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Unidirectional Photoinduced Shuttling in a Rotaxane with a Symmetric Stilbene Dumbbell**

Carol A. Stanier, Sara J. Alderman, Tim D. W. Claridge, and Harry L. Anderson*

Dedicated to Professor Fraser Stoddart on the occasion of his 60th birthday

A molecular machine is a molecular or supramolecular structure in which the components can be forced to move past each other, to achieve a functional outcome.[1–3] New insights into biological molecular motors[1] have stimulated a surge of activity towards the construction of artificial molecular machines.[2–11] Rotaxanes feature prominently among these prototypes, because they offer the possibility of long-range translational motion of a threaded macrocycle "shuttle" along the length of a dumbbell "rail track".[3–11] This shuttling motion can be driven chemically,[4] electrochemically,[5] or photochemically.[6–11] Use of light as the external stimulus or power source is particularly appealing because it can lead to a fast response without forming by-products. Light-driven translational motion has been achieved in rotaxanes using photoinduced electron transfer,[5, 6] excited-state changes in hydrogen-bonding,[7] and *E*/*Z* photoisomerization of azobenzene dumbbells.[8–11] Here we report the photochemical behavior of the azobenzene and stilbene rotaxanes shown in Scheme 1.[12] One of the stilbene rotaxanes (**3** ⊂ α-CD) exhibits unprecedented unidirectional shuttling, with the asymmetry of the cyclodextrin macrocycle determining its direction of motion on a symmetric dumbbell. Comparison of the *E*/*Z* photoisomerization of all four rotaxanes provides some general insights into the workings of a rudimentary molecular machine.

The *E*/*Z* photoisomerism of azobenzene rotaxane **1** ⊂ TM-α-CD, and its dumbbell analogue **1**, were investigated by monitoring the change in absorption during irradiation of the *E* isomers at 361 nm.[13] The dumbbell compound *E*-**1** underwent rapid photoisomerization to give a photostationary *E*/*Z* mixture characterized by the rise of a new absorption maximum at 255 nm, and a decrease in absorption at 361 nm; the photostationary equilibrium can be shifted back towards the *E* isomer by irradiation at 255 nm and displays excellent reversibility. In contrast, irradiation of rotaxane *E*-**1** ⊂ TM-α-CD under identical conditions results in no change in absorption. The cyclodextrin completely prevents $E \rightarrow Z$ photoisomerization. This may seem surprising, as

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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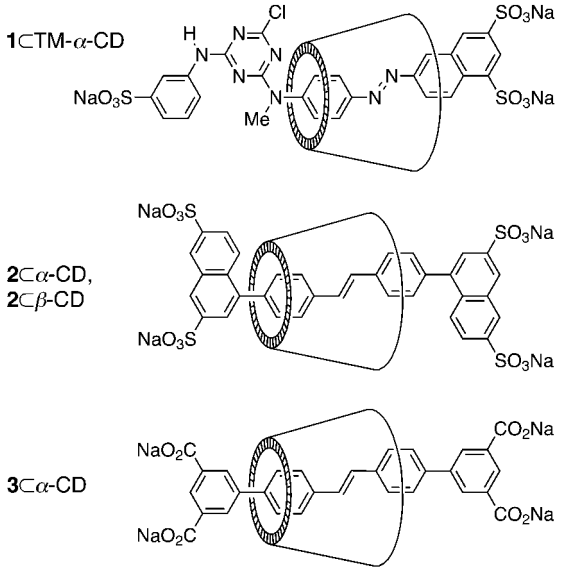


Scheme 1. Structures of rotaxanes studied. α-CD = α-cyclodextrin, β-CD = β-cyclodextrin, and TM-α-CD = hexakis(2,3,6-tri-*O*-methyl)-α-cyclodextrin. The cyclodextrins are drawn with a wide 2,3-rim and a narrow 6-rim; **1** ⊂ TM-α-CD is a single isomer. Compounds **1**, **2**, and **3** are the free dumbbells.[12]

azobenzene is known to photoisomerize in its α-CD inclusion complex,[14] and in Nakashima's rotaxane,[8] but these systems provide more freedom for translational motion and allow the azobenzene to move partly out of the cavity prior to photoisomerization, whereas in *E*-**1** ⊂ TM-α-CD it is difficult for the cyclodextrin to move away from the azo unit.

Next we turned our attention to the stilbene-based rotaxanes. The photochemistry of stilbenes is well studied,[15] but, as far as we know, there is no work on the photochemistry of stilbene rotaxanes.[16] Compounds **2** ⊂ β-CD, **3** ⊂ α-CD, **2**, and **3** all undergo reversible *E*/*Z* photoisomerization.[13] Irradiation at 340 nm generates the *Z* isomer, which leads to a decrease in absorption at around 340 nm and an increase in the absorption at 265 nm; irradiation at 265 nm shifts the system back towards the *E* isomer, as illustrated in Figure 1. No photoisomerization was detected with *E*-**2** ⊂ α-CD, which reflects the fact that it is the most tightly constrained of these three rotaxanes: the smaller endgroups in **3** ⊂ α-CD allow the cyclodextrin to shift away from the center of the stilbene unit, and the larger cyclodextrin in **2** ⊂ β-CD also gives the stilbene unit more space to move.[17] Prolonged irradiation leads eventually to irreversible degradation. NMR and mass spectrometric analysis of the products from prolonged irradiation of **3** showed the presence of the expected cyclobutane, as well as the hydrated stilbene unit.[18] Under the same conditions the rotaxane **3** ⊂ α-CD does not form any cyclobutane, and photohydration is about five times slower than with the dumbbell **3**, but gives a mixture of diastereomers.[19] Thus encapsulation enhances the fatigue-resistance of the chromophore.

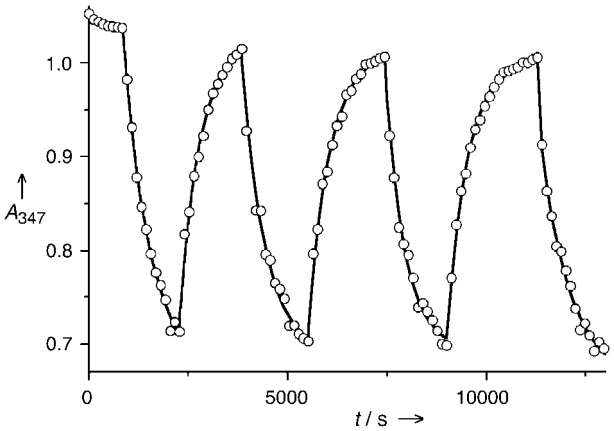
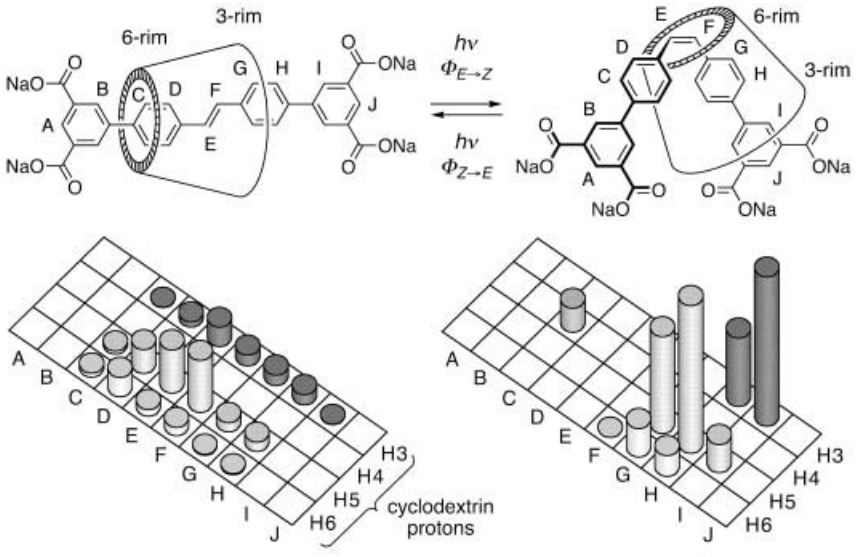


Figure 1. Plot of absorption at 347 nm versus time during alternating irradiation of an aqueous solution of **3** ⊂ α-CD at λ = 265 nm and λ = 347 nm.

The shuttling motion accompanying *E*/*Z* isomerization of **3** ⊂ α-CD is revealed by the pattern of NOEs for each isomer (Scheme 2).[20] Each rotaxane gives ten ^{1}H NMR resonance signals (arising from $H_A - H_J$) in the aromatic region, because of the asymmetry of the cyclodextrin.[12b] In the *E* isomer, many NOEs are observed from protons $H_C - H_I$ on the dumbbell to the internal protons H3, H5, and H6 of the cyclodextrin. This set of NOEs is not consistent with any single static geometry, and shows that the cyclodextrin rapidly glides up and down the dumbbell. A completely different pattern of NOEs is observed in the *Z* isomer; here the NOEs are much stronger and more selective. Only one end of the dumbbell ($H_G - H_I$) makes contact with the internal surface of



Scheme 2. Photoisomerization of *E*-**3** ⊂ α-CD to *Z*-**3** ⊂ α-CD, and key NOEs observed in these two isomers between $H_A - H_J$ of the dumbbell and H3 – H6 of the cyclodextrin; H3 and H5 are internal protons near the wide and narrow rim, respectively, H4 is on the external surface and H6 is on the narrow rim. The height of each column indicates the strength of the NOE (determined from the integrated NOE intensities, see Supporting Information).

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the cyclodextrin. An NOE is also observed between H_C, on the other end of the dumbbell, and H4, on the external surface of the cyclodextrin. All these NOEs are consistent with the geometry of the *Z* isomer shown in Scheme 2, with the *cis* alkene unit near the 6-rim of the cyclodextrin. Strong support for this geometry comes from the observation of NOEs from H_F to H6 (but not to H3), and from H_I to H3 (but not to H6). The alternative co-conformer, with the 6-rim of the cyclodextrin near an endgroup, is not detected. Although we do not yet know the origin of this remarkable directionality, we believe it could be useful in the construction of molecular machines; for example, it might enable cyclodextrins to be propelled in one direction along a polymer thread.

The kinetics of photoisomerization of **3** $\subset$ α-CD and **3** were investigated to determine the quantum yields for $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerization, $\Phi_{E\rightarrow Z}$ and $\Phi_{Z\rightarrow E}$ (Table 1).[21, 22]

Table 1. Photoisomerization and fluorescence quantum yields.[a]

Compound	$\Phi_{E\rightarrow Z}$	$\Phi_{Z\rightarrow E}$	$\Phi_{E,f}$
3 $\subset$ α-CD	0.06	0.71	0.94
3	0.17	0.79	0.67

[a] In N_2-saturated aqueous solutions (concentration $< 10\ \mu M$). $\Phi_{E,f}$ is the fluorescence quantum yield of the *E* isomer ($\pm 10\%$).[12b] The estimated uncertainty in these photoisomerization quantum yields is $\pm 20\%$.[21]

The presence of the cyclodextrin reduces $\Phi_{E\rightarrow Z}$ in the rotaxane to about a third of the value in the free dumbbell, while having no significant effect on $\Phi_{Z\rightarrow E}$. This result indicates that in the *E* isomer, the mobile cyclodextrin spends a third of its time sufficiently far from the center of the stilbene unit to permit *E*/*Z* photoisomerization. It appears that when the cyclodextrin sits directly over the alkene, it blocks photoisomerization by increasing the barrier for conversion of the initially formed S_1 state into the twisted p state.[23] Thus the decrease in $\Phi_{E\rightarrow Z}$ is accompanied by an increase in the fluorescence quantum yield $\Phi_{E,f}$ (Table 1). An even larger increase in $\Phi_{E,f}$ occurs in *E*-**2** $\subset$ α-CD, where $\Phi_{E\rightarrow Z}$ becomes negligible.[12b]

Two mechanisms for photoinduced shuttling in a photoisomerizable rotaxane are shown in Figure 2. In this model, the macrocycle prefers to sit on the photoactive unit in the *E* isomer (A is lower in energy than C), but it prefers to sit near one end in the *Z* isomer (D is lower in energy than B). In route 1 (A $\rightarrow$ B $\rightarrow$ D) photoisomerization occurs while the cyclodextrin is sitting round the photoactive unit, which forces it to relocate, like the piston of an engine. In route 2 (A $\rightarrow$ C $\rightarrow$ D), the photoactive unit waits until thermal motion has relocated the macrocycle, then photoisomerizes to block its return. Both mechanisms might sometimes apply, but our results indicate that photoisomerizable rotaxanes, such as **3** $\subset$ α-CD and Nakashima's rotaxane,[8] operate by route 2 rather than route 1. This mechanism illustrates how molecular machines can differ from their macroscopic analogues by utilizing random thermal motion.[1b]

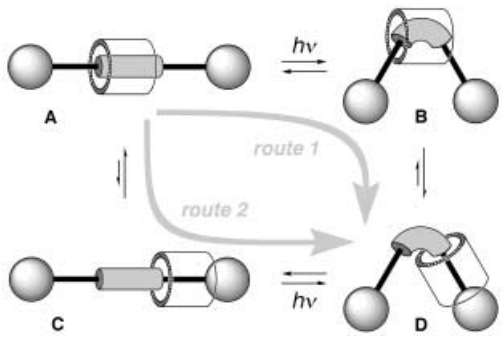

Figure 2. Two mechanisms for rotaxane photoisomerization. See text for details.

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[19] We have not detected phenanthrene formation from **3** or **3** $\subset \alpha$-CD, even after irradiation in the presence of iodine.

[20] We have been unable to separate the *E* and *Z* isomers of **3** $\subset \alpha$-CD. NOE measurements were carried out on a photogenerated mixture of both isomers, of known composition, which facilitates comparison of the strengths of NOEs in the two isomers; see Supporting Information.

[21] The ratios $\Phi_{E\rightarrow Z}/\Phi_{Z\rightarrow E}$ for **3** and **3** $\subset \alpha$-CD were evaluated from the *E*/*Z* ratios of their photostationary states. Values of $\Phi_{E\rightarrow Z}$ were obtained by comparing the initial rates of photoisomerization with that of *E*-stilbene in cyclohexane ($\Phi_{E\rightarrow Z} = 0.50$; S. Malkin, E. Fischer, *J. Phys. Chem.* **1964**, *68*, 1153 – 1163) during irradiation under identical conditions; see Supporting Information.

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[23] A similar reduction in $\Phi_{E\rightarrow Z}$ was reported in a cationic azobenzene rotaxane, compared to the free dumbbell, but in that case it was attributed to radiationless decay by charge-transfer states, rather than to steric hindrance.[9]

Samarium Diiodide-Induced Reductive Cross-Coupling of Nitrones with Aldehydes and Ketones**

Géraldine Masson, Sandrine Py,* and Yannick Vallée*

The use of nitrones as free-radical traps (spin traps) is well known. Nitrones have been designed to react with oxygen radicals to lengthen their half-lives and allow their detection in EPR studies.[1] They have also been used as in vivo protective agents against radicals generated by oxidative stress.[2] Surprisingly, nitrones have seldom been involved in radical reactions aimed to create C–C bonds,[3, 4] even though the addition of radicals to other C=N bonds is known.[5] We decided to explore the possibility of reductive cross-coupling between nitrones and carbonyl compounds, promoted by samarium diiodide, to produce vicinal amino alcohols. Vicinal amino alcohol fragments are common in natural products, and a preparation of these compounds by C–C bond formation (similar to the pinacol coupling reaction) is highly desirable.

The intramolecular reductive coupling of aldehydes or ketones with oximes,[6] hydrazones,[7] and imines[8] is well documented. These couplings have been accomplished with different degrees of stereoselectivity and generally yield the *trans* α-amino alcohol derivatives as the major products. The mechanism of this reaction is generally assumed to involve the initial formation of a ketyl radical by a single electron tranfer (SET) from the reducing agent, followed by its addition to the C=N double bond.

The intermolecular cross-coupling of C=O and C=N groups, on the other hand, has been far less successful in the past because of competitive homocoupling or formation of reduction products. Pedersen and Roskamp[9] used $NbCl_3 \cdot$ DME as a two-electron reducing agent to synthesize efficiently a variety of amino alcohols from the corresponding aldimines and ketones or aldehydes. The method was less efficient with aliphatic imines, and it failed with sterically hindered substrates. Electroreductive methods have also been employed to couple carbonyl compounds with aromatic aldimines, aliphatic aldoximes and ketoximes, and nitrones.[10] Samarium(II) diiodide (SmI_2) is another reducing agent which has been used with varying degrees of success in reductive cross-couplings involving carbonyl compounds and imine derivatives. It was initially reported to give poor selectivity in reductive couplings involving imines,[11, 12] the main side reaction being reduction to the corresponding amines. SmI_2 was employed for the aminomethylation of aliphatic aldehydes and ketones with *O*-benzylformaldoxime in the presence of hexamethylphosphoramide (HMPA) and an alcohol (2 equiv), but this reaction could not be extended to other oximes.[13] The cross-coupling of aromatic aldimines with nonaromatic ketones could be induced by SmI_2 under mild conditions, provided that NiI_2 was used as an additive in the reaction mixture.[14] Recently, Taniguchi and Uemura showed that SmI_2-promoted reductive coupling of aromatic aldehydes and imine derivatives was an efficient and selective way to prepare vicinal amino alcohols, provided that the imine derivatives were aromatic *N*-sulfonylimines, as these substrates exhibit a suitable redox potential for selective cross-coupling.[15]

Here we disclose our preliminary results on SmI_2-induced cross-coupling of nitrones with aldehydes or ketones. Because of its good oxophilicity, samarium(II) diiodide was chosen as the SET reagent to mediate the reductive coupling of nitrones with carbonyl compounds. It was supposed that coordination of a samarium(III) ketyl radical to the oxygen atom of the nitrone and of the C=O group would favor the reaction and might induce good stereoselectivities in the coupling reactions.

To verify these assumptions we first conducted an intramolecular reaction by treating a 0.04 M solution of ketonitrone **1**[16] in THF with 2 equiv of SmI_2 at $-78\,^{\circ}C$ (Scheme 1). Cyclization proceeded rapidly (1 h) to yield 2-[benzyl(hydroxy)amino]-1-methylcyclohexanol (**2**) as a single diastereoisomer in almost quantitative yield. Moreover, treatment

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