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Templating Photodimerization of *trans*-Cinnamic Acid Esters with a Water-Soluble Pd Nanocage

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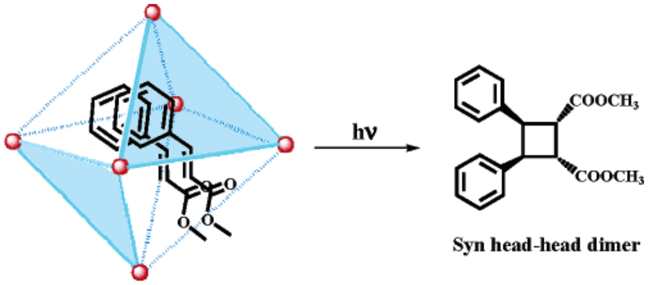

A water-soluble octahedral Pd nanocage acting as a reaction vessel templates the photodimerization of substituted *trans*-cinnamic acid methyl esters in water. Irradiation of the host−guest complexes of *trans*-cinnamic acid methyl esters with the Pd nanocage resulted in selective formation of a syn head−head dimer in addition to the corresponding cis isomer. These results suggest that the guest molecules are preoriented in a selective fashion with the hydrophilic ester group facing water and the hydrophobic aryl group tucked within the cavity of the host. Such an orientation occurs at the hydrophobic−hydrophilic interface between the nanocage exterior and interior. Weak intermolecular C−H−π and π−π interactions between the host and the guest(s) are likely to be responsible for the lack of mobility of the reactant olefins during their short excited-state lifetime.

Introduction

During the past two decades, there has been continued interest in controlling excited-state processes through the use of well-defined organized media. The media have included crystals, solid host−guest complexes, liquid crystals, polymers, micelles, zeolites, clays, and silica.[1] Quite recently, the impact of green chemistry has led chemists to explore water-soluble supramolecules based on hydrogen bonding, hydrophilic−hydrophobic interactions, and van der Waals forces as hosts to conduct chemical reactions.[2] Our group is currently investigating water-soluble hosts such as dendrimers, polymers, calixarenes, cucurbiturils, cavitands, and Pd-nanocage as media to conduct photochemical reactions.[3] In the present paper, we describe our attempts in controlling the stereochemistry of the cyclobutanes formed during the photodimerization of *trans*-cinnamic acid esters. These compounds belonging to a class of α,β-unsaturated carbonyl compounds when irradiated are known to undergo two types of reactions, namely, (a) geometric isomerization (unimolecular process) and (b) dimerization (bimolecular process). Geometric isomerization, however, is the main reaction in isotropic solutions. The photodimerization reactions involving C═C bonds could in principle give rise to more than 10 isomers; therefore, a strategy to favor dimerization and to obtain a single isomer in solution is highly desirable.[4] In this context, we first attempted to template the photodimerization of 3-methyl- and 4-methyl-*trans*-cinnamic acids through the use of a water-soluble octahedral Pd nanocage host. In spite of complexation of these two olefins with the host as evidenced by ^{1}H NMR data, none of these dimerized in aqueous solution (see Supporting Information). At this stage, we are not sure why *trans*-cinnamic acids

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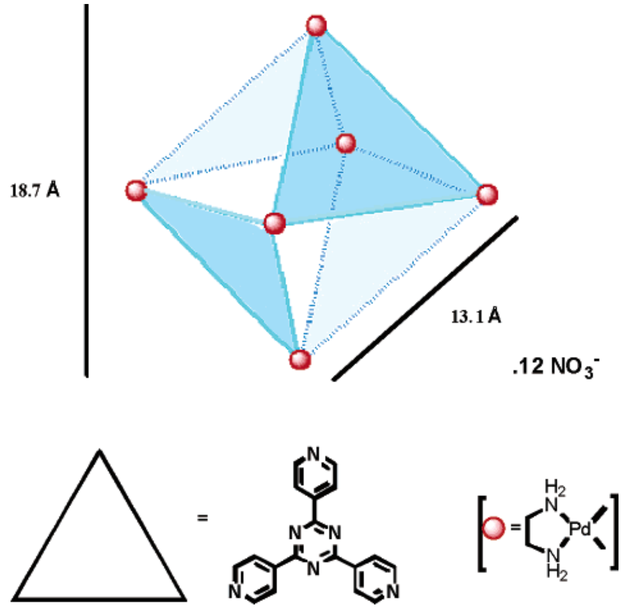

FIGURE 1. Structure of M_6L_4 octahedral host (Pd nanocage).

in spite of complexing with the nanocage did not dimerize. We believe that the water-soluble nature of the *trans*-cinnamic acids results in the guest spending considerable amount of time in water leading to geometric isomerization rather than dimerization. Currently, we do not have experimental evidence to confirm this proposition. To overcome this problem, we chose *trans*-cinnamic acid methyl esters for the templated dimerization reactions.

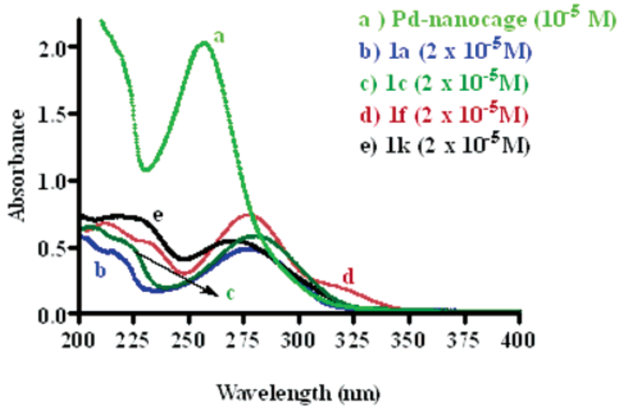

FIGURE 2. Absorption spectra of **1a**, **1c**, **1f**, and **1k** and Pd nanocage in water.

The Pd nanocage (the host compound used in this study) originally synthesized by Fujita and co-workers is a self-assembly of six metal ions (M) and four tridendate ligands (L) resulting in a water-soluble M_6L_4 octahedral cage (Figure 1).[5] This octahedral cage is comprised of four triangular tris(4-pyridyl)1,3,5-triazine panels connected to each other by the metal ions (Pd^{+2}) at the corners of the triangle (Figure 1). Four of the eight faces are open, and the other four faces present alternatively are covered by the triangular panel. Encapsulation of guest molecules within the hydrophobic cavity will occur through the empty faces of the octahedron. Adjacent metal ions of the cage are 13.1 Å apart, while the distance between metal ions opposite to each other is 18.7 Å. Eliminating the very narrow corners where the ligands are coordinated to the metal ions, we visualize the Pd nanocage to have a free space ~15 Å × 10 Å. The detailed investigations of Fujita and co-workers have found the Pd nanocage capable of encapsulating within its hydrophobic cavity varied dimensional organic molecules (e.g., *cis*-stilbene, adamantane carboxylate, acenaphthalene, 1,3,-5-tri-*tert*-butyl benzene, etc.).[6,8] The hydrophobic cavity of the Pd nanocage has been used for templating highly regioselective homo and hetero [2 + 2] photochemical dimerization of acenaphthalenes.[7] The host has also been used for alkane oxidation, catalysis, bimolecular recognition, etc.[8] We have recently reported the Pd nanocage templated photodimerization of coumarin derivatives that suggested that the cavity of the Pd nanocage is able to hold two coumarin molecules within its cavity in a fashion that on irradiation leads to the formation of a syn head−head dimer with >90% selectivity.[9] These results and the challenging possibility of controlling two reaction pathways (geometric isomerization and dimerization) prompted us to undertake the present study on the photodimerization of *trans*-cinnamic acid esters. Moreover, *trans*-cinnamic acid esters absorb at longer wavelengths as compared to the Pd nanocage. The absorption spectra of the cage and the four water-soluble cinnamic acid derivatives are shown in Figure 2. The absorption characteristics of these guest molecules suggest that direct excitation of the cage-included *trans*-cinnamic acid ester deriva-

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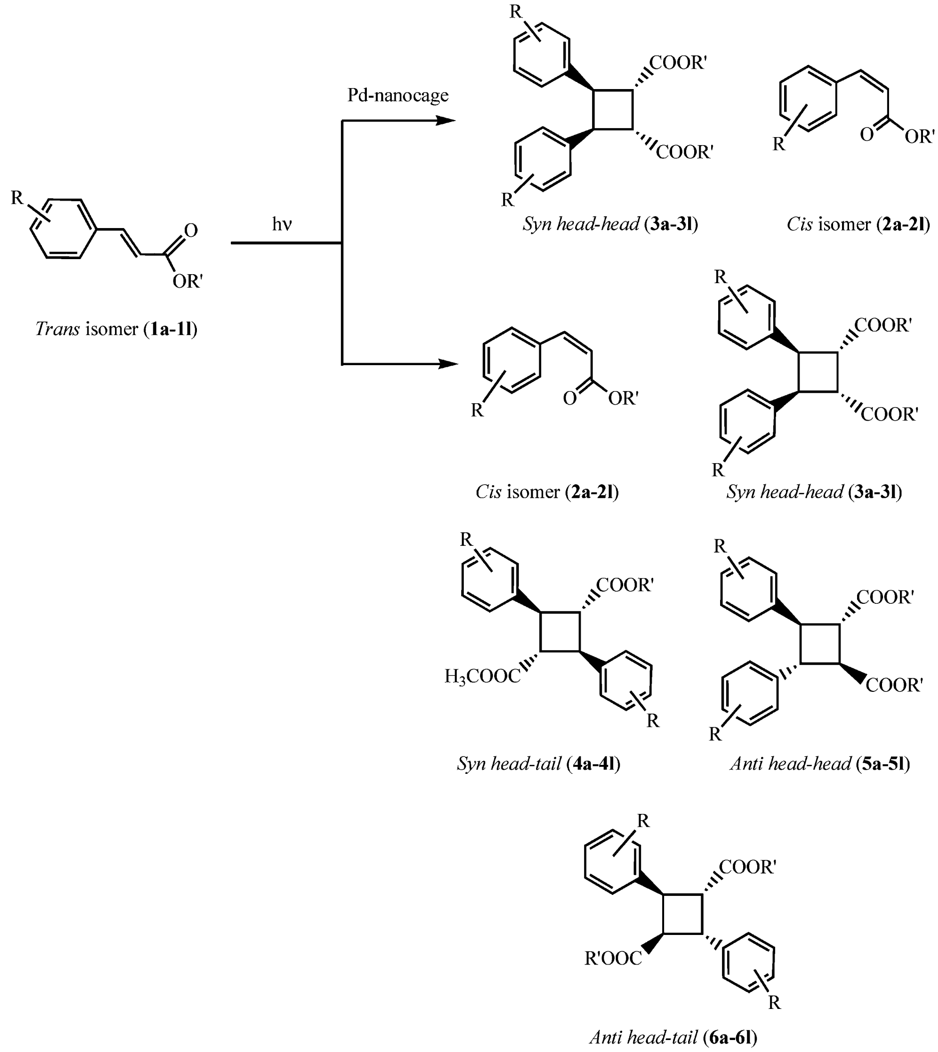
SCHEME 1. Photodimerization of *trans*-Cinnamic Acid Methyl Esters (1a−1l)



R' = CH_3, R = H (**1a**), *o*-CH_3 (**1b**), *m*-CH_3 (**1c**), *p*-CH_3 (**1d**), *o*-OCH_3 (**1e**), *m*-OCH_3 (**1f**), *p*-OCH_3 (**1g**),

R' = CH_3, R = *o*-OCH_2CH_3 (**1h**), *m*-OCH_2CH_3 (**1i**), *p*-OCH_2CH_3 (**1j**), *o*-$COOCH_3$ (**1k**), *m*-$COOCH_3$ (**1l**).

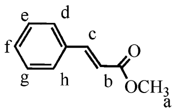
tives is possible. The other derivatives used in this study are expected to have similar absorption spectrum. Also, based on the absorption spectra, we believe that energy transfer from the excited singlet state of the host to the guest is likely. Thus, under our conditions, the *trans*-cinnamic acid ester derivatives are placed in reactive S_1 either by direct excitation or via an energy transfer pathway.

Results and Discussion

We have investigated the photodimerization of 12 *trans*-cinnamic acid esters (Scheme 1). Apart from controlling the photochemistry of these compounds, our interest in understanding how the substitutions in the cinnamic acid could influence its encapsulation behavior within the Pd nanocage prompted us to undertake studies with various derivatives. Methoxy (OCH_3), ethoxy (OCH_2CH_3), methyl (CH_3), and carbomethoxy ($COOCH_3$) groups were substituted at the ortho, meta, and para positions of the aromatic ring, and the alkyl groups of the ester were always maintained as methyl. The photochemical reactions of these molecules (**1a**−**1l**) are provided in Scheme 1. As illustrated in Scheme 1, these molecules on irradiation could undergo unimolecular geometric isomerization or dimerization leading to the formation of a cis isomer (**2a**−**2l**), syn head−head (**3a**−**3l**), syn head−tail (**4a**−**4l**), anti head−head (**5a**−**5l**), and anti head−tail (**6a**−**6l**) dimers. Despite the presence of the two reaction pathways, unimolecular geometric isomerization is the major pathway during solution-phase irradiation of these molecules.[4] The 1:2 host/guest (H/G) complexes of these *trans*-cinnamic acid esters (**1a**−**1l**) with the Pd nanocage were prepared by stirring required amounts of the two in 0.6 mL of D_2O at 60 °C. The exact amounts of host and guests (**1a**−**1l**) used for complexation are provided in the Experimental Procedures. The clear solution obtained indicative of the guest molecules' encapsulation within the hydrophobic cavity of the Pd nanocage was then filtered, and the complexation was confirmed by ^1H− NMR.

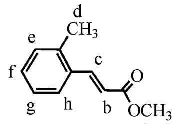
The ^1H− NMR spectra of the host−guest complexes recorded to confirm encapsulation of **1a**−**1l** with the Pd nanocage are provided in the Supporting Information. The changes in chemi-

SCHEME 2. Changes in Chemical Shift ($\delta_{solvent} - \delta_{Pd-nanocage}$) for 1a−1l upon Complexation with Pd Nanocage[a]



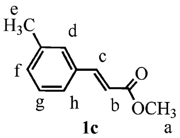
1a

H_a : 0.3, H_b : 2.5
H_c : 2.1, $H_{f, g}$: 2.3
$H_{d, h, e}$: 2.1



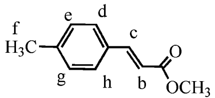
1b

H_a : 0.05, H_b : 2.0
H_c : 2.4, H_d : 2.2
$H_{e\text{-}h}$: 2.1-2.4



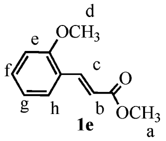
1c

H_a : 0.0, H_b : 2.5
H_c : 2.6, H_e : 1.75
$H_{d, f, g, h}$: 1.7-2.1



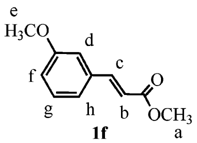
1d

H_a : 0.0, H_b : 2.2
H_c : 2.7, H_f : 1.6
$H_{d, e, g, h}$ - 2.0-2.3



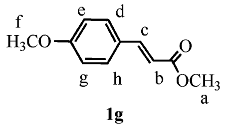
1e

H_a : 0.1, H_b : 1.7
H_c : 2.2, H_d : 1.5
$H_{e\text{-}h}$: 2.0-2.4



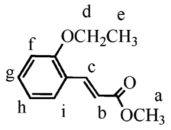
1f

H_a : 0.0, H_b : 2.3
H_c : 2.5, $H_{d, f\text{-}h}$: 2.4-2.6
H_e : 1.6



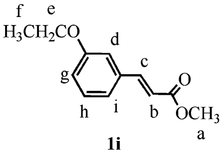
1g

H_a : 0.1, H_b : 2.2
H_c : 2.4, H_f : 0.5
$H_{d, h}$: 2.5, $H_{e, g}$: 1.8



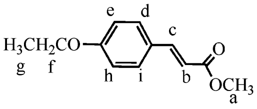
1h

H_a : - 0.2, H_b : 1.0
H_c : 1.7, H_d : 2.1
H_e : 2.2, $H_{f\text{-}i}$: 2.5-2.8



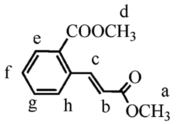
1i

H_a : - 0.2, H_b : 1.9
H_c : 2.1, $H_{g, i, d}$: 2.3-2.4
H_e : 1.8, H_f : 1.2, H_h : 2.3



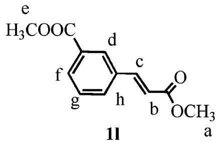
1j

H_a : 0.0, H_b : 1.7
H_c : 2.1, $H_{d, i}$: 2.4
$H_{e, h}$: 1.9, $H_{f, g}$: 0.9



1k

H_a : 0.2, H_b : 1.9
H_c : 1.75, H_d : 1.2
$H_{e\text{-}h}$: 1.5-2.0



1l

$H_{a, e}$: 0.2, H_b : 2.1
H_c : 2.4, $H_{d, f, g, h}$: 2.3-2.8

[a] In all cases, a H/G Ratio of 1:2 was used. The solvent used for comparison is either D_2O or $CDCl_3$. The guest molecules **1b**, **1g**, **1h**−**1j**, and **1l** are insoluble in water; hence, the changes in chemical shift reported here for these guest molecules is with respect to $CDCl_3$.

cal shift due to encapsulation of these guest molecules within the Pd nanocage are provided in Scheme 2. Because of the anisotropic ring current effect of the aromatic panels of the Pd nanocage, the olefin and the aromatic protons of the guest molecules are shifted upfield by 1.8−2.5 ppm, while the methyl protons of the ester group -$COOCH_3$ attached to the olefin showed a marginal shift (∼0.0−0.3 ppm) on encapsulation. The observed changes in chemical shift suggest that the ester group faces the water through the empty face of the octahedron, whereas aromatic and alkene parts of the guest molecule are cocooned within the hydrophobic cavity of the Pd nanocage. The possible structure of the host−guest complex based on the observed upfield chemical shift for the aromatic and alkene protons is provided in Figure 3. For the sake of clarity, only one of the two olefins is included in the figure.

The chemical shifts of the aromatic substituents were also dependent on the type (methoxy (OCH_3), ethoxy (OCH_2CH_3), methyl (CH_3), or carbomethoxy ($COOCH_3$) and position (ortho, meta, or para) on the aromatic ring. For example, in the case of methoxy substituted *trans*-cinnamic acid methyl esters (**1e**, **1f**, and **1g**), para substitution results in 0.5 ppm, while ortho or meta substitution results in a 1.5 ppm upfield chemical shift (Scheme 2) of the methyl protons of the methoxy group. To obtain insight on what governs the chemical shift of the protons of the substituents, we calculated the molecular dimensions of ortho, meta, and para methoxy *trans*-cinnamic acids methyl esters (**1e**−**1g**) using Chem 3-D ultra, which suggested that the para derivative (**1g**) was longer than the ortho and meta derivatives (**1e** and **1f**); **1g** was 12.7 Å and **1e** and **1f** were ∼11.0 Å, respectively.[10] Probably due to the molecular length differences and the orientation of the substituents, the protons of methoxy group in the ortho or meta position become situated close to one of the aromatic panels of the host, interacting strongly with the aromatic groups of the Pd nanocage, whereas

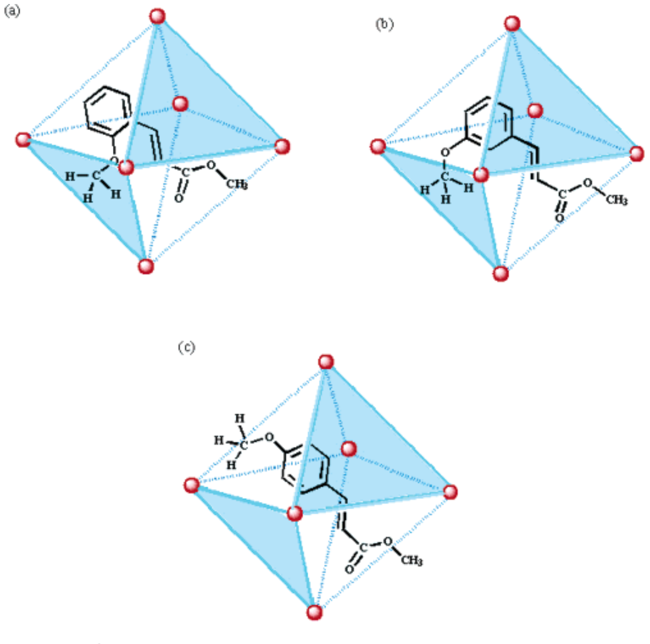


FIGURE 3. Possible orientation of (a) ortho-methoxy-*trans*-cinnamic-acid methyl ester (**1e**), meta-methoxy-*trans*-cinnamic-acid methyl ester (**1f**), and (c) para-methoxy-*trans*-cinnamic-acid methyl ester (**1g**) within Pd nanocage. For clarity, only one guest molecule is shown in the figure.

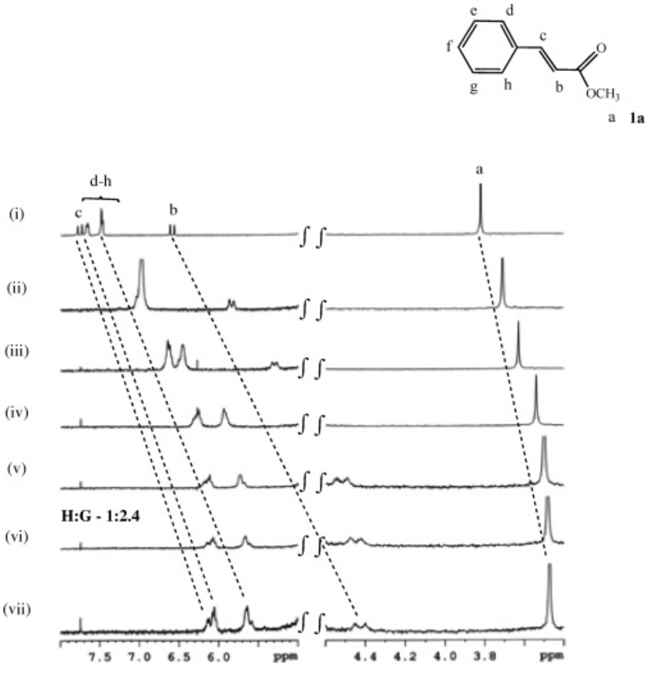


FIGURE 4. ^{1}H NMR (D_2O) spectra showing the changes in chemical shift for the protons of **1a** on addition of (i) 0, (ii) 0.09, (iii) 0.18, (iv) 0.27, (v) 0.36, (vi) 0.45, and (vii) 0.54 equiv of Pd nanocage. [**1a**] = 2.37 mM.

the methoxy group in the para position lacks such effective interaction. Our speculated mode of encapsulation of ortho, meta, and para methoxy *trans*-cinnamic acid methyl esters (**1e**−**1g**) within the Pd nanocage, based on observations from the ^{1}H NMR studies, is provided in Figure 3a−c. From Figure 3a,b, one can see that the encapsulation of the ortho and meta substituted derivatives within the Pd nanocage leads to orientation of the methyl protons of the methoxy group toward one of the aromatic panels, whereas for the para substituted derivative, the methyl protons of the methoxy group are not oriented toward the aromatic panels of the host.

To obtain additional information on the nature of the host−guest complex, the ^{1}H− NMR titration of the guest molecule (**1a**) was performed with the host (Figure 4). To the guest (**1a**) dissolved in water ([**1a**] = 2.37 mM), increasing amounts of the host (1.1×10^{-4} to 1.33×10^{-3} M) were added. After each addition of the host, the solution was sonicated for 10 min, and the ^{1}H− NMR spectrum was recorded. Addition of increasing amounts of the host to the guest molecule in D_2O led to an upfield shift of protons of aromatic and olefinic hydrogens of the guest molecule. The methyl protons of $COOCH_3$ attached to the olefin as indicated before underwent a marginal shift. Also, the absence of two independent signals, one due to the complexed and the other due to the uncomplexed guest molecule, suggests a fast exchange between these two types of guest molecules in the NMR time scale. The observed minimal shift beyond a host/guest ratio of 1:2.4 suggested maximum complexation of the guest molecule within the Pd nanocage. The exact stoichiometry of the host−guest complex is currently unknown. For our irradiation studies, generally the 1:2 host/guest ratio was used, although in one case, we had used a higher H/G ratio.

To gain additional insight on the structure of the host−guest complex and to predict the stereochemistry of the dimer that could be obtained from the Pd nanocage templated photodimerization of *trans*-cinnamic acid esters, modeling studies on the host−guest complex were carried out. Our modeling studies are based on NMR complexation results as well as the possible weak intermolecular interactions of the guest molecule encapsulated within the host.[11] The four possible arrangements of two guest molecules (**1g**) within the host leading to the formation of the syn head−head (**3g**), syn head−tail (**4g**), anti head−head (**5g**), and anti head−tail (**6g**) dimers are provided in Figure 5a−d. Of these four arrangements, due to the reasons outlined below, the ones leading to the formation of the syn head−head (Figure 5a) and syn head−tail (Figure 5b) dimers will be preferred within the Pd nanocage more than their anti counterparts. In these cases, the hydrophobic aromatic and alkene parts of the guest reside within the octahedral cavity of the Pd nanocage, while the hydrophilic ester group is exposed to the aqueous exterior through the empty face of the octahedron. Stabilization by hydrophobic effects of such an arrangement of guest molecules within the Pd nanocage will be augmented by weak intermolecular forces such as C−H−π and π−π interactions between the host and the guest(s).[11] The observed upfield shift of the protons of aromatic and olefin chromophores (1.8−2.5 ppm) is consistent with this model. On the contrary, the formation of anti dimers would require the hydrophobically unfavorable exposure of one of the aromatic groups to water (Figure 5c,d). Alternatively, the two reactive C═C bonds would be far away to interact in the excited state. Moreover, due to the positioning of the aromatic groups in water, stabilization of these complexes from weak intermolecular forces (C−H−π and π−π) between the host and the guest(s) would be considerably lower when compared to the corresponding syn arrangements. On the basis of these arguments, the existence of cinnamic acids in an anti orientation within the Pd nanocage seems less likely.

The arrangements leading to the formation of two syn dimers (head−head and head−tail) are equally favorable within the Pd nanocage except for the fact that in the latter case, the two C═C bonds are oriented in a criss−cross fashion. The former would be easily formed through an allowed [2 + 2] supra−supra addition without much change in the positions of various atoms of the olefins. On the other hand, the latter would have to undergo considerable motion to yield either syn head−tail or anti head−head dimers. One of the olefins in the criss−crossed oriented pairs will have to rotate by about ~90° to be able to form bonds at both ends. We believe that within the nanocage, large motions required for formation of these dimers from not-so-ideally oriented olefin pairs would be resisted by the cage. On this basis, we predict that the dimer of the syn head−head stereochemistry would be the most favored one from the Pd nanocage templated photodimerization of *trans*-cinnamic acid esters.

To verify our prediction, the host−guest complexes formed between Pd nanocage and guests (**1a**−**1l**) were irradiated with a 450 W medium-pressure Hg arc lamp for 3 h. The samples were then extracted by stirring with $CDCl_3$ for 1 h and analyzed by ^{1}H NMR for the products that indicated the formation of a syn head−head dimer and the corresponding cis isomer for guest

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(10) The molecular dimensions were calculated using Chem 3-D ultra software with a MM2 force field.

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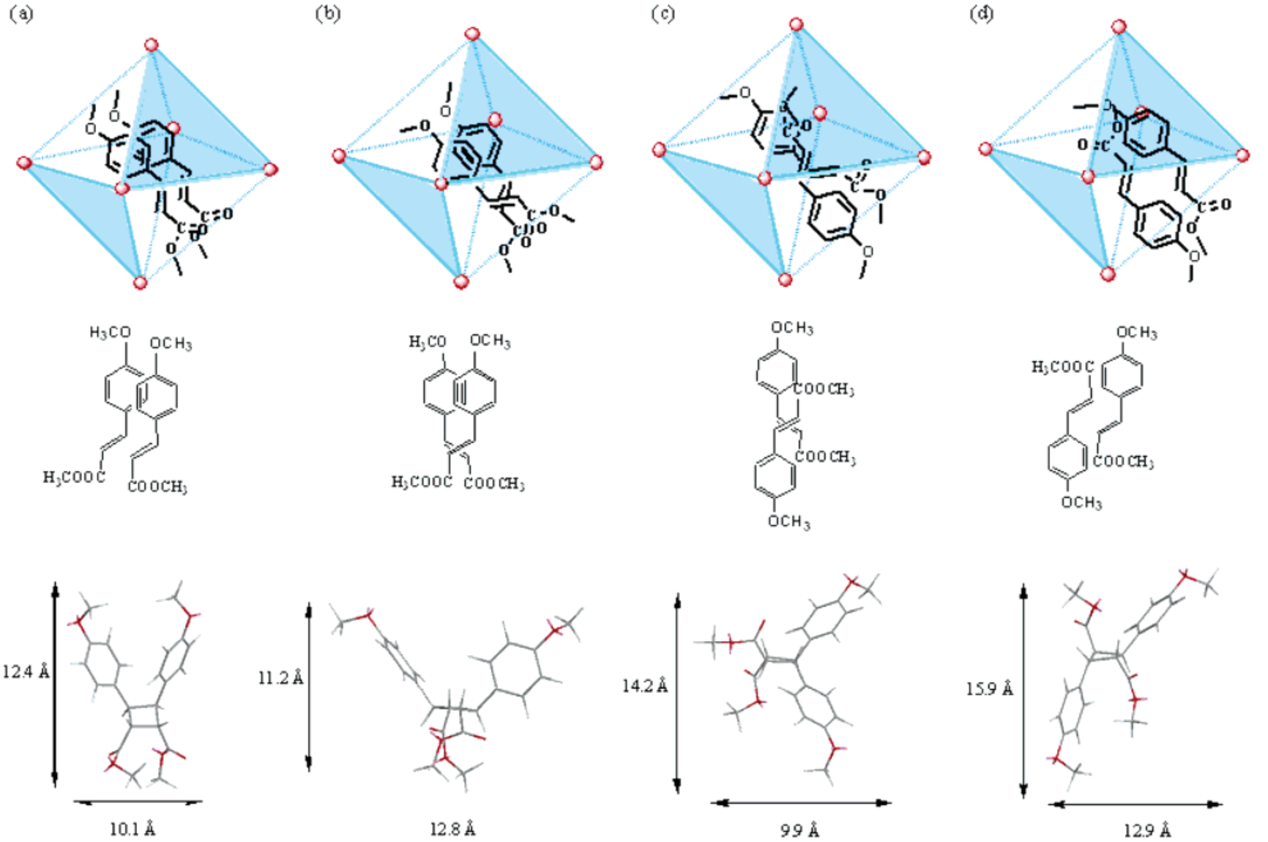

FIGURE 5. Possible orientations **1g** within Pd nanocage leading to the formation of (a) syn head−head dimer, (b) syn head−tail dimer, (c) anti head−head dimmer, and (d) anti head−tail dimer. The dimensions of the dimers were calculated using Chem 3-D ultra software using the MM2 force field.

TABLE 1. Photodimerization of 1a−1l within the Pd Nanocage[a]

Guest	% cis (2a−2l)	% dimers
1a	54	46 (**3a**/**6a**, 80:20)
1b	78	22 (**3b**)
1c	37	63 (**3c**)
1d	55	45 (**3d**)
1e	66	44 (**3e**/**6e**, 76:24)
1f	58	42 (**3f**)
1g	60	40 (**3g**)
1h	79	21 (**3h**)
1i	43	57 (**3i**)
1j	49	51 (**3j**)
1k	77	23 (**3k**)[b]
1l	40	60 (**3l**)

[a] The conversion was around 30−40% for 3 h irradiation. The H/G ratio of 1:2 was used in all the cases. The percent of the products formed was determined by integration of ^{1}H NMR signals. [b] The NMR analysis of the extracted sample indicated a peak at $\delta = 4.9$ ppm along with the cyclobutane protons of a syn head−head dimer. The splitting of the peak at $\delta = 4.9$ ppm resembled that of the cyclobutane protons of a dimer. The exact stereochemistry of this dimer is currently unknown. ^{1}H NMR integration indicated that this uncharacterirzed dimer and the syn head−head dimer are formed in equal amounts.

molecules **1b**−**1d**, **1f**−**1j**, and **1l**. For guest molecules **1a** and **1e**, the syn head−head dimer and anti head−tail dimers were formed in the ratio 80:20 and 76:24. In both cases, the syn head−head dimer was the major isomer formed. The results obtained on irradiation of substrates (**1a**−**1l**) as a host−guest complex with the Pd nanocage are provided in Table 1. The stereochemistry of the dimer formed was confirmed by comparing the ^{1}H NMR chemical shifts of cyclobutane protons of the dimer formed with the ^{1}H NMR chemical shifts of cyclobutane protons reported in the literature.[3j,4] The percent conversion for 3 h of irradiation was between 30 and 40. To ascertain that dimerization that is reported here occurs mainly within the cage and not from the olefins in an aqueous phase, we conducted irradiation of **1a** at two host/guest ratios (1:4 and 1:2). The host−guest complexes were prepared, irradiated, extracted, and analyzed by ^{1}H NMR. Analysis by ^{1}H NMR indicated no substantial difference in the dimer distribution between the previous two ratios. For H/G ratio of 1:2, we observed the formation of 54% of **2a** and 46% of dimers (**3a**/**6a**, 80:20). For a H/G ratio of 1:4, we observed 50% of **2a** and 50% of dimers (**3a**.**6a**, 76:24). To ensure that the photoreactions were uniform and that the observed products were not due to secondary photoreactions, we conducted irradiation of the host−guest complex (H/G, 1:2) for different durations (1, 1.5, and 3 h). Extraction of samples followed by ^{1}H NMR analyses indicated 40% (1 h), 50% (1.5 h), and 54% (3 h) of **2a** and 60% (**3a**/**6a**, 75:25), 50% (**3a**/**6a**, 76:24), and 46% (**3a**/**6a**, 80:20) of dimers. Importantly, the ratio of the two dimers remained nearly the same, suggesting that the dimer **6a** is also a primary photoproduct. The results obtained here are interesting given the fact that these guest molecules on solution irradiation undergo mainly geometric isomerization. The cavity of the Pd nanocage is unequivocally able to accommodate and bring two guest molecules in close proximity, leading to the formation of the syn head−head dimer as the major product.

The molecular dimensions of the syn head−head, syn head−tail, anti head−head, and anti head−tail dimers formed from **1g** were calculated to obtain additional support to our prediction.[10] Molecular dimension data of the dimers show that the pair of syn dimers (head−head: height 12.4 Å, width 10.1 Å and head−tail: height 11.2 Å, width 12.8 Å; Figure 4a,b) are more compact than their corresponding anti dimers (head−head: height 14.2 Å, width 9.9 Å and head−tail: height 15.9 Å, width 12.9 Å; Figure 4c,d). On the basis of these molecular dimensions and the free space available within the Pd nanocage (15 Å × 10 Å), the accommodation of olefins leading to both the anti dimers within the cavity of the Pd nanocage can easily be found to be difficult. Of the two syn dimers (head−head and head−tail), the former is slightly more compact, while the latter is slightly larger to fit the Pd nanocage. Also as stated previously for reasons of considerable motion of the double bonds, the syn head−tail dimer formation within the Pd nanocage seems to be a less favorable process. In our studies, probably for the previous reasons, the Pd nanocage templated irradiation of *trans*-cinnamic acid esters (**1a**−**1l**) resulted in the formation of only syn head−head dimer.

Summary

de Mayo and co-workers were the first ones to explore the use of weak interactions to control the regiochemistry of the photocycloaddition of enones in solution.[12] They were able to achieve modest control on the process using a micellar medium. The molecules were aligned at the interface between the hydrophobic interior and the hydrophilic exterior of a micelle. Similar attempts by Whitten and co-workers to obtain selective dimers from stilbazoles in conventional micellar media were not successful.[13] In contrast to normal micelles, when they employed a reverse micelle with much smaller size than the reaction medium, a syn HH dimer was obtained from stilbazole.[14] Whitten and co-workers speculate that the well-ordered and more constrained water pool in reverse micelles is able to provide a better orientation than conventional micelles. The previous results of de Mayo and Whitten's groups suggest that the hydrophobic−hydrophilic interface could be used to orient molecules but that the reaction space must be more rigid and less dynamic than a conventional micelle. Using the principles formulated by these pioneers, we have achieved superior control during the photocycloaddition of olefins through the rationale of confined spaces offered by cucurbiturils, calixarenes, and a Pd nanocage instead of a micelle.

In conclusion, we have used a self-assembled water-soluble octahedral host, namely, the Pd nanocage for conducting photodimerization of *trans*-cinnamic acid esters in water. The investigation reported in this paper complements the work of Fujita and co-workers on the photodimerization of acenaphthylenes within the Pd nanocage and our own on the photodimerization of coumarins.[7,9] One of the main advantages of this host (Pd nanocage) is its commercial availablility.[15] Considering the fact that some of the water-soluble supramolecular hosts reported in the literature require tedious, multistep syntheses and purification procedures, use of this commercially available host is a major advantage.[16] The main drawback in using the Pd nanocage as a reaction nanovessel for conducting photochemical studies is the similar absorption characteristics of both this host and most organic molecules.[7] Hence, it is essential to make a judicious choice of the substrates that would be photoactive when encapsulated and irradiated as a host−guest complex with the Pd nanocage. With the previous encouraging results with the Pd nanocage as a reaction vessel, we are currently investigating its utility in other photochemical reactions.

Experimental Procedures

Complexation of 1a−1l with Pd Nanocage and Irradiation Studies. Required amounts of the guest (G) (**1a**: 2.1 mg (21 × 10^{-3} M), **1b**/**1c**/**1d**: 1.7 mg (16.0 × 10^{-3} M), **1e**: 1.9 mg (16.4 × 10^{-3} M), **1f**/**1g**: 1.2 mg (10.4 × 10^{-3} M), **1h**/**1i**/**1j**: 1.1 mg (8.8 × 10^{-3} M), and **1k**/**1l**: 1.2 mg (9.09 × 10^{-3} M) were stirred with 10 mg (5.5 × 10^{-3} M for **1a**) or 20 mg (11 × 10^{-3} M for **1a**), 15 mg (8.3 × 10^{-3} M, for **1b**/**1c**/**1d**/**1e**), 9 mg (5.0 × 10^{-3} M, for **1f**/**1g**), 8 mg (4.45 × 10^{-3} M, for **1h**/**1i**/**1j**), and 10 mg (5.5 × 10^{-3} M, for **1k**/**1l**) of a Pd nanocage in 0.6 mL of D_2O in a hot water bath for 5 h to obtain a clear solution of the inclusion complex with a host/guest ratio of 1:2 or 1:4 (for **2a**). The ^{1}H NMR was recorded to confirm the complexation. The solution was then irradiated for 3 h using a 450 W medium-pressure Hg lamp. The products were extracted by stirring with $CDCl_3$ dried over anhydrous sodium sulfate and analyzed by ^{1}H NMR for the product formation. The conversion to the product was determined by NMR integration of peaks of the starting material (alkene protons) and that of the dimer formed (cyclobutane protons).

NMR Titration Studies. Known amounts of (2−3 mg) of **1a** were stirred with 1 mL of D_2O for 12 h. The solution was then filtered with filter paper of fine porosity, and the ^{1}H NMR was recorded. To this solution, the host was added sequentially (0.2 mg) and sonicated for 10 min before recording the ^{1}H NMR until the amount of added host was 2.4 mg. The H/G ratio was determined by integration of the peaks corresponding to the host and the guest.

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Supporting Information Available: ^{1}H NMR spectra of the host−guest complexes of **1a**−**1l** and 3-methyl- and 4-methyl-*trans*-cinnamic acids, syntheses and characterization of the guest molecules (**1b**−**1l**), and ^{1}H NMR characterization of the dimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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