Supramolecular control of the photochemistry of stilbenes by cyclodextrins

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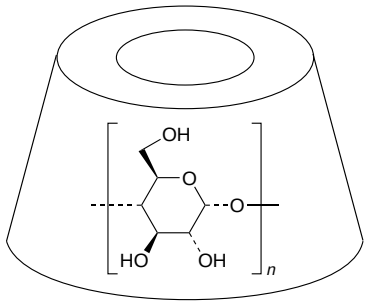
Upon UV irradiation in the presence of β-cyclodextrin, (*E*)-4,4′-bis(dimethylammoniomethyl)stilbene is transformed to the (*Z*)-isomer, but in the presence of γ-cyclodextrin only the [2 + 2]-cycloaddition products are obtained; the products are a molecular imprint of the cavity of the cyclodextrin.

Supramolecular assemblies are formed by the self organisation of complementary molecules, *e.g.* host and guest molecules.[1] They may show a high degree of short range order which allows chemical reactions to be performed with high specificity. Photochemical reactions can be especially well-controlled by supramolecular assembly of the reactive molecules as the close vicinity of the molecules makes the selective transformation of highly energetic intermediates possible.[2] Processes like energy[3] or electron transfer,[4] dimerisations[5–7] and polymerisations[8] have been successfully performed in organised media.[9] Here we report on the control of the photochemistry of stilbenes by inclusion in cyclodextrins.



1a *n* = 6
b *n* = 7
c in = *8*

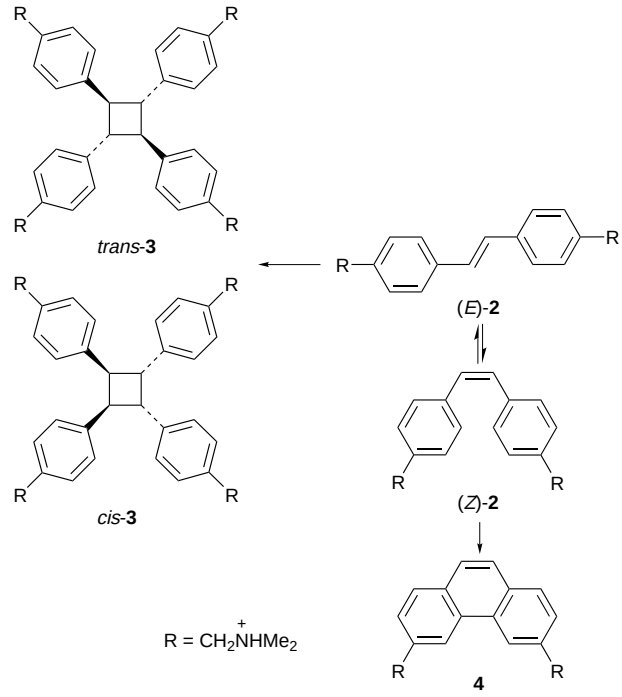
Cyclodextrins **1a**–**c** are torus shaped cyclic oligomers of glucose. They provide a hydrophobic cavity for the inclusion of hydrophobic guest molecules in aqueous solution.[10] The formation of ternary inclusion compounds of one cyclodextrin ring and two guests facilitates bimolecular reactions between the two guests:[11,12] the cyclodextrin ring acts like a molecular reaction vessel. Thus the photo-dimerisation of two anthracene,[13] acenaphthylene[14] or coumarin molecules[15] is accelerated by inclusion in **1c**. In contrast, the inclusion of stilbenes in **1b** leads to the prevention of the photo-dimerisation, as only one guest molecule is included.[16,17] Here the host **1b** seems to exert a shielding effect on the guest. We report on the influence of the ring size of a cyclodextrin on the photochemistry of the stilbene (*E*)-**2**. It is well suited for such investigations because of its high solubility in water.

The stilbene derivative[18] (*E*)-**2** was synthesised from 4,4-dimethylstilbene by bromination of the methyl groups and subsequent substitution with dimethylamine. UV irradiation† of an aqueous solution of [(*E*)-**2** afforded a mixture of products, mainly the (*Z*)-isomer (*Z*)-**2**, small amounts of the educt (*E*)-**2**, the tetraphenyl cyclobutanes *trans*-**3** and *cis*-**3** and phenanthrene **4**, as expected for stilbenes (Table 1 and Scheme 1).[19] The distribution of the products is dependent on the irradiation time (Fig. 1): the amount of the photo-stable products **3** and **4** increased with longer irradiation time.

Table 1 Distribution of products after the irradiation of (*E*)-**2** in aqueous solution with UV light (λ 312 nm) in the presence of cyclodextrins

		Content (%)				
Cyclodextrin	*t*/h	(*E*)-**2**	(*Z*)-**2**	*trans*-**3**	*cis*-**3**	**4**
none	24	10	62	7	2	19
1a	24	20	60	0	0	20
1b	24	16	83	0	0	1
1c	72	0	0	79	19	2

In the presence of hosts **1a** or **1b** the photo-dimerisation leading to cyclobutanes was totally restrained. Obviously, the stilbene moieties were shielded from each other by the formation of 1 : 1 inclusion compounds with **1a** or **1b**. Furthermore, inclusion in **1b** almost totally prevented the formation of phenanthrene **4**. Stilbenes **2** included in **1b** only show reversible photo-isomerisation with almost no side reactions. Consequently, **1b**–**2** is well suited for photo-switchable devices. In the presence of the larger host **1c**, the photo-dimerisation was found to be strongly favoured. After long irradiation times, high yields (up to 98%) of the cyclobutanes **3** were found (Table 1). For shorter times the (*Z*)-isomer (*Z*)-**2** of the educt appeared in the product mixture as an intermediate. Moreover, the presence of **1c** led to an increase of the rate of consumption of **2e**, *e.g.* after 1 h the product mixture contained 24% (44%) of (*E*)-**2** in the presence



Scheme 1

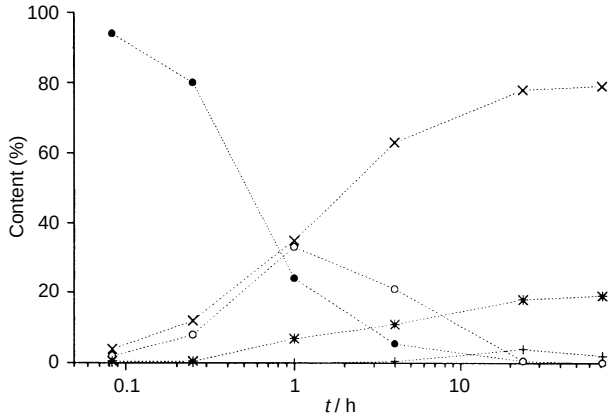


Fig. 1 The time dependence of the product distribution after irradiation of (*E*)-**2** in the presence of **1c**: (●) (*E*)-**2**, (○) (*Z*)-**2**, (×) *trans*-**3**, (∗) *cis*-**3** and (+)-**4**

Table 2 Thermodynamic parameters for the inclusion of the guests in cyclodextrins as determined by microcalorimetric titration (1 cal = 4.184 J)

	K_s/ dm³ mol	$-\Delta G°_m'$/ kcal mol^{-1}	$-\Delta H°_m'$/ kcal mol^{-1}	$T\Delta S°_m'$/ kcal mol^{-1}
1a–(*E*)-**2**	1520 ± 50	4.3	6.4 ± 0.1	−2.1
1a–(*Z*)-**2**	360 ± 110	3.5	1.9 ± 1.5	1.6
1b–(*E*)-**2**	705 ± 20	3.9	2.7 ± 0.1	1.2
1b–(*Z*)-**2**	540 ± 220	3.7	9.7 ± 8.4	−6.0
1c–(*E*)-**2**	385 ± 10	3.5	1.1 ± 0.3	2.4
1c–[(*E*)-**2**]$_2$	2730 ± 60	4.7	7.2 ± 0.1	−2.5
1c–*trans*-**3**	18 000 ± 6600	5.8	7.1 ± 1.2	−1.3
1c–*cis*-**3**	520 ± 700	3.7	−5.4 ± 11.0	9.1

(absence) of host **1c**. The selective formation of cyclobutanes **3** upon addition of **1c** was attributed to the preceding formation of the ternary inclusion compound **1c**–**2**$_2$. The close proximity of the two included stilbenes should strongly favour the [2 + 2] addition.

To confirm this assumption we investigated‡ the formation of inclusion compounds of stilbenes **2** by microcalorimetric titration.[20] Indeed, host **1c** includes two molecules of **2**. The binding constant for the formation of **1c**–**2**$_2$ is relatively high compared to the literature values for other guest molecules (Table 2).[21] In contrast, we observed the formation of 1 : 1 inclusion compounds of **2** in hosts **1a** and **1b**. For the smallest host **1a**, the inclusion enthalpy is strongly negative for (*E*)-**2**, accompanied by a loss of entropy which is typical for a rather tight axial inclusion compounds **1a**–(*E*)-**2**.[22] On the other hand, the formation of inclusion compound **1b**–(*E*)-**2** has a low enthalpy gain but also some entropy gain. These findings are attributed to the formation of a loose complex as guest (*E*)-**2** is too slim to completely fill the cavity of **1b**. Turro drew the same conclusion from fluorescence lifetime measurements.[23] In contrast, isomer (*Z*)-**2** is tightly bound by **1b**, presumably in a non-axial arrangement, as Ramamurthy has postulated.[17]

Consequently, the photo-dimerisation of stilbenes **2** is hindered by a 1 : 1 inclusion in hosts **1a** and **1b** but enhanced by an 1 : 2 inclusion in host **1c**. An excited stilbene in **1c**–[(*E*)-**2**]$_2$ can react rapidly with its neighbour. Furthermore, we found that dimerisation products **3**, especially *trans*-**3**, form stable 1 : 1 inclusion compounds with **1c**. The inclusion of *trans*-**3** is accompanied by an enthalpy gain and an entropy loss, typical of a tight fit between host and guest. Consequently, in the presence of hosts **1b** and **1c** the formation of the photo-product with the highest affinity towards the host was favoured most. The main photo-product is therefore a molecular imprint (replica) of the host.[24] The principle might be further exploited for the targeted photochemical synthesis of other molecules. The photo-chemical synthesis of poly(rotaxane)s is the subject of our current research.

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Footnotes and References

† A solution of (*E*)-**2**·(HCl)$_2$ (0.01 mol dm^{-3}; 10 cm³) was irradiated with UV light (λ 312 nm, source type D89008, 6 W, Bioblock Scientific, Illkirch Cedex, France) for 0.08, 0.25, 1.00, 5.00, 24.00 and 72 h. Afterwards, the solution was brought to pH 10 by addition of NaOH (2 mol dm^{-3}) and **2**–**4** were extracted with $CHCl_3$. The product distribution was determined by integration of the ^{1}H NMR signals of the crude product in $CDCl_3$. *Selected data* for (*E*)-**2** δ_H ($CDCl_3$, 400 MHz) 2.26 (s, 12 H, CH_3), 3.44 (s, 4 H, CH_2), 7.10 (s, 2 H, =CH), 7.30 (d, *J* 8.4, 4 H, ArH), 7.47 (d, *J* 7.9, 4 H, ArH). For (*Z*)-**2**: δ_H 2.23 (s, 12 H, CH_3), 3.37 (s, 4 H, CH_2), 6.56 (s, 2 H, =CH), 7.15 (d, *J* 8.0, 4 H, ArH), 7.21 (d, *J* 8.0, 4 H, ArH). For *trans*-**3**: δ_H ($CDCl_3$, 400 MHz) 2.17 (s, 24 H, CH_3), 3.30 (s, 8 H), 4.42 (s, 4 H, CH), 7.04 (s, 16 H, ArH). For *cis*-**3**: δ_H ($CDCl_3$, 400 MHz) 2.26 (s, 24 H, CH_3), 3.40 (s, 8 H, CH_2), 3.63 (s, 4 H, CH), 7.23 (s, 16 H, ArH). For **4**: δ_H ($CDCl_3$, 400 MHz) 2.32 (s, 12 H, CH_3), 3.69 (s, 4 H, CH_2), 7.57 (d, *J* 7.9, 2 H, ArH), 7.70 (s, 2 H, ArH), 7.84 (d, *J* 7.9, 2 H, ArH), 8.62 (s, 2 H, ArH).

‡ The microcalorimetric titrations were carried out using a Microcal Omega Titration Calorimeter, MicroCal Inc., Northampton Massachusetts. A solution of cyclodextrin (0.002 mol dm^{-3}; 1.336 cm³) was titrated with 20 portions of guest (0.045 mol dm^{-3}; 5 μl) ammonium acetate buffer (pH 5.7; 0.1 mol dm^{-3}) at 25 °C. The interaction heat data were fitted to models for either 1 : 1 or stepwise 1 : 2 inclusion processes by the program Origin ITC, MicroCal Inc. The binding constants and enthalpies were obtained as fitting parameters. We could not isolate pure (*Z*)-**2**. Thus we used a mixture of (*Z*)-**2** (64%) and (*E*)-**2** (36%) for the inclusion experiment and the data were fitted to the model 'two sets of sites' of the program package Origin ITC. This procedure was also applied for the mixture of *trans*-**3** (79%) and *cis*-**3** (21%).

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