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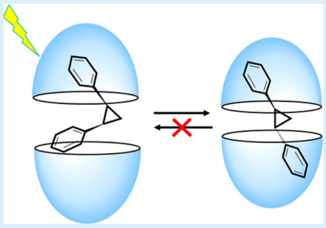
Space Constrained Stereoselective Geometric Isomerization of 1,2-Diphenylcyclopropane and Stilbenes in an Aqueous Medium

A. Mohan Raj, Gaurav Sharma, Rajeev Prabhakar, and V. Ramamurthy*

Department of Chemistry, University of Miami, Coral Gables, Florida 33124, United States

Supporting Information

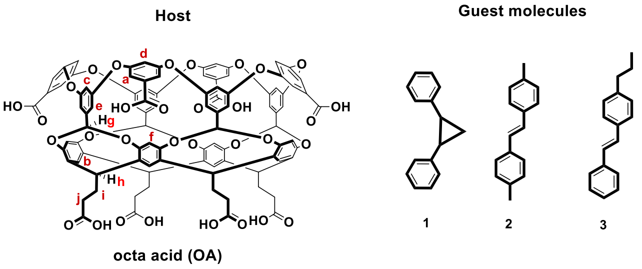
ABSTRACT: Confinement provided by the reaction space alters the photostationary state isomer distribution during the geometric isomerization of excited 1,2-diphenylcyclopropane and stilbenes. The selectivity in 1,2-diphenylcyclopropane is suggested to result from the supramolecular steric hindrance exerted by the medium for the rotational motion. The alteration in the selectivity between a dimethyl and *n*-propyl substituted stilbenes is attributed to the medium influence on the location of the transition state on the ground state surface.



Geometric isomerization of excited olefins and 1,2-disubstituted cyclopropanes, one of the most fundamental and mechanistically important photoreactions, results from the weakening of the π and σ bonds, respectively.[1−4] Generally the photostationary state (pss) mixture of *cis* and *trans* isomers in a photoisomerization reaction is controlled by excitation and decay ratios.[5] Isotropic and nonviscous media generally do not influence the composition of pss. In this Letter, we disclose the results of our study with 1,2-diphenyl cyclopropane and two alkyl substituted stilbenes that reveal the significant dependence of the pss mixture on the available free space wherein the isomerization occurs. Site-selective and one-way geometric isomerization replete in biological systems such as rhodopsin, bacteriorhodopsin, xanthopsin, and phytochrome[6,7] prompted research to explore the role of confined space using synthetic hosts such as zeolites, cyclodextrins, micelles, cavitands, and octa acid (OA).[8−20] Among these, OA, unlike cyclodextrins and related cavitands, forms a closed capsular assembly.[9,21] Results presented below demonstrate that photoisomerization of 1,2-diphenyl cyclopropane can be driven predominantly toward a single isomer when enclosed in the capsule formed by two molecules of OA. Similar striking selectivity was also noticed with stilbenes, but the isomer selectivity was dependent on both the size and location of the substituents on the phenyl ring. The structures of the host OA and the three guest molecules (1,2-diphenyl cyclopropane (**1**), 4,4′-dimethyl stilbene (**2**), and 4-propyl stilbene (**3**)) investigated are shown in Scheme 1.

In gas phase and in isotropic solution, the *cis* isomer of stilbenes, independent of the substituent (hydrogen, methyl, or propyl), is calculated to be slightly less stable than the corresponding *trans* isomer (Table S1). Structures and binding energies of the OA encapsulated *cis* and *trans* isomers of the three guest molecules obtained from computational modeling including molecular docking and molecular dynamics (MD) simulations performed using the Gaussian 09,[22] Autodock Vina 1.5.6,[23] and GROMACS 4.5.6[24] programs are provided in Figure 1 and Table 1. They reveal that in each case one isomer forms a stronger complex than the other. For example, in the case of **1**, the *trans* isomer is slightly more stable within OA (8 kJ/mol). Similarly, in the case of **2** the *trans* isomer is stabilized by 19 kJ/mol while in the case of **3** the *cis* isomer is more stable by 64 kJ/mol. These energies were calculated utilizing the Molecular Mechanics Poisson−Boltzmann Surface Area (MM-PBSA) method.[25] A comparison with the binding free energy calculated using the lambda (λ) particle approach[26−28] gave similar energy differences for **1** and unsubstituted stilbene.

Scheme 1. Structures of Host and Guest Molecules



Geometric isomerization of stilbenes and related olefins has been understood on the basis of the torsional rotational model illustrated in Scheme 2a and Figure 2a.[29−31] Volume conserving mechanisms such as hula-twist and a combination of rotation and pyramidalization pathways involving a conical intersection proposed recently are yet to gain full acceptance.[32−35] While such mechanisms are likely within a confined space, we believe, classical rotational process adequately explains the phenomenon. For stilbenes the geometry of the maximum in the ground state and minimum in the excited states, respectively, are suggested to be closer to the 90° twisted form. Owing to the varying extents of stabilization of the *cis* and *trans* isomers of **2** and **3** within OA and based on the well-known Hammond's postulate,[36,37] we envisioned the

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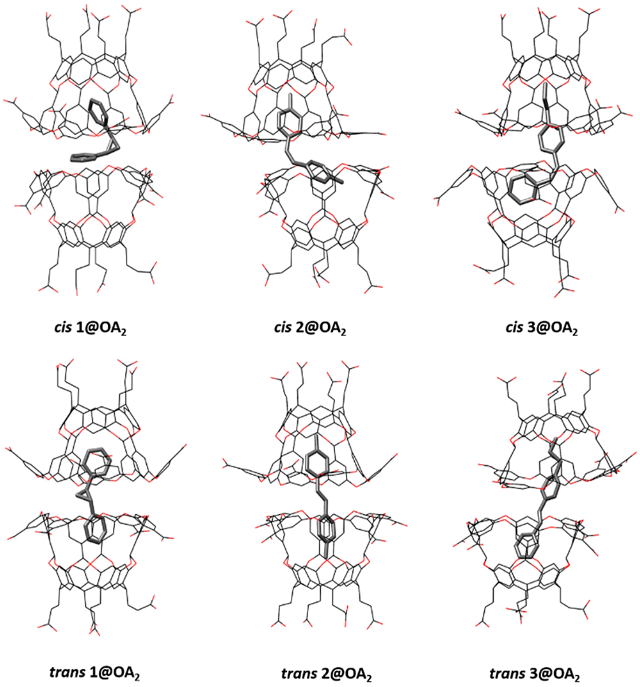

cis **1@OA$_2$** *cis* **2@OA$_2$** *cis* **3@OA$_2$**

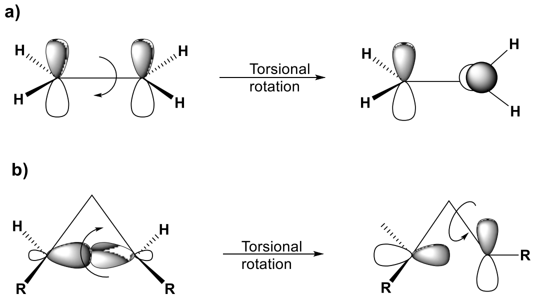
trans **1@OA$_2$** *trans* **2@OA$_2$** *trans* **3@OA$_2$**

Figure 1. Most representative structures of *cis* (top) and *trans* (bottom) isomer complexes within OA obtained from MD simulations.

Table 1. Binding Energies of the OA Complexes of *cis* and *trans* Isomers of 1−3

	binding free energy (kJ/mol)	
compd	*cis*@OA$_2$	*trans*@OA$_2$
1,2-diphenylcyclopropane (**1**)	−184.6	−192.4
4,4′-dimethylstilbene (**2**)	−196.3	−215.4
4-propylstilbene (**3**)	−212.0	−148.3

Scheme 2. Torsional Rotation Leading to *cis*−*trans* Isomerization



geometry at the transition state in the ground state during isomerization within the confined capsule would be different, for **2** to be closer to *cis* while closer to *trans* for **3** (Figures 2b and 2c). As per this model we expect the excited 90° twisted **2** to enter the ground state surface on the *trans* side and **3** to do so on the *cis* side. Based on Figure 2b and 2c, we anticipate that upon irradiation **2** and **3** would yield pss mixtures with different isomers in excess. The isomerization of 1,2-diphenylcyclopropane is different from that of stilbenes. In this case the breakage of the 1,2-σ bond and torsional rotation of either the 1,3 or 1,2 bond results in geometric isomerization (Scheme 2b).[2] The 1,3-diradical from **1** is expected to be more flexible than the 1,2-diradical arising from **2** and **3**. Therefore, the influence of the confinement on the energy diagram is not obvious (Figure 2).

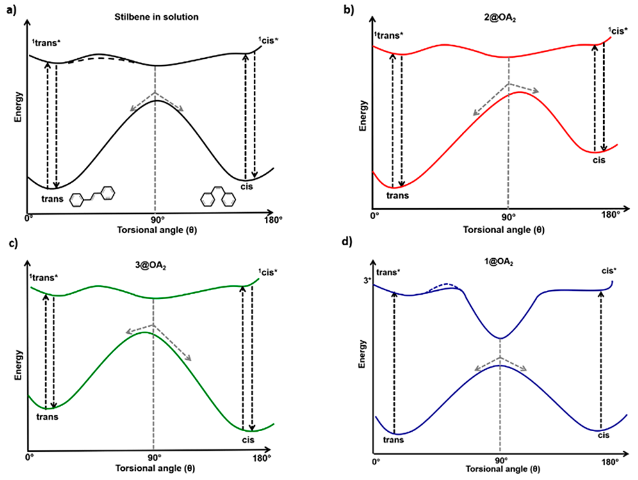


Figure 2. Modified potential energy diagrams for photoisomerization of OA encapsulated **1**−**3**.

Hydrophobic feebly water-soluble **1**, **2** and **3** formed transparent solutions in the presence of OA at pH ≈ 8.9 (borate buffer). Observed upfield shift of the cyclopropyl (in the case of **1**), and methyl and propyl in the case of **2** and **3** hydrogens confirmed the inclusion of the above guests within OA (Figure 3 and Figures S1−S6). Diffusion constant data (Table S2) as measured by 2D-DOSY NMR experiments (Figures S7−S13) revealed them to be 2:1 (host to guest) capsules. The diffusion constants in the range of 1.27 to $\sim 1.45 \times 10^{-6}$ cm^2/s are lower than that for free OA (1.88×10^{-6} cm^2/s) and the 1:1 cavitandplex ($\sim 1.7{-}1.9 \times 10^{-6}$ cm^2/s).[38,39] Furthermore, ^{1}H NMR titration experiments supported the above conclusion (Figures S1−S6). As expected for a 2:1 complex, the integrations of the NMR peaks of the host (H$_f$) and the guest aliphatic protons of the solution containing no free host or guest were 2:1 (Figures S14−S16).

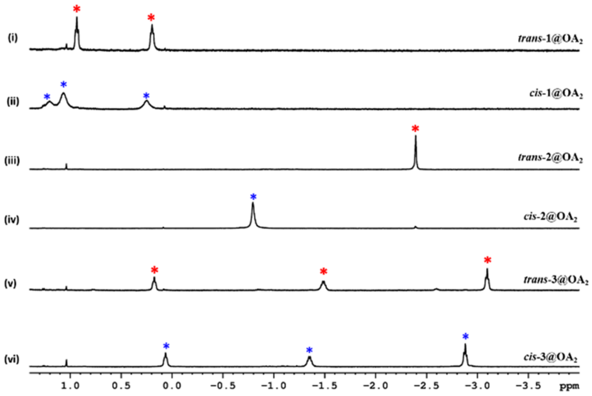


Figure 3. Partial ^{1}H NMR (500 MHz) spectra of (i) 1:2 complex of *trans*-**1**@OA$_2$; (ii) 1:2 complex of *cis*-**1**@OA$_2$; (iii) 1:2 complex of *trans*-**2**@OA$_2$; (iv) 1:2 complex of *cis*-**2**@OA$_2$; (v) 1:2 complex of *cis*-**3**@OA$_2$; (vi) 1:2 complex of *trans*-**3**@OA$_2$. Red * symbols represent the bound protons of *trans* isomers, and blue * symbols represent the bound protons of *cis* isomers.

The results of competition experiments (monitored by ^{1}H NMR (Figures S17−S21) are consistent with the calculated binding energy data (Table 1). Addition of *trans*-**1** to the OA complex of *cis*-**1** displaced the latter to the exterior aqueous phase while *cis*-**1** did not show such displacement with *trans*-**1**@OA$_2$. Similar behavior was observed in the case of **2** as well.[40] This suggested a stronger complex of the *trans* isomers of **1** and **2** with OA than the corresponding *cis* isomers. On the other hand, *cis*-**3** displaced OA encapsulated *trans*-**3**.

It has been established that the pss during triplet sensitization of **1** in isotropic solution consists of 45% *cis* and 55% *trans*,[2,41] while reaction upon direct excitation gave multiple products.[42,43] We reported earlier that the photoisomerization could be driven to >90% *cis* isomer within zeolites.[44] Contrary to this finding the results presented in this article show that within the OA capsule the photoisomerization of **1** proceeds to >90% *trans*.

It is clear from the overlapping absorption spectra of OA and **1** (Figure S22) that under our experimental conditions the incident light would be absorbed by both OA and **1** (>280 nm; Pyrex NMR tube; see SI for details). Although the singlet energy of OA and **1** are similar, the triplet energy of OA (305 kJ/mol) is higher than that of **1** (222 kJ/mol).[40,44] Based on the established feasibility of triplet energy transfer from OA to included guests[45] we believe that upon irradiation the triplet of **1** would be generated within the OA capsule. The progress of irradiation of the OA complexes of *cis* and *trans* **1** (1 mM of OA and 0.5 mM of 1; Pyrex NMR tube) was monitored by recording ^{1}H NMR spectra. As per the spectra presented in Figures 4 and 5, *cis*-**1** was almost quantitatively converted to the *trans* while the *trans* remained unchanged even after 5 h of irradiation. This is a strikingly different behavior from the one observed in solution[2,41] and within zeolites.[44] Following clean one-way isomerization from *cis* to *trans*, the product *trans*-**1** was isolated from the capsule with chloroform and identified by ^{1}H NMR.

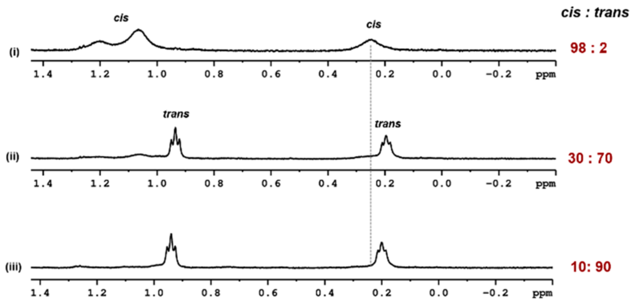


Figure 4. Partial ^{1}H NMR (500 MHz) spectra of (i) 1:2 complex of *cis*-**1**@ OA$_2$ before irradiation; (ii) after 2 h irradiation; (iii) after 5 h irradiation (irradiation wavelength >280 nm).

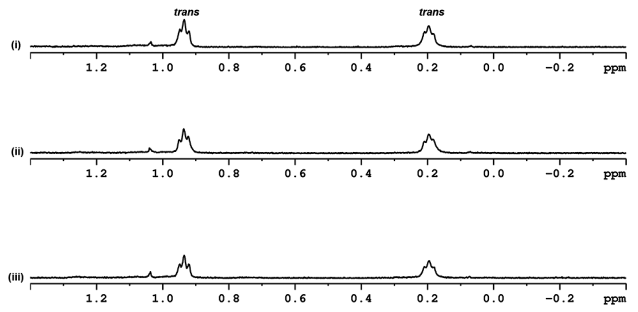


Figure 5. Partial ^{1}H NMR (500 MHz) spectra of (i) 1:2 complex of *trans*-**1**@ OA$_2$ before irradiation; (ii) after 2 h irradiation; (iii) after 5 h irradiation (irradiation wavelength >280 nm).

We attribute the origin of the *trans* selectivity in **1** to the restriction imposed by the capsule for the required torsional rotation of the 1,3 and/or 1,2 bond on the excited surface (Scheme 2b). The snug fit of *trans*-**1** within the capsule and absence of free space surrounding the phenyl groups (Figure 1a) likely hinders the displacement of the phenyl from the *trans* to *cis* geometry. We hypothesize, in the case of the *cis* isomer, the placement of the two phenyl groups, one at the narrower end and the other at the wider median of the capsule (Figure 1) with larger free space surrounding it, facilitates conversion from the *cis* to *trans* isomer.

Although absorption spectra of stilbenes **2** and **3** overlap with that of OA, the absorption due to stilbene is still visible at the tail end (Figure S22). With both the singlet and triplet states of stilbenes being lower in energy (S$_1$: 364 kJ/mol and T$_1$: 230 kJ/mol) than OA, we believe that even if the host absorbs most of the light the energy would be transferred to the guest stilbenes. An aqueous solution of the 2:1 OA−guest complex (1 mM host and 0.5 mM guest) maintained at pH ≈ 8.9 using borate buffer was irradiated for about 8 h, and the progress of the photoreaction was monitored by ^{1}H NMR spectra. The pss reached in about 6 h in OA were found to be 80:20 and 3:97 *trans* to *cis* for **2** and **3**, respectively, while in solution (acetonitrile) they were 20:80 and 15:85 (Table-S3), in favor of the *cis* isomer. Clearly, in the presence of OA the *trans* isomer favored in the case of **2** differs from the *cis* isomer favored in isotropic solution; the results in the case of **3**@OA$_2$ are reversed. The possibility of photoisomerization occurring from uncomplexed stilbenes and one of the resulting isomers preferentially being adsorbed within the OA capsule was ruled out by irradiating solutions containing excess OA (3:1 and 4:1, OA to guest ratio in solution). Under all conditions, the pss ratios were the same as the 2:1 mixture. Even if the above phenomenon occurs, the question of why *trans*-**2** does not isomerize to *cis*-**2** and *cis*-**3** to the *trans*-**3** remains to be addressed. First, the guests are hydrophobic and are poorly soluble in water; only the *cis* isomer that is liquid can be readily dispersed in water. Furthermore, ^{1}H NMR spectra of the solutions before and after irradiation did not show the presence of free **2** and **3** in solution. These results led us to conclude that photoisomerization does not occur outside the capsule.

We believe that enrichment of the *trans* in **2** and the *cis* in **3** can be rationalized on the basis of the well-established Hammond postulate using the diagrams displayed in Figure 2.[36,37] The main assumption is excited molecules enter the ground surface at the 90° twisted geometry. In the case of **2**, when the excited state enters the ground surface it would be on the *trans*-slanting side favoring the formation of the *trans* isomer. In the case of **3**, entry would be on the *cis*-slanting side which would favor *cis*. Most likely the free space plays a minor role in the selectivity. Examination of Figure 1 reveals that in the case *cis*-**2** and *cis*-**3** the free space around one of the phenyl rings is similar, yet *cis*-**3** does not isomerize to the *trans*. Whether there are any barriers for torsional motion in the excited state can only be revealed via ultrafast studies which are underway.[35]

The current study has established that photoisomerization of stilbenes and 1,2-diphenyl cyclopropane is selective within the OA capsule. As illustrated with 4,4′-dimethyl and 4-propyl stilbenes, a small change in the alkyl substituent can direct the photoisomerization toward the opposite isomer. A similar dramatic shift in the pss was also observed with 1,2-diphenylcyclopropane. Results presented with stilbenes and diphenylcyclopropane highlight the importance of considering the reactant (guest) and the host as a whole (supramolecule) while visualizing the photochemical behavior of a guest included in a capsule. The impressive alkyl group (dimethyl vs *n*-propyl) dependent pss composition in OA exhibits resemblance to the highly selective photoisomerization of protein embedded substrates.[6,7]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01176.

> Experimental and computational details, absorption spectra, titration of guest to the host and competition for OA host between *cis* and *trans* isomers-all followed by NMR (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: murthy1@miami.edu.

ORCID

Rajeev Prabhakar: 0000-0003-1137-1272
V. Ramamurthy: 0000-0002-3168-2185

Notes

The authors declare no competing financial interest.

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