

## Azobenzene-bridged calix[8]arenes

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**Abstract**—An azobenzene bridge was introduced into the lower (or smaller) rim of *p*-*tert*-butylcalix[8]arene (**1**) and 1,5-calix[8]-crown-3 (**2**) to form 1,4-singly bridged (**3**) and 1,5:3,7-doubly bridged (**4**) calix[8]arene derivatives, respectively. *Trans* and *cis* isomers of conformationally rigid **4** were isolated. The quantum yields of the *trans*–*cis* photoisomerisation reactions have been measured.

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Development of molecular machines and switches whose motion can be induced by light is a focus of interest in supramolecular chemistry.<sup>1</sup> Azobenzene is one of the typical photochromic units whose *cis*–*trans* isomerisation has been the basis for many functional molecules and materials.<sup>2</sup> In order to produce light-driven structures, azobenzene moieties have been chemically introduced into molecular systems such as macrocycles.<sup>3</sup> Thus, calix[4,6]arenes<sup>4</sup> and calix[4]resorcinarenes<sup>5</sup> with azobenzene functionalities have been reported and their complexing and photoresponsive properties have been demonstrated.

Light-induced conformational change of a photoresponsive unit is efficiently conveyed to other parts of the molecule in some cyclic systems with consequent changes of chemical and physical properties.<sup>6</sup> To the contrary, it is also known that the isomerisation of responsive units in some macrocycles is strictly controlled by the size and the conformation of the rest part of the ring.<sup>4c,7</sup> Considering this, we wished to investigate the effect of the introduction of an azobenzene bridging unit into the conformationally flexible calix[8]arene macrocycle (**1**).<sup>8</sup> Intrabridging of calix[8]arene is a valid approach to effectively preorganise this macrocycle and has provided highly selective ionophores.<sup>9</sup> It is conceivable that combining the well-known calixarene host

ability and the azobenzene photochromic properties, novel light-driven molecular switches may be produced.

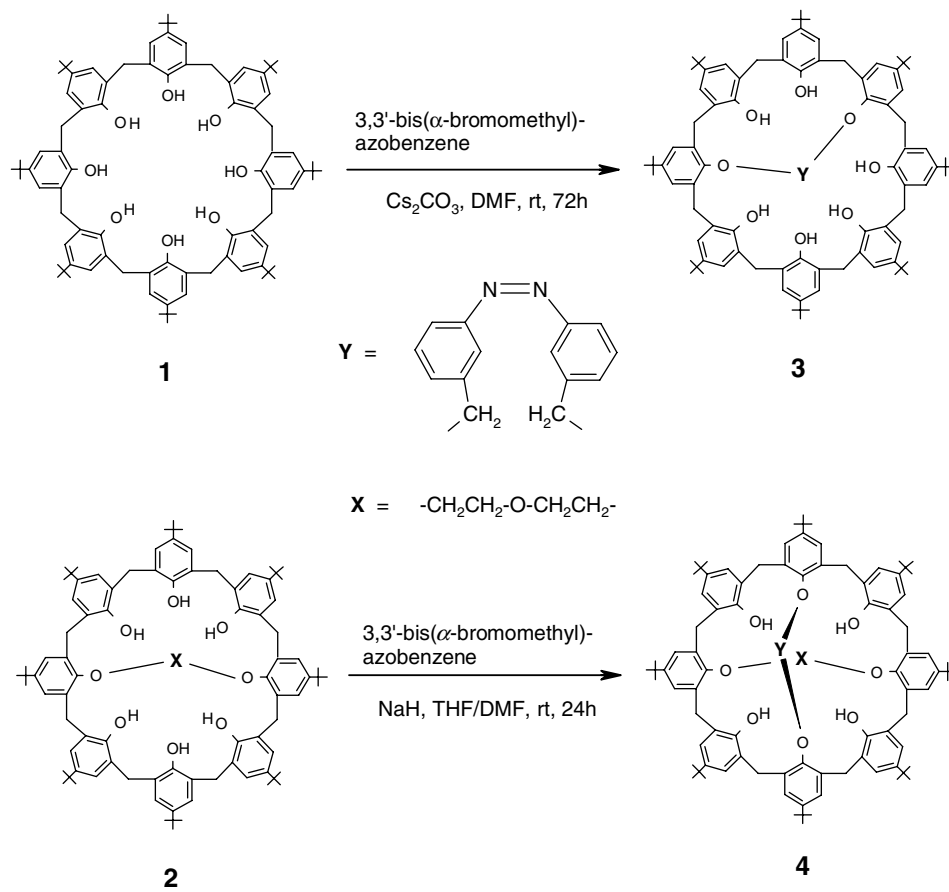
Because the azo group is usually considered to be a chromogenic centre but a modest metal-chelating site, we decided to insert an azobenzene bridge also in the singly bridged 1,5-calix[8]crown-3 **2**.<sup>10</sup> The presence of an additional crown ether spanner could result advantageous in both conferring to the hybrid system a higher rigidity and reinforcing its metal-chelating ability.

To introduce an azobenzene bridge into the calix[8]arene lower rim, we adapted previously reported procedures for the preparation of singly and doubly bridged calix[8]arenes.<sup>9b,c,10,11</sup> Thus, treatment of substrate **1** or **2** with 3,3'-bis( $\alpha$ -bromomethyl)azobenzene<sup>12</sup> in the presence of a base and under UV irradiation (Scheme 1) afforded 1,4-singly bridged calix[8]arene **3** (33% yield) and 1,5:3,7-doubly bridged calix[8]arene **4** (30% yield).<sup>13</sup> Lower yields were usually obtained in the absence of UV irradiation. The obtained orange coloured compounds were characterised by FAB-MS, NMR and UV analysis.

Considering that calix[8]arene **1** in solution likely assumes a *pleated loop* conformation,<sup>14</sup> molecular modelling suggested that the spanning azobenzene can potentially cross-link the 1,4 or 1,5-phenoxy groups of **1** (Fig. 1). Identity of the obtained compound **3** was established on the basis of its NMR data<sup>15</sup> and molecular weight, fitting for a singly bridged calix[8]arene

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Scheme 1. Synthesis of azobenzene-bridged calix[8]arenes.

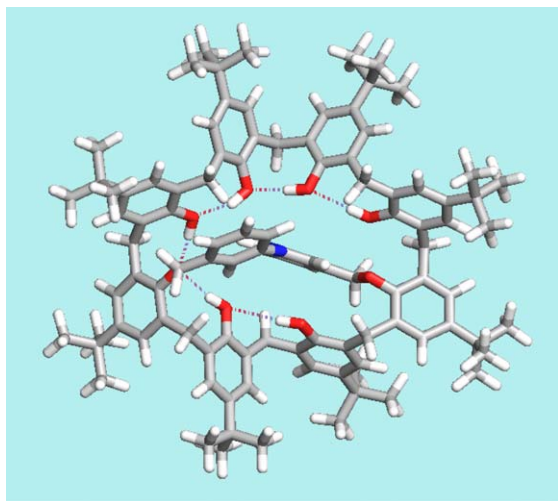


Figure 1. Computer model of idealised conformation of **3** in the trans configuration.

derivative. Among the four possible singly bridged regioisomers (1,2, 1,3, 1,4 or 1,5), the presence of four singlets for the *t*-Bu groups and eight signals for C–O and C–Bu quaternary carbons (147–153 ppm) was indicative of a CH<sub>2</sub>–CH<sub>2</sub> symmetry<sup>16</sup> compatible with a 1,2- or 1,4-bridged derivative. Discrimination between these two regioisomers was obtained from the chemical shift of the phenolic hydroxyls on the basis of a well docu-

mented rule.<sup>17</sup> The occurrence of a resonance at 8.29 ppm in the protonic spectrum of **3** can be considered diagnostic of the relegated singly bonded hydroxyls characteristic of 1,4-bridging.<sup>17</sup> Interestingly, the methylene region of the <sup>1</sup>H NMR spectrum of **3**, at room temperature in CDCl<sub>3</sub>, displayed five AX/AB systems for ArCH<sub>2</sub>Ar groups indicating that conformational motion of the calixarene skeleton is hampered. This is attributable to the presence of the bridge associated with a stabilising hydrogen bonding network (Fig. 1).

The azobenzene group in compound **3** can exist in either a trans or cis configuration. Proton NMR spectrum of the isolated compound **3** appeared consistent with the trans isomer on the basis of the chemical shift of the azobenzene aromatic protons.<sup>18</sup> In addition, low intensity broad resonances were also observed, which could be ascribed to the cis isomer. This is in accordance with MM2 calculations (GB/SA model solvent for CHCl<sub>3</sub>) that favoured the trans over the cis isomer of **3** (Fig. 1). Attempts to isolate the pure cis isomer have not been successful probably because of a fast cis–trans interconversion.

The known caesium cation conformational templation in 1,5-bridged calix[8]arene derivatives,<sup>19</sup> which folds the calixarene skeleton in the *tube-shaped* conformation,<sup>20</sup> addressed also the introduction of the azobenzene bridge into substrate **2**, affording 1,5:3,7-doubly

bridged regioisomer **4**. It was univocally identified on the sole basis of the NMR signal patterns.<sup>21</sup> The presence of three *tert*-butyl signals (1:2:1 ratio) and two AX/AB systems for ArCH<sub>2</sub>Ar groups in the proton spectrum (CDCl<sub>3</sub>, 297 K) of **4** was a clear evidence of its molecular structure bisected by two orthogonal 2-fold symmetry elements (C<sub>2v</sub>-symmetry). The introduction of the second bridge in compound **4** was also confirmed by FAB-MS.

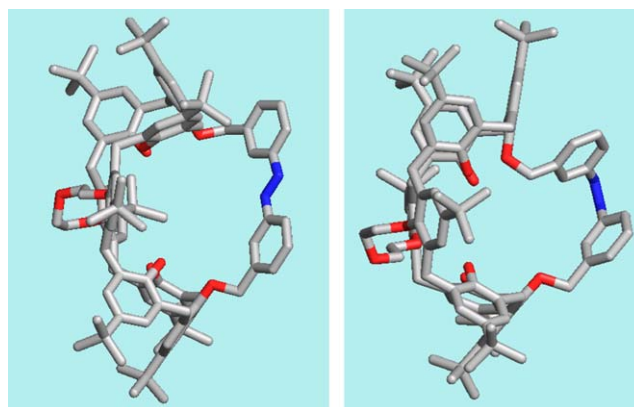
In doubly bridged derivative **4**, calixarene macrocycle undergoes a strong reduction of its conformational mobility as evidenced by the appearance of one AB and one AX system for ArCH<sub>2</sub>Ar groups in the protonic spectrum in CDCl<sub>3</sub>. NMR data suggested that analogously to other doubly bridged calix[8]arenes,<sup>9,22</sup> compound **4** assumes a folded conformation in which the triads of contiguous aromatic rings in positions 2–4 and 6–8 adopt a 3/4 *cone* geometry (AX system with  $\Delta\delta = 0.97$  ppm and carbon resonances at 30.4 and 30.9 ppm for ArCH<sub>2</sub>Ar groups), while the bridge-head aryls bearing the crown bridge are in an *out* orientation (AB system with  $\Delta\delta = 0.05$  ppm for ArCH<sub>2</sub>Ar groups).

Also for compound **4**, the presence of the azobenzene moiety allows the existence of *trans* and *cis* isomers that were separated by preparative TLC (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>). The two isomers were characterised on the basis of their NMR<sup>21</sup> and UV spectra. Because the aromatic protons of a *trans* azobenzene unit generally resonate at a lower magnetic field with respect to the *cis* form,<sup>18</sup> we assigned the *cis* configuration to the more polar compound, whose azobenzene aromatic protons resonate at 6.41, 7.42, 7.75 and 7.98 ppm. Consequently, the *trans* geometry was assigned to the other isomer showing azobenzene proton resonances at 7.57, 7.58, 7.94 and 8.31 ppm. *Trans*–*cis* geometry influences also the resonances relative to the calixarene ArH and crown OCH<sub>2</sub> groups, both of which undergo upfield shift in the *cis* isomer.<sup>21</sup>

Isomerisation of both pure *trans* and *cis* forms of **4** occurred at room temperature in CDCl<sub>3</sub> solution to give in both instances a final 36:64 *trans*–*cis* equilibrium ratio as found by integration of their NMR signals.

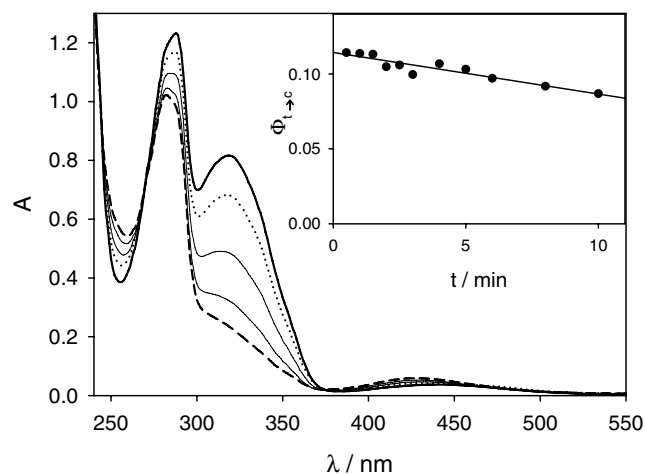
Also in this instance, MM2 energy-minimisation (GB/SA model solvent for CHCl<sub>3</sub>) favoured the *trans* with respect to the *cis* isomer of **4** (Fig. 2) by 28 kJ/mol.

To evaluate the influence of the calixarene macrocycle on the photoisomerisation of the azobenzene moiety, experiments were performed in dichloromethane solution on compounds **3** and **4** and on azobenzene as reference compound. Irradiation was carried out with 320 and 432 nm light obtained with a monochromator from a xenon lamp. Since the calixarene moiety does not absorb above 300 nm in compounds **3** and **4**, there is no overlap with the relevant bands of the azobenzene unit (320 and 430 nm) that have indeed the same shape and are assumed to have the same intensities as those of the free azobenzene moiety. From the absorption spectra, we have estimated that the investigated samples of



**Figure 2.** Computer model of idealised conformation of **4** (side view) in the *trans* (left) and *cis* (right) configurations (H atoms omitted).

compounds **3** and **4** contained 85% and 80% of the *trans* isomer, respectively, before irradiation.<sup>23</sup> The photoisomerisation reactions were monitored from the spectral variations (see Fig. 3) at  $\lambda = 320$  nm that corresponds to the largest difference in absorbance of the two isomers. Because of the partial overlap of the spectra of the two isomers, upon irradiation a stationary state is reached in which the *trans*/*cis* concentration ratio (Table 1) depends on the molar absorption coefficients of the two isomers at the excitation wavelength and on the quantum yields of the forward and reverse reactions. The true quantum yields (Table 1) were obtained by extrapolation to zero irradiation time (Fig. 3, inset) after suitable correction. The rate of the thermal *cis* → *trans* back reaction at 35 °C was also measured for azobenzene and compound **3**. In the case of **4**, however, the back thermal isomerisation reaction was accompanied by decomposition. The results obtained, gathered in Table 1, show that the photochemical behaviour of the azobenzene moiety of compounds **3** and **4** is substantially the same as that of free azobenzene. Within the experimental error ( $\pm 15\%$ ), the quantum yields for the



**Figure 3.** Absorption changes of a dichloromethane solution of **4** upon irradiation at 320 nm: solid line represents the absorption spectrum of the non-irradiated solution and dashed line corresponds to the photostationary state. The dotted curve corresponds to the photostationary state upon irradiation at 432 nm. Inset shows the quantum yield of *trans* → *cis* photoreaction as a function of time.

**Table 1.** Isomerisation reactions in dichloromethane solution<sup>a</sup>

	$\lambda_{\text{irr}} = 320 \text{ nm}$		$\lambda_{\text{irr}} = 432 \text{ nm}$		$k_{\text{c} \rightarrow \text{t}} (\text{s}^{-1})^{\text{c}}$
	$\Phi_{\text{t} \rightarrow \text{c}}$	% trans <sup>b</sup>	$\Phi_{\text{c} \rightarrow \text{t}}$	% trans <sup>b</sup>	
Azobenzene	0.12	16	0.33	80	$3 \times 10^{-6}$
<b>3</b>	0.13	19	0.49	83	$1 \times 10^{-6}$
<b>4</b>	0.13	18	0.44	65	—

<sup>a</sup> At rt, unless otherwise noted.<sup>b</sup> At photostationary state.<sup>c</sup> Initial reaction rate at 308 K. Compound **4** undergoes decomposition.

trans  $\rightarrow$  cis photoisomerisation at 320 nm are the same as those of free azobenzene, whereas the quantum yield for the cis  $\rightarrow$  trans photoisomerisation at 432 nm is slightly higher for the azobenzene-bridged derivatives. As far as the values of % trans at the stationary states are concerned, they are difficult to rationalise since they depend not only on the quantum yield values, but also on values of the molar absorption coefficients that have been taken to be those of free azobenzene for all the investigated compounds.

In conclusion, the first azobenzene-bridged calix[8]-arenes have been synthesised and trans–cis isomers of the conformationally rigid 1,5:3,7-doubly bridged derivative **4** have been isolated. The photoresponsive behaviour of these compounds has also been investigated. More in depth studies to evaluate the photoswitching and complexing properties of **3** and **4** and to design analogues with improved photophysical characteristics are in progress.

### Acknowledgements

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- by filtration and purified by column chromatography (SiO<sub>2</sub>, gradient from 15:85 to 60:40 CH<sub>2</sub>Cl<sub>2</sub>/hexane) to afford compound **4** in 30% yield (pure trans plus a trans–cis mixture). Pure cis isomer of **4** was obtained by purification on preparative TLC (SiO<sub>2</sub>, 100% CH<sub>2</sub>Cl<sub>2</sub>).
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  - <sup>1</sup>H NMR data for compound **4** (400 MHz, CDCl<sub>3</sub>, 297 K): **trans isomer** δ 1.20 [s, C(CH<sub>3</sub>)<sub>3</sub>, 36H], 1.22, 1.25 [s, C(CH<sub>3</sub>)<sub>3</sub>, 18H each], 3.52/4.53 (AX system, ArCH<sub>2</sub>Ar, *J* = 14.2 Hz, 8H), 3.79 (br t, OCH<sub>2</sub>, 4H), 3.81/3.86 (AB system, ArCH<sub>2</sub>Ar, *J* = 14.8 Hz, 8H), 4.09 (br t, OCH<sub>2</sub>, 4H), 5.31 (s, azoBn OCH<sub>2</sub>, 4H), 7.04 (br d, ArH, 4H), 7.13 (br d, ArH, 4H), 7.16 (s, ArH, 4H), 7.21 (s, ArH, 4H), 7.31 (s, OH, 4H) 7.55–7.59 (overlapped, azoBn ArH, 4H), 7.95 (d, azoBn ArH, *J* = 6.5 Hz, 2H), 8.32 (s, azoBn ArH, 2H); **cis isomer** δ 1.21 [s, C(CH<sub>3</sub>)<sub>3</sub>, 36H], 1.22, 1.24 [s, C(CH<sub>3</sub>)<sub>3</sub>, 18H each], 3.50, 3.52 (br t, OCH<sub>2</sub>, 4H each), 3.56/4.54 (AX system, ArCH<sub>2</sub>Ar, *J* = 14.1 Hz, 8H), 3.88/3.95 (AB system, ArCH<sub>2</sub>Ar, *J* = 15.2 Hz, 8H), 5.19 (s, azoBn OCH<sub>2</sub>, 4H), 6.41 (d, azoBn ArH, *J* = 7.9 Hz, 2H), 7.02 (br s, ArH, 4H), 7.13 (s, ArH, 8H), 7.34 (s, OH, 4H), 7.35 (br s, ArH, 4H), 7.42 (t, azoBn ArH, *J* = 7.6 Hz, 2H), 7.75 (s, azoBn ArH, 2H), 7.98 (d, azoBn ArH, *J* = 7.5 Hz, 2H).
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