 to 0.5. Magnitudes of anisotropic thermal parameters (guest molecules) were varied up to the maximum of 0.5, which is acceptable for guest molecules in the cage.

Complex **A**: Data collected at 125 K up to $2\theta = 56.6°$. Plates $0.5 \times 0.5 \times 0.2$ mm crystallize in the tetragonal space group $P4/nnc$, with lattice dimensions of $a = 15.5151(12)$ $c = 22.708(4)$ Å, and unit-cell volume 5466.2(10) Å^3. Final residual factors are $R1 = 0.0998$, $wR2 = 0.2672$, GOF = 1.119 (56943 reflections measured, 3405 independent reflections, 2331 observed reflections $I > 2\sigma(I)$, 265 parameters).

Complex **B**: Data collected at 125 K up to $2\theta = 44.6°$. Plates $0.45 \times 0.4 \times 0.2$ mm crystallize in the tetragonal space group $P4/nnc$, with lattice dimensions of $a = 15.5167(16)$ $c = 22.315(5)$ Å, and unit-cell volume 5372.7(14) Å^3. Final residual factors are $R1 = 0.1247$, $wR2 = 0.3789$, GOF = 1.951 (31920 reflections measured, 1728 independent reflections, 1115 observed reflections $I > 2\sigma(I)$, 421 parameters).

Complex **C**: Data collected at 125 K up to $2\theta = 56.8°$. Plates $0.5 \times 0.35 \times 0.35$ mm crystallize in the monoclinic space group $P2_1/n$, with lattice dimensions of $a = 15.579(2)$ $b = 22.136(3)$ $c = 15.952(2)$ Å, $\beta = 90.965(2)°$, and unit-cell volume 5500.5(12) Å^3. Final residual factors are $R1 = 0.1047$, $wR2 = 0.3204$, GOF = 1.344 (61667 reflections measured, 13618 independent reflections, 7254 observed reflections $I > 2\sigma(I)$, 856 parameters).

Crystal data and structure refinement parameters are reported in the Supporting Information. CCDC-281734, -281735, and -281736 contain the supplementary crystallographic data for complexes **A**, **B**, and **C**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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