Original Article

Cyclodextrin Complexation of the Stilbene 4-(2-(4-*Tert*-butylphenyl)ethen-1-yl)-benzoate and the Self-assembly of Molecular Devices

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Abstract

E-4-(2-(4-*tert*-butylphenyl)ethen-1-yl)benzoate, *E*-1^-, photoisomerizes to the *Z*-1^- isomer and *vice versa* in the free state and in the binary complexes **2**·*E*-1^-, **2**·*Z*-1^-, **3**·*E*-1^- and **3**·*Z*-1^- where **2** is the urea-linked cyclodextrin *N*-(6^A-deoxy-α-cyclodextrin-6^A-yl)-*N*′-(6^A-deoxy-β-cyclodextrin-6^A-yl)urea and **3** is *N*,*N*-bis(6^A-deoxy-β-cyclodextrin-6^A-yl)urea. In **2**·*E*-1^- and **3**·*E*-1^- the stilbene occupies both cyclodextrin (CD) components of **2** and **3**, whereas in **2**·*Z*-1^- and **3**·*Z*-1^- it only occupies one CD component while the other CD component is unoccupied. 4-*tert*-Butylphenolate, 4^-, and its carboxylate, 5^-, and sulfonate, 6^-, analogues form the ternary complex **2**·*Z*-1^-·4^- and its analogues and also **3**·*Z*-1^-·4^- and its analogues. These photoisomerize to **2**·*E*-1^- and **3**·*E*-1^- and either free 4^-, 5^- or 6^- and thereby function as molecular devices.

Introduction

The interactions of hydrophobic guests with native cyclodextrins and modified cyclodextrins have been extensively explored [1, 2] and raise the possibility of the self-assembly of complexes which may be switched between two states at will and thereby constitute molecular devices [3]. One way in which this might be achieved is to amplify a simple transformation such as an isomerization about a double bond within a binary complex. This we have sought to do through the complexation of *E*- and *Z*-4-(2-(4-*tert*-butylphenyl)-ethen-1-yl)benzoate, *E*-1^- and *Z*-1^-, by the urea linked cyclodextrins, *N*-(6^A-deoxy-α-cyclodextrin-6^A-yl)-*N*′-(6^A-deoxy-β-cyclodextrin-6^A-yl)urea, **2**, and *N*,*N*-bis(6^A-deoxy-β-cyclodextrin-6^A-yl)urea, **3** [4] (Scheme 1). Thus, isomerization of *E*-1^- and *Z*-1^- within the binary complexes **2**·*E*-1^- and **2**·*Z*-1^- and in **3**·*E*-1^- and **3**·*Z*-1^- may produce the desired two states of a molecular device which performs a specific function. As stilbenes are subject to photoisomerization [5], we have studied this aspect of *E*-1^- and *Z*-1^- and the extent to which their complexes act as molecular devices.

Experimental

General

^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were run on a Varian Gemini 300 spectrometer and chemical shifts were referenced against internal TMS in CDCl$_3$ and against the ^{1}H residue multiplet ($\delta = 2.49$ ppm) the solvent ^{13}C multiplet ($\delta = 39.5$ ppm) in d_6-DMSO. ^{1}H (600 MHz) NMR spectra were run on a Varian Inova 600 spectrometer and chemical shifts were referenced against the HOD resonance ($\delta = 4.72$ ppm). ESI-MS studies were made in positive ion mode with a Finnigan MAT ion trap LC-Q mass spectrometer fitted with an electrospray ionization source. Accurate mass spectrometry was carried out at the University of Tasmania, Hobart. ESI-MS samples were dissolved in water for injection. Infrared spectra were recorded on an ATI Mattson Genesis FT-IR. The abbreviations strong (s), medium (m), weak (w) and broad (b) are used for reporting the intensity of the bands observed. UV/VIS spectra were recorded on a Cary 300 Bio spectrophotometer. Irradiation of solutions of the *E*-1^- and *Z*-1^- complexes were carried out in a quartz cuvette in a Perkin Elmer LS50B fluorimeter. Elemental analyses were performed by the Microanalytical Service of the Chemistry Department, University of Otago, Dunedin, New Zealand. α-CD and β-CD (Nihon Shokhuin Kako Co.) were dried by heating at 100 °C under vacuum for

E-1⁻

αCD; X = OH, n = 1
βCD; X = OH, n = 2
2; n =1
3; n = 2
and for both **2** and **3**,

X =
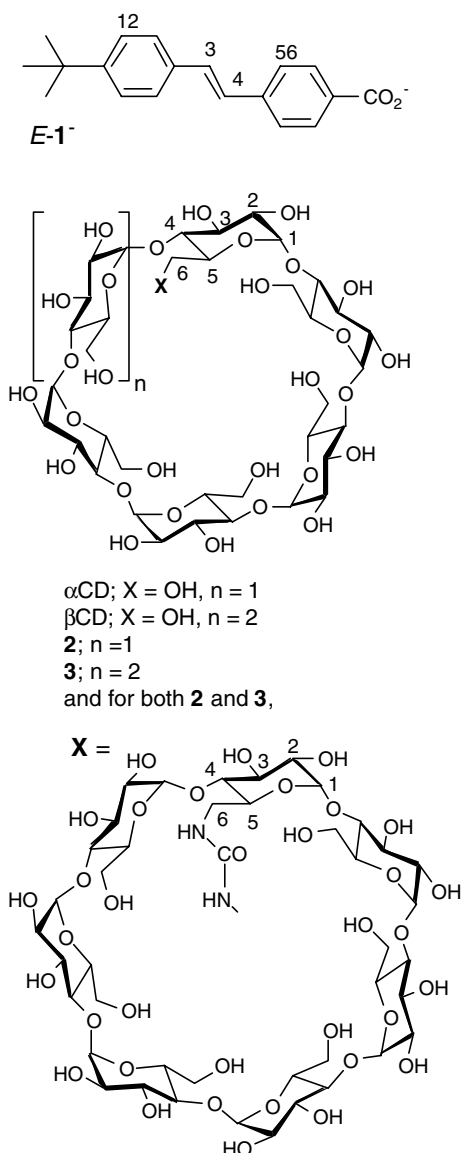
Scheme 1. The numbering shown for *E-1⁻* corresponds to the numbering of resonances in its ¹H NMR spectrum.

18 h. Both **2** and **3** were prepared as previously described [4]. The solvents used in syntheses were redistilled and dried by standard methods [6].

*Preparation of methyl E- and methyl Z-4-(2-(4-*tert-*butylphenyl)ethen-1-yl)benzoate*

(a) 4-*tert*-Butylbenzylbromide (0.992 g, 4.37 mmol) and triphenylphosphine (1.34 g, 5.11 mmol) were added to dry benzene (12 cm³) and stirred under nitrogen at room temperature for 72 h. Toluene was removed under reduced pressure and the solid product was washed several times with hexane to give 4-*tert*-butylbenzyl(tri-phenyl)phosphonium bromide as white crystals (1.87 g, 87%), δ_H(CDCl₃) 7.60–7.78 (m, 15H, PPh₃); 7.14 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 2H, ArH); 7.05 (d, $J = 8.4$ Hz, 2H, ArH); 5.31 (d, $J = 13.8$ Hz, 2H, CH₂P); 1.23 (s, 9H, C(CH₃)₃).

(b) A solution of sodium methoxide was prepared by adding sodium (0.115 g, 5.0 mmol) to dry methanol (2.7 cm³). After dissolution of the sodium, the solution was added dropwise to 4-*tert*-butylbenzyl(tri-phenyl)phosphonium bromide (1.03 g, 2.1 mmol) in methanol (5.5 cm³) at 0 °C. The solution was stirred at 40–45 °C for 40 min, then cooled to 0 °C, and a solution of 4-formylmethyl benzoate (0.298 g, 1.82 mmol) in methanol (3.5 cm³) was added dropwise. Once the addition was complete, the mixture was refluxed for 3.5 h. The solution was cooled to 0 °C and concentrated hydrochloric acid (0.55 cm³) was added dropwise. The resulting precipitate (which was mostly methyl *E*-4-(2-(4-*tert*-butylphenyl)ethen-1-yl)benzoate was filtered by vacuum filtration and washed with 10% sodium bicarbonate solution (10 cm³), water (2 × 10 cm³) and methanol (2 × 10 cm³). Further purification was achieved by flash column chromatography (5% ethyl acetate/hexane) to give methyl *E*-4-(2-(4-*tert*-butylphenyl)ethen-1-yl)benzo-ate as white crystals (0.202 g, 38%), mp 145–147 °C; FAB-MS m/z 294.4 (M⁺); [Found: C, 81.59; H, 7.53%. Calcd. C, 81.64; H 7.54%]; δ_H(CDCl₃) 8.16 (d, $J = 4.2$ Hz, 2H, ArH6); 7.55 (d, $J = 4.2$ Hz, 2H, ArH5); 7.40 (δ_A), 7.47 (δ_B) (ABq, $J = 9.0$ Hz, 4H, ArH1,2); 7.21 (d, $J = 16.2$ Hz, 1H, C=CH); 7.08 (d, $J = 16.2$ Hz, 1H, C=CH); 3.92 (s, 3H, CH₃—O); 1.33 (s, 9H, C(CH₃)₃); δ_C(CDCl₃) 166.87 (C=O); 151.52, 142.09, 134.01, (ArC); 131.10 (C=C); 129.99, 128.74 (ArC); 126.81 (C=C); 126.55, 126.19, 125.70 (ArC); 51.97 (CH₃—O); 34.67 (C(CH₃)₃); 31.24 (C(CH₃)₃); ν_{max} (Nujol/cm⁻¹) 1718 s (C=O); 1599 m (C=C); 1502 w (Ar); 849 (Ar).

The filtrate remaining after precipitation of methyl *E*-4-(2-(4-*tert*-butylphenyl)ethen-1-yl)benzoate contained mainly the *Z*-isomer. This was concentrated and the residue was extracted with toluene (15 cm³), ethyl acetate (15 cm³) and chloroform (15 cm³). The solvents were removed under reduced pressure and the crude material was purified by flash column chroma-tography (2.5–5.0% ethyl acetate/hexane) to give methyl *Z*-4-(2-(4-*tert*-butylphenyl)ethen-1-yl)benzoate as a white sticky solid which was hydrolysed without further purification (0.110 g, 21%); FAB-MS m/z 295.4 (M + H⁺); δ_H(CDCl₃) 7.91 (d, $J = 8.1$ Hz, 2H, ArH6); 7.35 (d, $J = 8.1$ Hz, 2H, ArH5); 7.24 (d, $J = 8.4$ Hz, 2H, ArH); 7.16 (d, $J = 8.4$ Hz, 2H, ArH); 6.66 (d, $J = 12$ Hz, 1H, C=CH); 6.56 (d, $J = 12$ Hz, 1H, C=CH); 3.90 (s, 3H, CH₃—O); 1.29 (s, 9H, C(CH₃)₃); δ_C(CDCl₃) 166.94 (C=O); 150.69, 142.48, 133.64, (ArC); 132.05 (C=C); 129.50, 128.80, 128.58 (ArC); 128.51 (C=C); 125.19 (ArC); 51.96 (CH₃—O); 34.56 (C(CH₃)₃); 31.22 (C(CH₃)₃).

*Preparation of E-4-(2-(4-*tert-*butylphenyl)ethen-1-yl) benzoic acid, E-1H*

Methyl *E*-4-(2-(4-*tert*-butylphenyl)ethen-1-yl)benzoate (0.110 g, 0.374 mmol) was suspended in a mixture of ethylene glycol (3 cm³) and water (2 cm³) and sodium

hydroxide (0.250 g, 6.25 mmol) was added. The mixture was stirred at reflux (16 h), diluted with water (20 cm³) and heated further at reflux (1 h). After cooling the mixture to room temperature, it was acidified (concentrated hydrochloric acid) to pH 1. The product was extracted with ether (6 × 20 cm³), dried (sodium sulfate) and concentrated. The residue was dissolved in THF (1 cm³) and added dropwise to hexane (10 cm³), the precipitate was collected by vacuum filtration and washed with hexane (2 cm³) to give the product as white crystals (0.065 g, 62%), mp > 206 °C (decomposition); FAB-MS m/z 280.4 (M^+); [found: C, 81.61; H, 7.11%. Calcd. C, 81.31; H 7.19%]; δ_H(d_6-DMSO) 7.93 (d, $J = 8.1$ Hz, 2H, ArH6); 7.70 (d, $J = 8.1$ Hz, 2H, ArH5); 7.57 (d, $J = 8.4$ Hz, 2H, ArH2); 7.42 (d, $J = 8.4$ Hz, 2H, ArH1); 7.39 (d, $J = 16.5$ Hz, 1H, C=CH); 7.27 (d, $J = 16.5$ Hz, 1H, C=CH); 1.29 (s, 9H, C(CH₃)₃); δ_C(d_6-DMSO) 166.96 (C=O); 150.81, 141.50, 133.81 (ArC); 130.73 (C=C); 129.66, 129.24 (ArC); 126.51 (C=C, ArC); 126.5, 120.44 (ArC); 34.31 (C(CH₃)₃); 30.95 (C(CH_3)₃); ν_{max} (Nujol/cm⁻¹) 2500–2900b (OH), 1681s (C=O); 1601m (C=C); 1594w, 1502w (Ar); 850 (Ar) cm⁻¹.

Preparation of Z-4-(2-(4-tert-butylphenyl)ethen-1-yl)-benzoic acid, Z-1H

Methyl-Z-4-(2-(4-*tert*-butylphenyl)ethen-1-yl)benzoate (0.055 g, 0.186 mmol) was suspended in a mixture of ethylene glycol (1.5 cm³) and water (0.5 cm³) and sodium hydroxide (0.100 g, 2.50 mmol) was added. The mixture was stirred at reflux (5 h) in the dark, diluted with water (2 cm³) and heated further at reflux (1 h). After cooling the mixture to room temperature, it was acidified (concentrated hydrochloric acid) to pH 1. The precipitate was collected by vacuum filtration and washed with water (2 cm³) and cold ethanol (1 cm³) to give the product as a white powder (0.043 g, 82%), FAB-MS m/z 281.4 ($M + H^+$); [found: C, 79.79; H, 7.11%. Calc. for ($C_{19}H_{20}O_2$)₃H₂O, 79.67; H 7.27%]; δ_H(d_6-DMSO) 7.83 (d, $J = 8.1$ Hz, 2H, ArH6); 7.34 (d, $J = 8.1$ Hz, 2H, ArH5); 7.28 (d, $J = 8.4$ Hz, 2H, ArH1); 7.14 (d, $J = 8.4$ Hz, 2H, ArH2); 6.71 (δ_A), 6.62 (δ_B) (ABq, $J_{AB} = 12$ Hz, 2H, HC=CH); 1.24 (s, 9H, C(CH₃)₃); δ_C(d_6-DMSO) 167.08 (C=O); 150.13, 141.49, 133.34 (ArC); 131.43 (C=C); 129.83, 129.33 (ArC); 128.55 (C=C); 128.42, 128.30, 125.08 (ArC); 34.25 (C(CH₃)₃); 30.96 (C(CH_3)₃).

Results and discussion

The isomerization of E-1⁻ and Z-1⁻. The preparation of 4-(2-(4-*tert*-butylphenyl)ethen-1-carboxylic acid, yields both *E*-1H and *Z*-1H isomers which may be separated through a combination of fractional crystallization and chromatography as described in the Experimental section. Both isomers have a very low water solubility, but

are more soluble when deprotonated to give *E*-1⁻ and *Z*-1⁻. For convenience, their UV–VIS spectra are shown in their 2·*E*-1⁻ and 2·*Z*-1⁻ binary complexes (to which their free state spectra are very similar) in figure 1. Irradiation of *E*-1⁻ at 340 nm and of *Z*-1⁻ at 275 nm produces photostationary states between the isomers dominated by *Z*-1⁻ and *E*-1⁻, respectively. Switching between the two photostationary states is achieved by irradiation at these wavelengths. Similar UV–VIS absorption changes occur for 3·*E*-1⁻ and 3·*Z*-1⁻ and
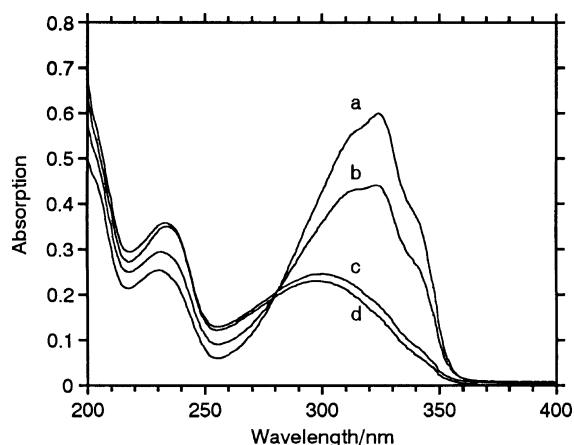

Figure 1. The UV–visible spectral variation accompanying changes in the position of equilibrium between *E*-1⁻ and *Z*-1⁻ for an aqueous:methanol, 97.5:2.5%, v/v solution in which total [*E*-1⁻ and *Z*-1⁻], [2] and [NaOH] = 1.8×10^{-5}, 2.3×10^{-5} and 1.2×10^{-4} mol dm⁻³, respectively. (a) Initially prepared solution where the stilbene was exclusively *E*-1⁻. (d) Initially prepared solution where the stilbene was exclusively *Z*-1⁻. The spectra (b) and (c) are those of photostationary equilibria between *E*-1⁻ and *Z*-1⁻ after irradiation of either solution (a) or (d) for 3.5 h at 275 and 340 nm, respectively.
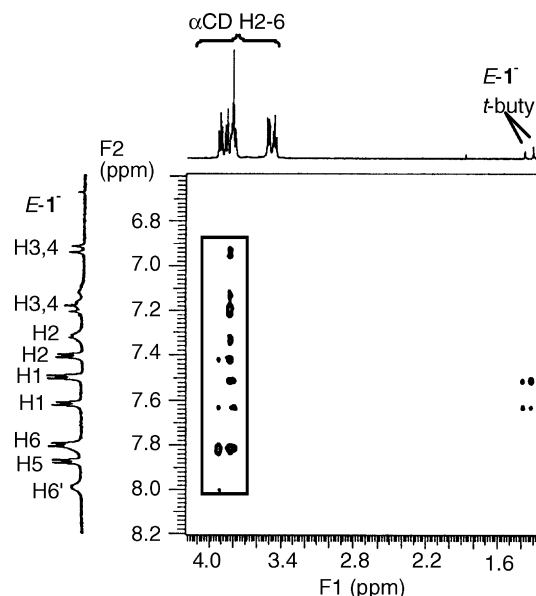

Figure 2. ¹H 600 MHz ROESY NMR spectrum at 298 K of a D₂O solution in which total [α-CD], [*E*-1⁻] and [NaOD] = 0.010, 0.0034 and 0.15 mol dm⁻³, respectively. The cross-peaks enclosed in the rectangles arise from dipolar interactions between the protons indicated on the F1 and F2 axes.
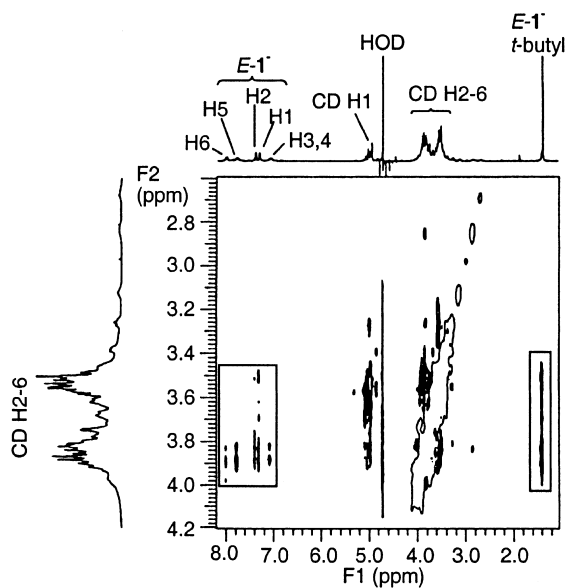
Figure 3. ^{1}H 600 MHz ROESY NMR spectrum at 298 K of a D$_2$O solution in which total [**2**], [*E*-**1**$^-$] and [NaOD] = 0.016, 0.015 and 0.15 mol dm^{-3}, respectively. The cross-peaks enclosed in the rectangles arise from dipolar interactions between the protons indicated on the F1 and F2 axes.
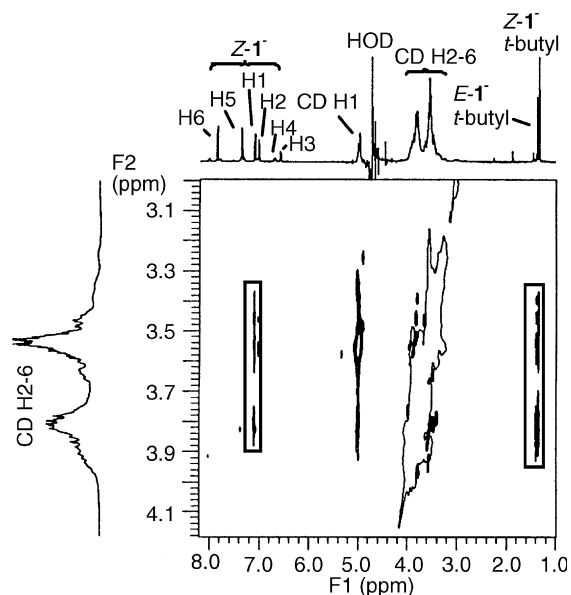

Figure. 4. ^{1}H 600 MHz ROESY NMR spectrum at 298 K of the same solution as in Figure 3 after 24 h exposure to daylight in an NMR tube. The **2**·*E*-**1**$^-$ to **2**·*Z*-**1**$^-$ ratio is 30:70. The cross-peaks enclosed in the rectangles arise from dipolar interactions between the protons of **2** and *Z*-**1**$^-$indicated on the F1 and F2 axes. Some of the cross-peaks arising from **2**·*E*-**1**$^-$ also appear within the rectangles, but are of lesser intensity.
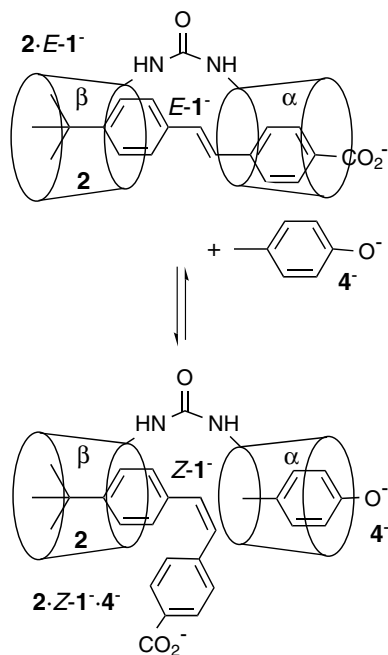
Scheme 2. Photoisomerization to give photostationary states in which **2**·*E*-**1**$^-$ and **2**·*Z*-**1**$^-$ dominate under 275 and 340 nm, respectively. The vacated α-CD component annulus of **2**·*Z*-**1**$^-$ may be occupied by 4-methylphenolate, **4**$^-$, to form **2**·*Z*-**1**$^-$·**4**$^-$ but does not enter the α-CD component annulus of **2**·*E*-**1**$^-$. Both **2**·*Z*-**1**$^-$·**5**$^-$ and **2**·*Z*-**1**$^-$·**6**$^-$ are similarly formed as are the analogous complexes of **3**.

for both systems in the presence of **4**$^-$, **5**$^-$ and **6**$^-$, as is also the case for the α-CD and β-CD complexes of *E*-**1**$^-$ and *Z*-**1**$^-$. This is consistent with complexation having little effect on the photoisomerization. Daylight irradi-

ation in Pyrex vessels (which cut out most light with $\lambda \le 300$ nm) also causes photoisomerization to give a preponderance of the *Z*-**1**$^-$ isomer in the free state and when complexed by a cyclodextrin.

^{1}H NMR spectroscopic studies of the complexation of *E*-**1**$^-$ by α-CD and β-CD

Both *E*-**1**$^-$ and *Z*-**1**$^-$ are insufficiently soluble in D$_2$O for ^{1}H NMR spectra to be obtained. However, both are solubilized by α-CD, β-CD, **2** and **3** consistent with the formation of complexes, but to obtain sufficiently high concentrations to give good signal to noise ratios for their ^{1}H NMR spectra a [NaOD] = 0.15 mol dm^{-3} was required. This may indicate that it is necessary to deprotonate a CD hydroxy group (which is expected to have a p$K_a \ge 12$ on the basis that the pK_as of OH(2) and OH(3) are 12.33 for α-CD [1]) to increase solubility of the complexes.

The ^{1}H 600 MHz ROESY NMR spectrum of a solution in which total [α-CD], [*E*-**1**$^-$] and [NaOD] = 0.010, 0.0034 and 0.15 mol dm^{-3}, respectively, shows all of the *E*-**1**$^-$ resonances to be duplicated and cross-peaks arising from dipolar interactions of the *E*-**1**$^-$ aromatic protons and the H3, H5 and H6 protons of the interior of the α-CD annulus but only very weak cross-peaks are observed for the *E*-**1**$^-$ *t*-butyl protons (figure 2). This is consistent with α-CD being centered on the *E*-**1**$^-$ double bond in each of two α-CD·*E*-**1**$^-$ complexes in which the narrow end of the α-CD annulus
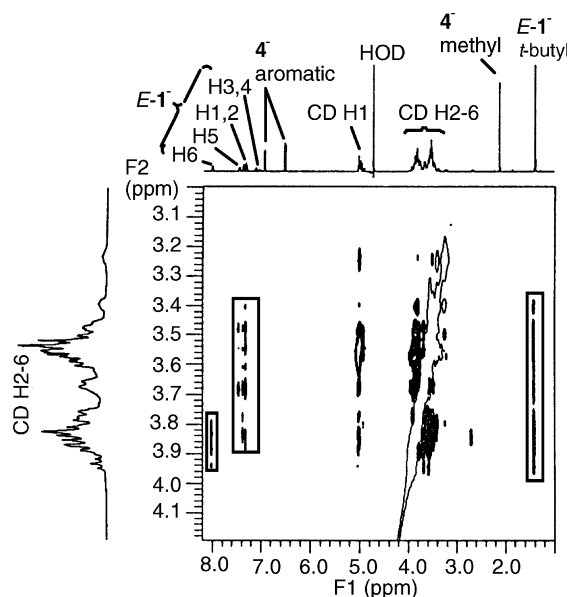
Figure 5. ^{1}H 600 MHz ROESY NMR spectrum at 298 K of a D$_2$O solution in which total [**3**], [*E*-**1**$^-$], [**4**$^-$] and [NaOD] = 0.016, 0.015, 0.024 and 0.15 mol dm^{-3}, respectively. The cross-peaks enclosed in the rectangles arise from dipolar interactions between the protons indicated on the F1 and F2 axes.

Figure 6. ^{1}H 600 MHz ROESY NMR spectrum at 298 K of a D$_2$O solution in which total [**3**], [*Z*-**1**$^-$], [**4**$^-$] and [NaOD] = 0.016, 0.015, 0.024 and 0.15 mol dm^{-3}, respectively. The cross-peaks enclosed in the rectangles arise from dipolar interactions between the protons indicated on the F1 and F2 axes.

is adjacent to either the 4-*tert*-butylphenyl or benzoate end of *E*-**1**$^-$. While the duplicated *E*-**1**$^-$ resonances are narrow at 298 K, they broaden with increasing temperature up to 323 K consistent with the exchange of *E*-**1**$^-$ between its two complexed environments. In contrast, the analogous spectrum of a D$_2$O solution in which total [β-CD], [*E*-**1**$^-$] and [NaOD] = 0.016, 0.015 and 0.15 mol dm^{-3}, respectively, shows cross-peaks arising from the aromatic H1 and H2 and *t*-butyl protons of *E*-**1**$^-$ and the H3, H5 and H6 protons of β-CD, but the *E*-**1**$^-$ resonances are not duplicated. This is consistent with β-CD being centered on the 4-*tert*-butylphenyl moiety of *E*-**1**$^-$ in a single β-CD·*E*-**1**$^-$ complex or of two such complexes with opposite β-CD orientations being in fast exchange.

^{1}H NMR studies of the complexation of E-1$^-$ and Z-1$^-$ by 2 and 3

The ^{1}H 600 MHz ROESY NMR spectrum of **2**·*E*-**1**$^-$ shows strong cross-peaks arising from dipolar interactions between all of the *E*-**1**$^-$ protons and the H3, H5 and H6 protons of the α-CD and β-CD component annuli of **2** (figure 3). As the above studies of the *E*-**1**$^-$ complexes indicate that α-CD is positioned away from the *t*-butyl group of *E*-**1**$^-$ in α-CD·*E*-**1**$^-$ whereas β-CD preferentially complexes the 4-*tert*-butylphenyl moiety of *E*-**1**$^-$ in β-CD·*E*-**1**$^-$, it is assumed that these preferences are also exercized in **2**·*E*-**1**$^-$ as shown in Scheme 2. In contrast, the ^{1}H 600 MHz ROESY NMR spectrum of the same solution after exposure to daylight for 24 h shows resonances arising from **2**·*E*-**1**$^-$ and **2**·*Z*-**1**$^-$ in the ratio 30:70 (figure 4). Strong cross-peaks arise from the *Z*-**1**$^-$ H1, H2 and *t*-butyl protons (and appear adjacent
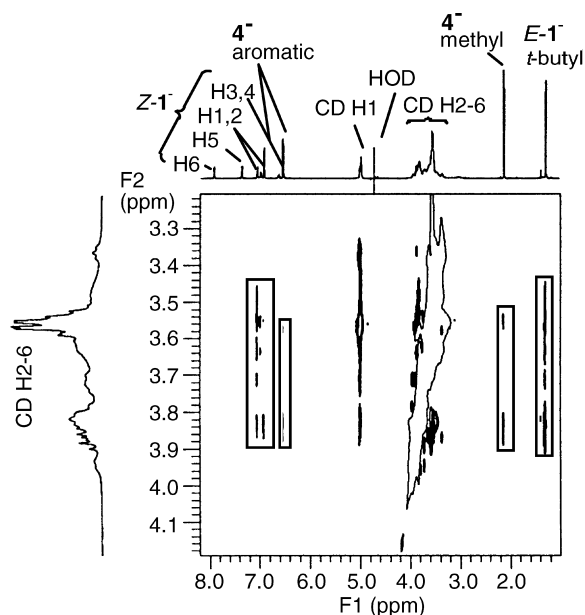
to the weaker *E*-**1**$^-$ H1, H2 and *t*-butyl proton cross-peaks) consistent with the 4-tert-butylphenyl moiety of *Z*-**1**$^-$ occupying the β-CD component annulus of **2** and the α-CD component annulus being vacated by the benzoate moiety as shown in Scheme 2. The much decreased *E*-**1**$^-$ H5 and H6 cross-peaks are also seen in Figure 4. Similar differences are observed between the analogous spectra of **3**·*E*-**1**$^-$ and **3**·*Z*-**1**$^-$.

In the presence of **4**$^-$, **5**$^-$ and **6**$^-$, no ^{1}H 600 MHz ROESY NMR cross-peaks arising from interactions of their protons with the H3, H5 and H6 protons of the α-CD and β-CD component annuli of **2**·*E*-**1**$^-$ and **3**·*E*-**1**$^-$ are observed consistent with *E*-**1**$^-$ being too strongly complexed for either **4**$^-$, **5**$^-$ or **6**$^-$ to compete for their occupancy (figure 5). However, **4**$^-$, **5**$^-$ and **6**$^-$ occupy the vacated β-CD component annuli of **2**·*Z*-**1**$^-$ and **3**·*Z*-**1**$^-$ to form the ternary complexes, **2**·*Z*-**1**$^-$·**4**$^-$ and **3**·*Z*-**1**$^-$·**4** and their **5**$^-$ and **6**$^-$ analogues, as shown by cross-peaks arising from the **4**$^-$, **5**$^-$ and **6**$^-$ aromatic and methyl proton dipolar interactions with the H3, H5 and H6 protons of the vacated α-CD and β-CD component annuli (figure 6 and Scheme 2). The cross-peaks arising from the continued occupancy of the β-CD component annuli of **2**·*Z*-**1**$^-$ and **3**·*Z*-**1**$^-$ by the *Z*-**1**$^-$ 4-*tert*-butylphenyl group remain.

Upon irradiation of a solution of **2**·*E*-**1**$^-$ and **4**$^-$ at 340 nm ^{1}H NMR resonances and cross-peaks arising from **2**·*Z*-**1**$^-$·**4**$^-$ appear, and irradiation of a solution of **2**·*Z*-**1**$^-$·**4**$^-$ at 275 nm produces resonances and cross-peaks arising from **2**·*E*-**1**$^-$ and **4**$^-$. The photostationary states achieved by irradiation at these wavelengths differ in their relative concentrations of **2**·*E*-**1**$^-$ and **4**$^-$ and **2**·*Z*-**1**$^-$·**4**$^-$ as expected and switching between photo-

stationary states is achieved by choosing the appropriate irradiation wavelength. Similar ^{1}H NMR spectral changes are observed in the photo-switching between the stationary states achieved in the presence of **5**$^-$ and **6**$^-$, in the analogous systems formed by **3**, and also when *E*-**1**$^-$ and *Z*-**1**$^-$ are replaced by *E*- and *Z*-4-(2-(4-*tert*-butylphenyl)ethen-1-yl)phenoxide [7].

Conclusion

The photoswitching between the stationary states exemplified in Scheme 2 constitutes the operation of a molecular device. It is based on the amplification of the *Z*-**1**$^-$ and *E*-**1**$^-$ photoisomerization within urea-linked CDs and the interactions between the components of the self-assembling molecular device are entirely intermolecular. There appears to be considerable potential for the amplification of such isomerizations in molecular device design.

Acknowledgements

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