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Synthesis of a ditopic cyclophane based on the cyclobutane ring by chalcone photocycloaddition

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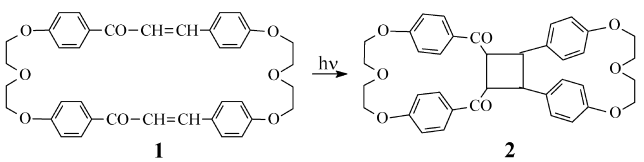
Abstract—The intramolecular photocycloaddition of chalcones to give cyclobutanes has proven to be a fast and simple method to shrink a cyclophane ring to a tricyclic system, in order to prepare potential ditopic receptors. In particular, the chalcone **1**, having dioxyethylene chains as spacers, is converted in high yield to the cyclobutane **2**. NOESY spectroscopy indicates that the formation of **2** occurs by a head-to-head *syn* ring closure.

1. Introduction

The cyclobutane ring may constitute a rigid nucleus for the insertion of a variety of cyclic ligand moieties, in order to build complex ditopic receptors.

A fast method to obtain cyclobutane rings is the photochemical dimerization of α,β-unsaturated carbonyl or carboxyl compounds and in particular of benzalacetophenones (chalcones). These reactions can be carried out in solution, solid state and molten state by sunlight or UV–vis irradiation, with variable results in terms of yield and product composition.[1–11]

Due to our interest in host–guest chemistry,[12–16] we have tested the feasibility to produce ditopic cyclophanes that could act as receptors, exploiting the intramolecular photocycloaddition of the cyclic chalcone **1** to cyclobutane **2** (Scheme 1).

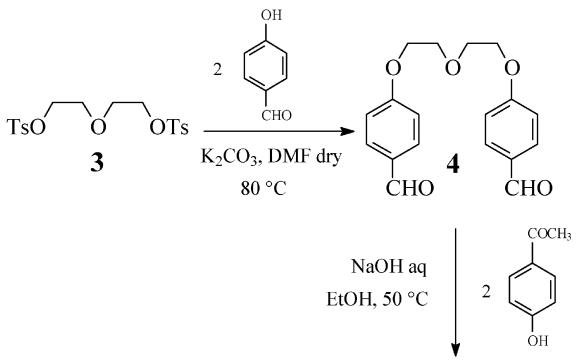


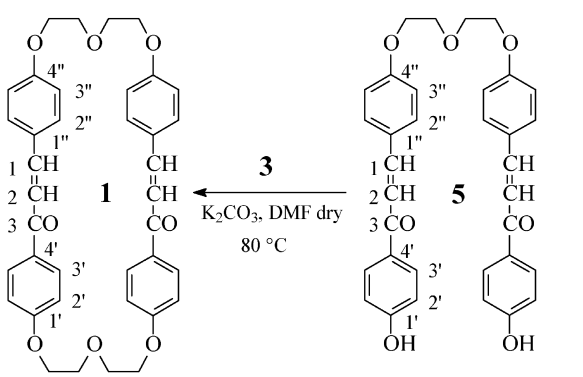
Scheme 1.

2. Results and discussion

The dioxyethylene substituted *trans*-benzalacetophenone (chalcone) **1** has been synthesized according to the route indicated in Scheme 2.

A 4×10^{-3} mol dm^{-3} chloroform solution of this compound, that showed an intense UV absorption band centred at





Scheme 2.

Keywords: cyclophanes; enones; carbocycles; cycloaddition; photochemistry.

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334 nm, after ~1 h exposure to sunlight on a sunny day in July, yielded **2** in 74% yield. The irradiation for ~20 min of a 6.5×10^{-3} mol dm^{-3} chloroform solution in a Rayonet apparatus, with fourteen 350 nm centred lamps, gave the cyclobutane **2** in 92% yield. Thermal treatment in the absence of light was ineffective.

The ready occurrence of this cyclization with respect to the examples reported in Refs. 1–11, is related to its intramolecular nature, that favors the approach of the reacting groups. This feature was already observed in the photocycloaddition of cinnamoyl derivatives, where the photoactive groups were linked together by a short spacer,[17–19] and could account for the different behaviour shown from 4,4′-dimethoxybenzalacetophenone, which is electronically very similar to **2**, but that under irradiation yields only brown resin.[3]

The cycloaddition of *trans*-chalcones may give four possible stereoisomers, namely *syn*/*anti* head-to-head and head-to-tail (Fig. 1). Since we had difficulties obtaining suitable crystals of **2** for X-ray studies, we resorted to ^{1}H NMR spectrometry to gain information about its stereochemistry.

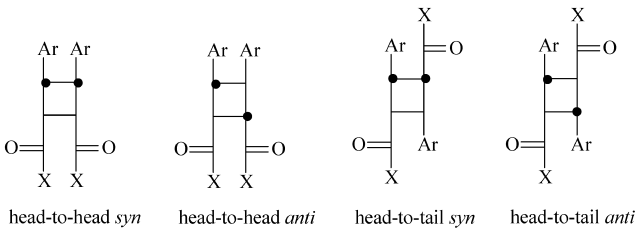

Figure 1.

Two symmetrical multiplets (AA′BB′ system) were observed for the cyclobutyl protons. Simulation of these NMR patterns has allowed the estimation of the coupling constants of the cyclobutyl protons (Fig. 2): $J_{AA'}$=11.3 Hz, J_{AB}=6.3 Hz, $J_{AB'}$=-0.8 Hz, $J_{BB'}$=10.5 Hz.[20]

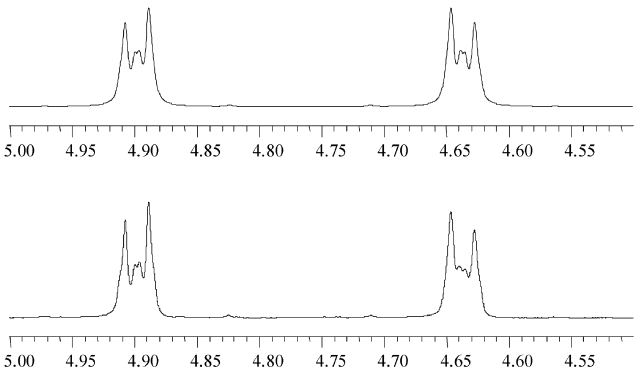

Figure 2. Simulated (above) and experimental (below) ^{1}H NMR spectra of cyclobutyl protons of **2**.

The values of these coupling constants suggest that **2** was formed by the head-to-head coupling, but they do not allow a certain assignment with respect to the *syn*/*anti* stereochemistry.[21,22]

A more accurate structural determination has been attained by (H,H)-COSY, (H,C)-COSY and NOESY-Phase sensitive spectra.

^{1}H and ^{13}C NMR spectra showed that the *ortho* and *meta* protons (and carbons), of the phenylene groups directly bonded to the cyclobutane ring of **2**, are not chemically equivalent (Figs. 3 and 4), because of the restricted rotations of the aromatic rings due to the short spacer.[†]

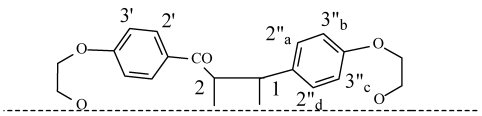

Figure 3.

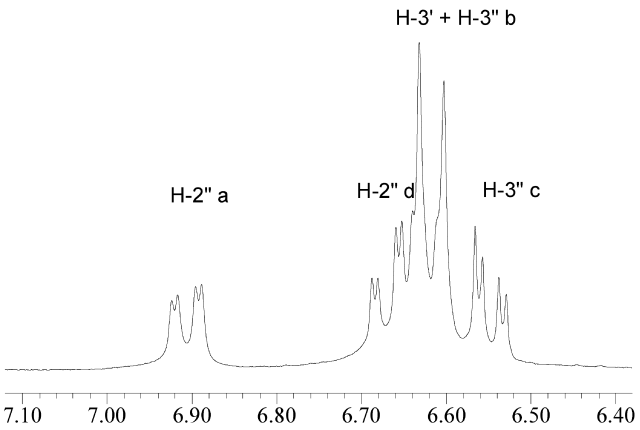

Figure 4. ^{1}H NMR of **2** in $CDCl_3$ (detail).

The upfield shift of H-2″$_d$ and to a lesser extent of H-3″$_c$, suggests that these protons are in some degree directed inwards to the opposite phenylene group, experiencing its ring current shielding effect.

The non-chemical equivalence of the H-2″ protons allowed us to distinguish the through-space interactions of proton 2″$_a$ from those of 2″$_d$. In particular, the NOESY spectrum of **2** shows, inter alia, that the protons that we have named H-2″$_a$, have a through-space coupling exclusively with the protons H-2, whereas the protons that we have named H-2″$_d$, couple through the space only with the protons H-1 (Fig. 5, filled contours).

These results are in accordance with a *trans* relationship between protons H-1 and H-2, and with a *cis* relationship between the two H-1 protons (and obviously between the two H-2 protons), caused by a head-to-head *syn* junction (Fig. 6, **2** h–h *syn*). Results obtained from 15 ns of molecular dynamics simulations indicate (see Table 1) that, for the **2** h–h *syn* stereoisomer, the atomic distances between H-2″$_a$–H-2 and H-2″$_d$–H-1 are lower than 3.5 Å, whereas the distances H-2″$_a$–H-1 and H-2″$_d$–H-2 are greater. In this situation we should observe exactly the correlation pattern reported in Figure 5.

[†] The atom numbers indicated in Figures 3–7, do not follow the IUPAC rules used in Section 3 for naming the compounds, and were utilized only for the sake of simplicity.

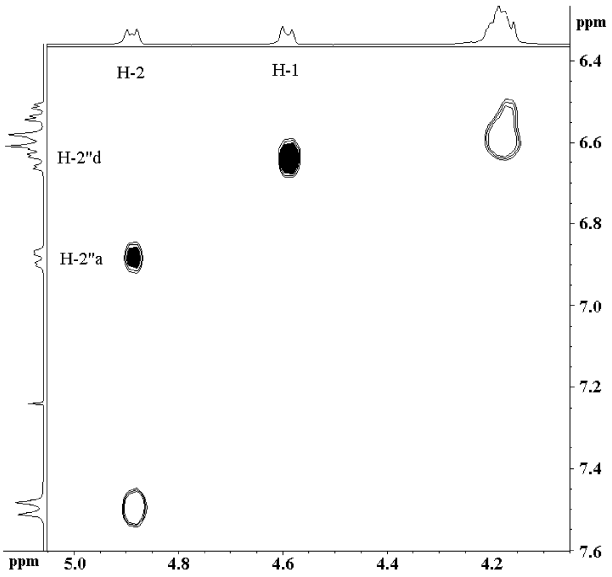

Figure 5. NOESY spectrum of **2** (detail).

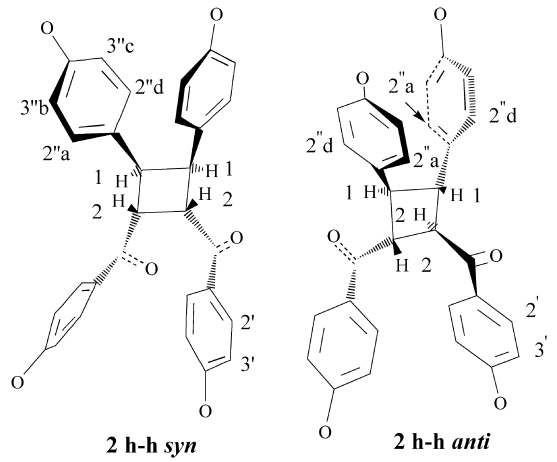

Figure 6. Head-to-head *syn* and *anti* structures (the dioxyethylene chains have been omitted).

Table 1. Relative average energies ($\langle E\rangle$) and average distances obtained from 15 ns of molecular dynamics simulations for *syn* and *anti* stereoisomers of **2**, at 298 K in $CHCl_3$. Distances greater than 3.5 Å are not reported (see Section 3 for details)

	2 h–h *syn*		**2** h–h *anti*	
$\langle E\rangle$ (kJ/mol)	0		36.28	
Atom pair type	$\langle d\rangle$ (Å)	$(1/\langle d^{-6}\rangle)^{1/6}$ (Å)	$\langle d\rangle$ (Å)	$(1/\langle d^{-6}\rangle)^{1/6}$ (Å)
H2a″–H2	2.409	2.338	2.827	2.745
	–	2.714	–	–
	3.324	2.593	2.870	2.783
	2.434	2.359	–	–
H2a″–H1	–	–	–	–
	–	–	2.438	2.375
	–	–	–	–
	–	–	2.441	2.350
H2d″–H1	2.645	2.574	2.416	2.373
	–	3.427	–	–
	–	–	2.420	2.379
	2.599	2.537	–	–
H2d″–H2	–	–	–	–
	–	–	–	–
	–	–	–	–
	–	–	–	–

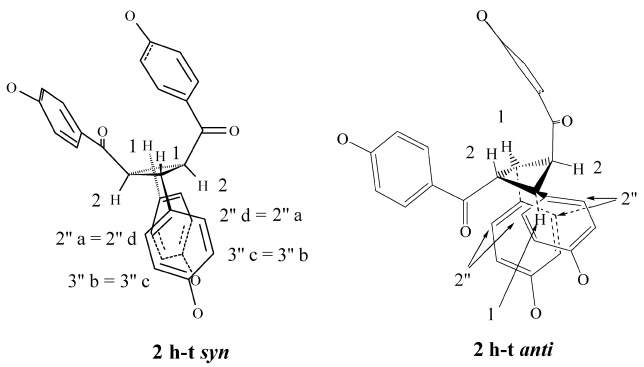

Figure 7. Head-to-tail *syn* and *anti* structures (the dioxyethylene chains have been omitted).

On the contrary, for the **2** h–h *anti* stereoisomer, (Fig. 6, **2** h–h *anti*), both the H-2″$_a$–H-1 and the H-2″$_a$–H-2 atomic distances are lower than 3.5 Å and therefore the protons H-2″$_a$ would show cross peaks with both H-1 and H-2.

The NOESY pattern confirms that the head-to-tail junction does not occur, because in this case the H-2 protons should correlate with both the H-2″ protons, either in the *syn* structure or the highly strained *anti* structure (Fig. 7). In particular, in **2** h–t *syn*, symmetry considerations show that H-2″$_a$ and H-2″$_d$ (H-3″$_b$ and H-3″$_c$) protons would be chemically equivalent, in contrast with the NMR results.

In the photocycloadditions of cinnamoyl derivatives linked with short spacers, the cyclobutane products were formed by head-to-head *syn* coupling.[17–19] It is noteworthy that also for the chalcone **1** the only kind of coupling process observed again allows a *syn* relationship for the two carbonyl groups. This feature is of importance because it could have implications on the potential ligand properties of the corresponding cyclophane moiety, and could be exploited to construct more complex structures.

3. Experimental

3.1. General and instrumentation

Melting points were determined with a Büchi capillary instrument and are uncorrected. Thin-layer chromatography (TLC) was carried out on Merck precoated 60 Kiesegel F_{254} silica gel plates and Merck precoated RP-18 F_{254S} reverse phase plates. Flash chromatography was carried out on columns with flash silica gel 60 Merck (40–63 μm). All reactions requiring anhydrous conditions were conducted in flame-dried apparatus. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AC 200 or a Bruker AC 300 spectrometer, at 25°C if not specified. Chemical shifts are expressed in ppm with reference to the solvent signals. 2D

NMR spectra (H,H-COSY, H,C-COSY, NOESY-Phase sensitive) were measured using standard Bruker software. NOESY-Phase sensitive spectra in TPPI mode, were recorded with mixing-times of 50–800 ms. IS-MS spectra were obtained on a Perkin–Elmer SCIEX API 365 triple quadrupole spectrometer. UV–vis spectra were carried out on a Cary 300, at 25°C. IR spectra were recorded on an FT-IR Nicolet 510. Microanalyses were performed on a Carlo Erba EA 1110 CHNS-O analyser. Photoreactions were carried out in a Rayonet apparatus.

3.2. Molecular modeling

Molecular dynamics calculations were carried out with the MacroModel 6.0 molecular modeling system,[23] running on a Silicon Graphics O2 R10000 workstation. The MMFF force field[24] was used in all the calculations. The electrostatic interactions were calculated by using the partial atomic charges of the MMFF force field. The effect of the solvent was taken into account by using the GB/SA model for chloroform as implemented in the MacroModel package.[25] A time step of 0.5 fs was chosen without the use of SHAKE.

3.3. Materials

4-Hydroxybenzaldehyde (98%), 4′-hydroxyacetophenone (99%), *p*-toluenesulphonyl chloride (98%) and diethyleneglycol (99%) were purchased from Aldrich and have been used without further purification. Dry K_2CO_3 was obtained by overnight heating analytical grade K_2CO_3 (Carlo Erba) at 110°C. Dry DMF was purchased from Fluka. Spectroscopy grade chloroform (Carlo Erba) was used in the synthetic and kinetic experiments without further purification.

3.3.1. 1,7-Bis-(4-formylphenyl)-1,4,7-trioxaheptane (4). A dry DMF solution (50 mL) containing the diethylene glycol bis-(*p*-toluenesulfonate) **3** (14.63 g, 35.3 mmol),[26] was added dropwise (ca. 1 h), to a stirred suspension in dry DMF (50 mL) of 4-hydroxybenzaldehyde (9.40 g, 77 mmol) and dry K_2CO_3 (26 g, 188 mmol), kept under argon at 80°C. The stirring was continued at this temperature for 3.5 h. The resulting mixture was cooled and poured on ice water. The precipitate was filtered and washed with cold water to remove K_2CO_3. The solid residue was crystallized from AcOEt affording **4** (9.32 g, 29.6 mmol, 84%, mp 141–143°C); lit. (60%, 140–141°C).[27]

3.3.2. 1,7-Bis-(4-[*trans* 3-(4-hydroxyphenyl)-3-oxo-propenyl]-phenyl)-1,4,7-trioxaheptane (5). 4′-Hydroxyacetophenone (1.51 g, 11.1 mmol) and the aldehyde **4** (1.16 g, 3.69 mmol), were added to a stirred solution of NaOH (1.34 g, 33.5 mmol) in EtOH/H_2O (8/2, 25 mL), kept at ~5°C under argon atmosphere. After the addition, the suspension was stirred at 75°C for ~3 h until complete dissolution of **4**. The solution was subsequently stirred at 50°C for 70 h, until complete consumption of the bis-aldehyde **4**, as established by reverse phase TLC (eluent: CH_3CN/H_2O 6/4+0.1% TFA). The mixture was cooled, carefully acidified to pH 5.5 by HCl 6 M and then ice water was added until complete separation of a yellow powdered solid, that was filtered and repeatedly washed with ice water. Recrystallization from MeOH yielded the bis-(4-hydroxychalcone) **5** as a yellow solid (62%, mp 188–190°C).

^{1}H NMR (DMSO, 40°C),‡ δ 3.3 [bs, O*H*], 3.81–3.86 [m, 4H, –O–CH_2], 4.16–4.21 [m, 4H, –O–CH_2], 6.88 [AA′XX′, $^3J_{H-H}$=8.8 Hz, 4H, *H*-3′], 7.01 [AA′XX′, $^3J_{H-H}$=8.8 Hz, 4H, *H*-3″], 7.63 [d, $^3J_{H-H}$=15.6 Hz, 2H, *H*-1], 7.72 [d, $^3J_{H-H}$=15.6 Hz, 2H, *H*-2], 7.78 [AA′XX′, $^3J_{H-H}$=8.3 Hz, 4H, *H*-2′], 8.03 [AA′XX′, $^3J_{H-H}$=8.8 Hz, 4H, *H*-2″].

^{13}C NMR (DMSO, 50°C),‡ δ 67.26 [–O–*C*H_2], 68.77 [–O–*C*H_2], 114.75 [*C*-3″], 115.00 [*C*-3′], 119.82 [*C*-2], 127.46 [*C*-quat.], 129.24 [*C*-2″], 129.96 [*C*-2′], 130.50 [*C*-quat.], 142.09 [*C*-1], 160.05 [*C*-quat.], 161.57 [*C*-quat.], 186.96 [*C*=O].

IR ($CHCl_3$), $\nu_{max\ (C=O)}$ 1652 cm^{-1}.

MS (IS) m/z=551 $(M+H)^+$.

Elemental analysis was unsatisfactory owing to the presence, in traces, of non removable impurities.

3.3.3. 9,12,15,27,30,33-Hexaoxapentacyclo [32.2.2.2^{5,8}.2^{16,19}.2^{23,26}] tetratetraconta-1(36), 3,5,7,16,18,20,23,25,34,37,39,41,43-tetradecaene-2,22-dione (1). A solution containing **3** (0.414 g, 1 mmol) in dry DMF (200 mL) was added dropwise (ca. 5 h), to a stirred suspension of **5** (1 mmol) and dry K_2CO_3 (690 mg, 1 mmol) in dry DMF (800 mL) and kept under argon at 80°C. The stirring was continued at this temperature for ~3 days until complete consumption of **5**, as established by reverse phase TLC (CH_3CN/H_2O 6/4). The resulting mixture was cooled and filtered to remove K_2CO_3. The recovered K_2CO_3 was washed with DMF, the organic phases were collected and solvent removed in vacuo to yield a solid residue that was dissolved in $CHCl_3$, washed with water and dried on Na_2SO_4. The solvent was removed in vacuo to yield a solid that was purified by flash chromatography ($CHCl_3$/acetone 9/1). Recrystallization from $CHCl_3$/MeOH yielded the cyclic bis-chalcone **1** as yellow solid (68%, mp 191–192°C).

^{1}H NMR ($CDCl_3$),‡ δ=3.86–3.96 [m, 8H, –O–CH_2], 4.14–4.24 [m, 8H, –O–CH_2], 6.77 [AA′XX′, $^3J_{H-H}$=8.7 Hz, 4H, *H*-3″], 6.83 [AA′XX′, $^3J_{H-H}$=8.8 Hz, 4H, *H*-3′], 7.30 [d, $^3J_{H-H}$=15.6 Hz, 2H, *H*-2], 7.44 [AA′XX′, $^3J_{H-H}$=8.5 Hz, 4H, *H*-2″], 7.73 [d, $^3J_{H-H}$=15.6 Hz, 2H, *H*-1], 7.89 [AA′XX′, $^3J_{H-H}$=8.8 Hz, 4H, *H*-2′].

^{13}C NMR ($CDCl_3$),‡ δ 67.81 [–O–*C*H_2], 69.95 [–O–*C*H_2], 114.64 [*C*-3″], 115.34 [*C*-3′], 118.99 [*C*-2], 127.80 [*C*-quat.], 129.86 [*C*-2″], 130.41 [*C*-2′], 131.30 [*C*-quat.], 143.80 [*C*-1], 160.67 [*C*-quat.], 162.43 [*C*-quat.], 188.26 [*C*=O].

‡ For the sake of simplicity, the atom numbers indicated in NMR spectra are referred to those indicated in Scheme 2 (compounds **1** and **5**), and Figure 3 (compound **2**).

IR ($CHCl_3$), $\nu_{max(C=O)}$ 1655 cm^{-1}.

UV–vis ($CHCl_3$), λ_{max} 334 nm, ε 5.8×10^4 cm^{-1} - dm^3 mol^{-1}.

MS (IS) m/z=621 $(M+H)^+$.

Calcd. C 73.53, H 5.85; Found C 73.80, H 5.95.

3.3.4. 9,12,15,27,30,33-Hexaoxaheptacyclo-[32.2.2.$2^{5,8}$.$2^{16,19}$.$2^{23,26}$.$0^{2,22}$.$0^{3,21}$]-tetratetraconta-1(36),5,7,16,18,23,25, 34,37,39,41,43-dodecaene-4,20-dione (2). *Photoisomerization in sunlight*. A solution of **1** (98 mg, 0.163 mmol) in 50 mL of chloroform, kept in a Pyrex flask, was exposed to sunlight on a sunny day in July. The progress of the reaction was followed by silica gel TLC ($CHCl_3$/acetone 9/1) and reverse phase TLC (CH_3CN/H_2O 8/2). The reaction was stopped after ~1 h. The solution was evaporated and the residue purified by flash chromatography ($CHCl_3$/acetone 94/6, 72 mg, 74%). Recrystallization from chloroform–methanol gave microscopic white needles of an analytically pure sample (mp 258–259°C).

Photoisomerization at 350 nm. A 6.44×10^{-3} mol dm^{-3} solution of **1** (0.100 g in 25 mL) in chloroform, contained in a Pyrex flask, was irradiated in a Rayonet reactor by 14 lamps whose emission was centred at 350 nm. After ca. 30 min the reaction appeared to be complete. The solvent was removed and the residue purified by flash chromatography (yield: 92%).

^{1}H NMR ($CDCl_3$),‡ δ=3.55–3.65 [m, 4H, –O–CH_2], 3.70–3.85 [m, 4H, –O–CH_2], 4.15–4.30 [m, 8H, –O–CH_2], 4.60–4.65 [m, 2H, *H*-1],§ 4.87–4.91 [m, 2H, *H*-2],§ 6.55 [dd, $^3J_{H-H}$=8.4 Hz, $^4J_{H-H}$=2.5 Hz, 2H, *H*-3″c], 6.62 and 6.63 [AA′XX′, $^3J_{H-H}$=8.9 Hz, 6H, *H*-3′ and superimposed *H*-3″b], 6.67 [dd, $^3J_{H-H}$=8.5 Hz, $^4J_{H-H}$=2.0 Hz, 2H, *H*-2″d], 6.91 [dd, $^3J_{H-H}$=8.5 Hz, $^4J_{H-H}$=2.0 Hz, 2H, *H*-2″a], 7.52 [AA′XX′, $^3J_{H-H}$=8.9 Hz, 4H, *H*-2′].

^{13}C NMR ($CDCl_3$),‡ δ=42.61 [*C*-1], 45.60 [*C*-2)], 68.01 [–O–CH_2], 68.81 [–O–CH_2], 69.92 [–O–CH_2], 70.32 [–O–CH_2], 114.27 [*C*-3′], 115.49 [*C*-3″b], 115.95 [*C*-3″c], 126.77 [*C*-2″a], 130.17 [*C*-quat.], 130.35 [*C*-2′], 131.29 [*C*-2″d], 132.25 [*C*-quat.], 156.75 [*C*-quat.], 162.31 [*C*-quat.], 197.09 [*C*=O].

IR ($CHCl_3$), $\nu_{max(C=O)}$ 1679 cm^{-1}.

UV–vis ($CHCl_3$), λ_{max} 272 nm, ε 3.1×10^4 cm^{-1} dm^3 mol^{-1}.

MS (IS) m/z=621 $(M+H)^+$.

Calcd. C 73.53, H 5.85. Found C 73.39, H 5.91.

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§ The estimated *J* values for this AA′BB′ scheme are reported in the text.