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Synthesis and Complexation Properties towards Alkali Cations of a Photosensitive Azo-modified Calix[4]Crown Ether in the 1,3-Alternate Conformation

MOHAMED SAADIOUI[1], NATHALIE REYNIER[2], JEAN-FRANÇOIS DOZOL[2], ZOUHAIR ASFARI[1] and JACQUES VICENS[1]
[1]*E.C.P.M., Laboratoire de Chimie Minérale et de Chimie Analytique, associé au CNRS, 1, Rue Blaise Pascal, F-67000 Strasbourg, France.*
[2]*D.C.C./D.E.S.D./S.E.P. Commissariat à l'Energie Atomique, CEA-Cadarache F-13108 Saint-Paul-lez-Durance, France.*

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Abstract. We report the synthesis and complexation properties towards alkali cations of a photosensitive azo-modified calix[4]crown **5** in the 1,3-alternate conformation. Selectivity of the *cis*-isomer towards Cs^+ and Rb^+ was observed.

Key words: Calix[4]arene, calixcrowns, *cis-trans* azobenzene, photoresponsive.

1. Introduction

The first step in decreasing the volume and the toxicity of radioactive waste arising from the reprocessing of nuclear fuel consists in separating long-lived radionuclides from shorter-lived ones [1]. This partitioning of toxic radioelements can be achieved by specific complexation through liquid-liquid extraction [2]. During such processes decomplexation of some cations at the water-solvent interface sometimes appears to be difficult when strong binding ligands are used as carriers [3]. One solution to this problem could be to induce a structural modification of the geometry of the complexing cavity of the extractant between the complexation and decomplexation steps of the cation. In this respect many examples of photosensitive extracting agents containing *azobenzene* units in their framework, allowing photo-induced modifications of the complexing cavities through *cis-trans* isomerization, have been reported in the literature [4]. On the other hand, calixarenes have been shown to exhibit very high complexation selectivities towards a given cation when functionalized by chosen ligating functions [5]. More particularly calix[4]crowns which combine the calix[4]arene unit in the 1,3-alternate conformation with crown ether units have been observed to selectively transport cesium cation through synthetic liquid membranes [6]. These observations drove

us to introduce an azobenzene unit in the crown ether bridge of a 1,3-alternate calix[4]crown. Thus, once the crown ether is modified by the introduction of the azobenzene unit, the azo-modified calixcrown produced should not only combine the properties of preorganization of calixcrowns with the complementarity properties of classical crown ethers [7], but also should benefit from the properties of the azobenzene function which changes its geometry with UV irradiation and thermal isomerization [8].

In this paper, we report the synthesis and complexation properties of photoresponsive 1,3-calix[4]azobenzene crown-6 (**5**) combining a calix[4]arene in the 1,3-alternate conformation with a 2,2′-azobenzene crown ether chain.

2. Experimental

2.1. Material for synthesis

2,2′-Dihydroxyazobenzene, 2-(2-chloro-ethoxy)-ethanol, 2-(2-methoxy-ethoxy)-ethanol-*p*-toluene sulfonate, *p*-toluene sulfonyl chloride, potassium carbonate and the solvents were commercial reagents and used without further purification. Calix[4]arene was prepared according to the literature [9].

2.2. Analytical procedures

The melting points (mps) were taken on a Büchi apparatus in capillaries sealed under nitrogen. Silica columns were prepared with Merck Kieselgel (Art.11567). Thin layer chromatography (TLC) was carried out on Merck TLC plates (Art. 6484). The eluent is specified in the experimental procedure. Elemental analyses were performed at the Service de Microanalyse of the Institute de Chimie de Strasbourg. The ^{1}H-NMR spectra were recorded at 200 MHz on a Bruker AC 200 spectrometer and at 400 MHz on a Bruker AM 400 spectrometer. The FAB mass spectra were obtained on a VG-Analytical ZAB HF apparatus. UV-Visible spectra were recorded on a Cary13 spectrophotometer.

2.3. Synthesis of 1,3-calix[4]azobenzene crown-6 (**5**)

2.3.1. *2,2′-Di-[2-(2-hydroxy-ethoxy-ethoxy)]-azobenzene* (**1**)

2,2′-Dihydroxyazobenzene (4.00 g, 18.67 mmol) and 10.32 g of K_2CO_3(74.68 mmol) were dissolved in 150 mL CH_3CN. The mixture was stirred for 24 h at r.t. 2-(2-chloro-ethoxy)-ethanol (5.80 g, 46.50 mmol) was added. After refluxing for 12 days the solvents were removed. The residue was dissolved in CH_2Cl_2. The solution was neutralized with 1N HCl. The organic phase was separated and dried (Na_2SO_4). After evaporation of the solvents the residue was triturated with methanol, yielding, after filtration, 10.00 g (quantitative) of **1**, mp 68–69°C.

^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.63 dd (2 H, J = 8.0 Hz, 2.0 Hz, Ar—*H* azobenzene), 7.40 (t, 2H, J = 7.0 Hz, Ar—*H* azobenzene), 7.11–6.99 (m, 4H,

Ar—*H* azobenzene), 4.36 (t, 4H, *J* = 4.4 Hz, ArOC*H*$_2$CH$_2$O), 3.97 (t, 4H, *J* = 4.3 Hz, ArOCH$_2$C*H*$_2$O), 3.71–3.66 (m, 8H, OC*H*$_2$C*H*$_2$OH), 2.47 (s, 2H, O*H*, exchangeable with D$_2$O). *Anal. Calcd*. for $C_{20}H_{26}N_2O_6$. CH_3OH: C, 61.51; H, 6.72. *Found*: C, 61.55; H, 6.60. *UV-Visible* (benzene): $c = 3 \times 10^{-4}$ M, λ_{max} = 363 nm (4780) and 451 nm (1020).

2.3.2. *Ditosylate of 2,2′-di-[2-(2-hydroxyethoxy)-ethoxy]-azobenzene* (**2**)

Compound **1** (3.13 g, 8.00 mmol) and tosylchloride (3.05 g, 16.00 mmole) were dissolved in 100 mL CH_2Cl_2. NEt_3 (4.6 mL, 32.00 mmol) was slowly added at 0°C. The reaction mixture was stirred at r.t. for 48 h. The excess of NEt_3 was neutralized with 1N HCl. The organic phase was separated and dried (Na_2SO_4). After evaporation the residue was chromatographed on silica (90/10 chloroform/acetone) to afford 4.06 g (67%) of **2** as a red powder, mp 99–100°C (CH_2Cl_2–methanol).

^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.76 (d, 4H, *J* = 8.3 Hz, Ts*H*), 7.58 (dd, 2H, *J* = 7.9 Hz, 1.6 Hz, Ar—*H* azobenzene), 7.43–7.35 (m, 2H, Ar—*H* azobenzene), 7.26 (d, 4 H, *J* = 8.4 Hz, Ts*H*), 7.08–6.97 (m, 4H, Ar—*H* azobenzene), 4.27 (t, 4H, *J* = 4.7 Hz, ArOC*H*$_2$CH$_2$O), 4.16 (t, 4H, *J* = 4.7 Hz, ArOCH$_2$C*H*$_2$O), 3.90–3.80 (m, 8H, OC*H*$_2$C*H*$_2$OTs), 2.39 (s, 6H, C H_3); *Anal. Calcd*. for $C_{34}H_{38}N_2O_{10}S_2$: C, 58.40; H, 5.48. *Found*: C, 58.30; H, 5.44. *UV-Visible* (benzene): $c = 3 \times 10^{-4}$ M, λ_{max} = 360 nm (6301) and 440 nm (740).

2.3.3. *1,3-Calix[4]-(2,2′-azobenzene)-crown-6* (**3**)

Calix[4]arene (2.00 g, 4.71 mmol) and K_2CO_3 (0.657 g, 4.75 mmol) were dissolved in 150 mL CH_3CN. After stirring for 24 h at r.t 3.30 g of **2** (4.71 mmol) was added and the reaction mixture was refluxed for 7 days. After evaporation of the solvent the residue was solubilized in CH_2Cl_2, and the solution was neutralized with 1N HCl. The organic phase was separated and dried (Na_2SO_4). The filtrate was evaporated to give a red oil which was purified by chromatography on silica (90/10 chloroform/acetone) to afford 0.700 g (19%) of **3** as a red powder, mp 117–118 °C.

^{1}H-NMR (200 MHz, $CDCl_3$) δ 8.16 (s, 2H, ArO*H*, exchangeable with D$_2$O), 7.63 (dd, 2H, *J* = 8.0 Hz, 2.0 Hz, Ar*H* azobenzene), 7.33 (t, 2H, *J* = 9.0 Hz, Ar*H* azobenzene), 7.10–6.59 (m, 16H, Ar*H*), 4.37 (d, 4H, *J* = 13.0 Hz, AB system for ArC*H*$_2$Ar), 4.23–3.95 (m, 16H, glycolic C*H*$_2$), 3.34 (d, 4H, *J* = 13.0 Hz, AB system for ArC*H*$_2$Ar). FAB (+) MS: m/z 779.4 (M + H$^+$). *Anal. Calcd*. for $C_{48}H_{46}N_2O_8$: C, 74.02; H, 5.95. *Found*: C, 74.12; H, 5.96. *UV-Visible* (87/13 1,2-dichlorobenzene/*n*-butanol) $c = 2 \times 10^{-4}$M, λ_{max} = 355 nm (10800).

2.3.4. *1,3-Di-(ethoxy-ethoxy-methoxy)-calix[4]arene* (**4**)

Calix[4]arene (10.61 g, 25.00 mmol) and of K_2CO_3 (3.46 g, 25.00 mmol) were dissolved in 350 mL CH_3CN. The mixture was stirred for 24 h at r.t. A solution of 13.72 g of the tosylate of 2-(2-methoxyethoxy)-ethanol (50.00 mmol) in 200 mL

CH_3CN was added dropwise. After 7 days of reflux the work up was carried out as for **3**. Chromatography on silica (95/5 chloroform/acetone) afforded 6.55 g (42%) of **4** as a white solid, mp 133–134 °C (methanol).

^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.74 (s, 2H, ArOH, exchangeable with D_2O), 7.05 (d, 4H, J = 7.4 Hz, ArH), 6.88 (d, 4H, J = 7.3 Hz, ArH), 6.75-6.61 (m, 4H, ArH), 4.44 (d, 4H, J = 13.0 Hz, AB system for ArCH_2Ar), 4.45 4.20 (t, 4H, J = 4.6 Hz, ArOCH_2CH_2O), 4.46 4.01 (t, 4H, J = 4.6 Hz, ArOCH$_2$CH_2O), 3.85 (t, 4H, J = 4.6 Hz, OCH_2CH$_2$OCH$_3$), 3.62 (t, 4H, J = 4.6 Hz, OCH$_2$CH_2OCH$_3$), 3.37 (s, 6H, OCH_3), 3.36 (d, 4H, J = 13.0 Hz, AB system for ArCH_2Ar). 3.37 FAB (+) MS: m/z 629.3 (M + H$^+$). *Anal. Calcd*. for $C_{38}H_{44}O_8$: C, 72.58; H, 7.07. *Found*: C, 72.50; H, 7.31.

2.3.5. *1,3-Di-(ethoxy-ethoxy-methoxy)-calix[4]-(2,2′-azobenzene)-crown-6* (**5**) *from 3*

K_2CO_3 (0.138 g, 1.00 mmol) was added to a solution of **3** (0.200 g, 0.25 mmol) in 150 mL CH_3CN. After 24 h of stirring at r.t., a solution of the tosylate of 2-(2-methoxy-ethoxy)-ethanol (0.205 g, 0.75 mmol) was added and the reaction mixture was refluxed for 14 days. The work up was performed as for **3**. Chromatography on silica (93/7 dichloromethane/acetone) afforded 0.068 g (28%) of **5** as a red oil. ^{1}H-NMR spectroscopy (200 MHz and 400 MHz) showed that **5** is a mixture of *trans* and *cis* isomers. The detailed ^{1}H-NMR spectrum (400MHz, $CDCl_3$) of **5** in the aromatic region is given in Figure 3. We only give here the data of the *trans*-**5** isomer because it is the major isomer.

^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.68 (dd, 2H, J = 8.0 Hz, 2.0 Hz, ArH azobenzene), 7.39 (t, 2H, J = 9.0 Hz, ArH, azobenzene), 7.21–6.80 (m,12H, ArH), 6.69 (t, 2H, J = 7.5 Hz, ArH), 6.32 (t, 2H, J = 7.5 Hz, ArH), 4.40 (t, 4H, J = 5.5 Hz, ArOCH_2), 4.00–3.52 (m, 24H, glycolic CH_2), 3.49 (s, 8H, ArCH_2Ar), 3.41 (s, 6H, OCH_3), 3.12–3.03 (m, 4H, glycolic CH_2). FAB (+) MS m/z 983.2 (M$^+$). *Anal.Calc*.for $C_{58}H_{66}N_2O_{12}.CH_2Cl_2$: C, 66.09; H, 6.31. *Found*: C, 65.94; H, 6.56. *UV-Visible* (87/13 1,2-dichlorobenzene/*n*-butanol): c = 10^{-4}M, λ_{max} = 360 nm (11800) and 452 nm (1600).

2.3.6. *1,3-Di-(ethoxy-ethoxy-methoxy)-calix[4]-(2,2′-azobenzene)-crown-6* (**5**) *from* **4**

K_2CO_3 (2.76 g, 20.00 mmol) was added to a solution of **4** (1,26 g, 2.00 mmol) dissolved in 150 mL CH_3CN. The mixture was stirred at r.t. for 24 h under nitrogen. A solution of **2** (1.40 g, 2.00 mmol) in 50 mL CH_3CN was added dropwise. The mixture was refluxed and stirred for 4 days. The work up was performed as described for **3**. Chromatography on silica (93/7 dichloromethane/acetone) afforded 1.23 g (63%) of **5** as a red oil.

2.4. PHOTOISOMERIZATION OF **5**

The spectrophotometric cell was irradiated with a 500 W high-pressure Hg lamp. The absorption band of *trans*-**5** in 1,2-dichlorobenzene (λ_{max} = 360 nm, ϵ_{trans} = 11 900) rapidly decreased with photoirradiation time and finally reached a constant intensity after 5 min: the photostationary state. All experiments were recorded on a Varian Cary13E spectrophotometer. The distance between the lamp and the sample tube was 12 cm.

2.5. THERMAL ISOMERIZATION OF **5**

The absorption spectrum of an irradiated solution of **5** (10^{-4} M in 1,2-dichlorobenzene) was recorded on a Varian Cary13E spectrophotometer (experimental conditions: 5 min of irradiation at 20°C with a 500 W high-pressure Hg lamp). The spectrophotometer was thermostatted at 30°C and the absorption spectrum of the solution was recorded at regular intervals (20 min). In the course of time, we observed the increase of the *trans*-**5** absorption band (at 360 nm) and after about 80 min, the initial spectrum was totally recovered. The *cis*-**5** concentration, plotted against time, satisfied a first order equation, the correlation coefficient being usually better than 0.99. The thermal recovery of *trans*-**5** in the dark was slow ($t_{1/2}$ = 29 min at 30°C and $t_{1/2}$ = 40 min at 25°C).

2.6. PHOTO- AND THERMAL ISOMERIZATIONS IN THE PRESENCE OF ALKALI METAL CATIONS

Alkali cations were introduced in the organic phase as carboxylate salts of dodecanoic acid. The diluent used was a mixture of 87/13 1,2-dichlorobenzene/*n*-butanol. *n*-Butanol was used to dissolve the salts in the organic phase. Each organic solution was prepared at constant concentration of **5** (10^{-4} M) and with varying concentrations of one alkali cation. Each organic solution was irradiated for 5 min to attain the photostationary state.

2.7. SOLVENT EXTRACTION PROCEDURE

Organic solutions were irradiated prior to extraction. Equal volumes of organic solutions containing **5** (10^{-2} M in 1,2-dichlorobenzene) and of aqueous solutions containing either one or several radionuclides (^{22}Na, ^{86}Rb and ^{137}Cs at trace level), picric acid (7×10^{-3} M in 1 M lithium nitrate, pH = 3.4) were mixed for 20 min (25 $\pm$ 2 °C) in dark polypropylene, stoppered centrifuge tubes on a rotative agitation device (60 r.p.m). After centrifugation both phases were separated and aliquots were analysed by gamma spectrometry. Activity concentrations (expressed in kBq L^{-1}) were thus determined for every radionuclide in every sample. Distribution coefficients were directly calculated as the ratios of the organic phase activities and

aqueous phase activities at equilibrium. Total activity balance allowed estimation of an experimental error of 5–10%.

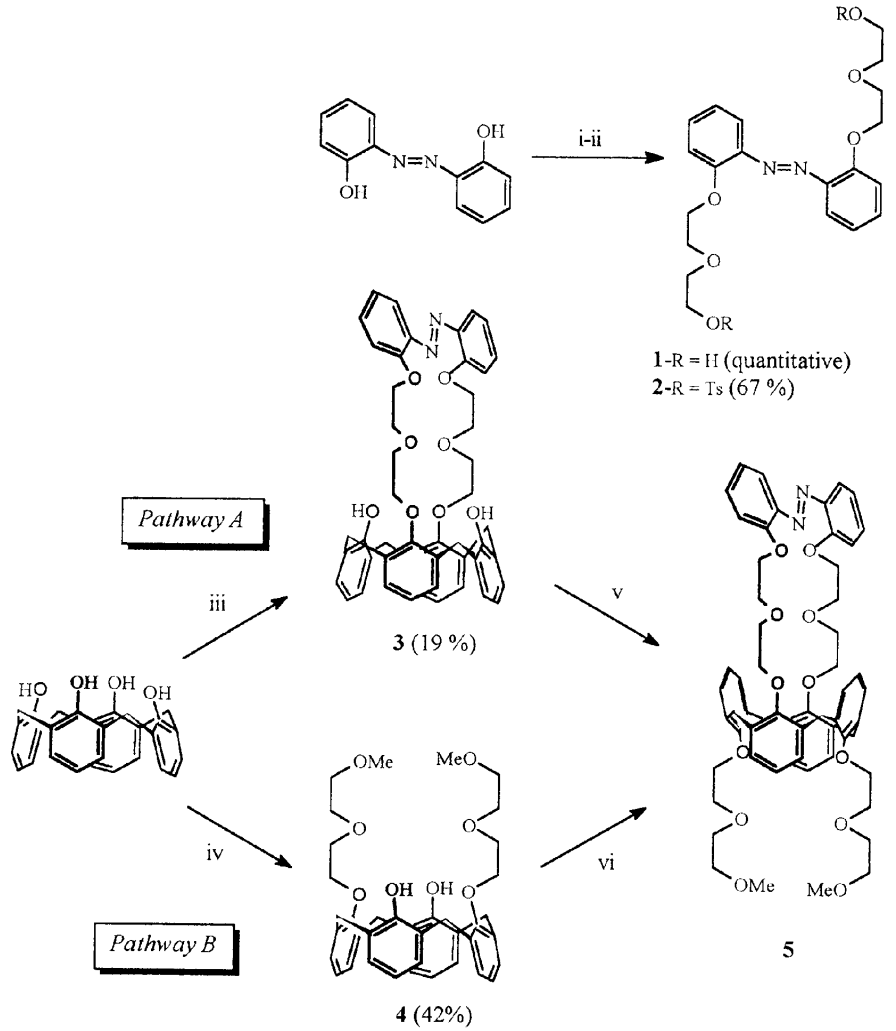
3. Results and Discussion

3.1. SYNTHESIS OF 1,3-CALIX[4]AZOBENZENE CROWN-6 (**5**)

As shown in Scheme 1 the synthesis of ligand **5** began with the *O*-alkylation of commercial *trans*-2,2′-dihydroxyazobenzene with 2.5 equiv. of 2-(2-chloroethoxy)-ethanol in the presence of K_2CO_3 (acetonitrile, 12 days reflux) to produce the azo diol **1** (mp. 68–69°C) quantitatively, which was treated with 2 equiv. of tosylchloride in the presence of 4 equiv. of NEt_3 (CH_2Cl_2, 0 °C, 48 h at r.t.). The oily residue was eluted from silica (90/10 chloroform/acetone) and recrystallisation from dichloromethane/methanol gave the azo ditosylate **2** as a red powder (mp.99–100° C; 67%). From this point, the synthesis of macrocycle **5** has been achieved along two different pathways (see Scheme 1).

In pathway A: calix[4]arene was condensed with 1 equiv. of **2** in the presence of 1.05 equiv. of K_2CO_3 (acetonitrile, 7 days reflux). Purification of the crude mixture by silicagel chromatography with 90/10 chloroform/acetone lead to pure **3** (mp.117–118 ° C; 19%). The red powder obtained (**3**) was analyzed by thin layer chromatography (95/5: dichloromethane/acetone) and two red spots were observed, R_f = 0.58 and 0.51 corresponding to the *trans* and *cis* isomers, respectively. By comparing the intensity of each spot it was concluded that the *trans*-**3** was mainly formed. This was in agreement with the ^{1}H-NMRdata as deduced by the presence of a pair of doublets at 7.63 ppm (J = 8.0 Hz, coupling between H_6 and H_5, and J = 2.0 Hz, coupling between H_6 and H_4) for the aromatic protons of the azobenzene moiety at low magnetic field as noticed in Ref. [10]. Selective 1,3-capping and cone conformation were deduced by the presence of one pair of doublets at 4.37 ppm and 3.34 ppm (J = 13.0 Hz) for the methylene ArCH_2Ar. Subsequently, derivative **3** was 1,3-O-dialkylated with 3 equiv. of the tosylate of 2-(2-methoxy-ethoxy)-ethanol in the presence of 4 equiv. of K_2CO_3 (acetonitrile, 14 days reflux) to afford, after chromatography on silica (97/3 dichloromethane/acetone) in the dark, pure **5** (red oil; 28%).

In *pathway B*: calix[4]arene was first 1,3-*O*-dialkylated with 2 equiv. of the tosylate of 2-(2-methoxy-ethoxy)-ethanol in the presence of 1 equiv. of K_2CO_3 (acetonitrile, 7 days reflux), after chromatography on silica column and recrystallization from methanol, which yielded **4** as a white solid (mp 133–134 °C; 42%). Compound **4** was shown to be in the cone conformation by the presence in its ^{1}H-NMR spectrum of the characteristic AB system at 4.44 ppm and 3.36 ppm (J = 13.0 Hz) corresponding to the ArCH_2Ar protons. Condensation of **4** with 1 equiv. of **2** in the presence of an excess of K_2CO_3 (acetonitrile, 4 days reflux), after chromatography on a silica column in the dark, afforded ligand **5** in 63% yield. The ^{1}H-NMR spectrum of **5** revealed that both 1,3-*O*-dialkylation of **3** or distal 1,3-capping of **4** occured with a change from the cone conformation into



Scheme 1. Synthesis of ligand **5**.

the 1,3-alternate one due to the presence of one singlet at 3.49 ppm for methylene ArCH_2Ar. Azocalix-crown **5** was analysed by TLC (85/15 CH_2Cl_2/acetone) and two red spots were also observed R_f = 0.61 and 0.48 showing *trans*-**5** to be the major product. This was confirmed by the presence in the ^{1}H-NMR spectrum of a pair of doublets at 7.68 ppm (J = 8.0 Hz, coupling between H_6 and H_5, and J = 2.0 Hz, coupling between H_6 and H_4) for the aromatic protons H_6 of the azobenzene moiety at low magnetic field as noticed in reference [10] for the *trans* form.

3.2. PHOTOISOMERIZATION OF **5**

Photosensitive azo calixcrown **5** exists as a mixture of *trans* and *cis* forms at equilibrium, as depicted in Figure 1. *Trans*-**5** is the major form, because it is the more thermodynamically stable. The azobenzene unit possesses a low intensity absorption band in the visible spectrum and a high intensity absorption band in the UV spectrum [11]. In the case of **5**, the absorption maximum of *trans*-**5** appeared at 360 nm ($\pi - \pi^*$ transition), whereas that of *cis-5*, with a much lower intensity, appeared at 460 nm ($n - \pi^*$ transition). The *cis* isomer also absorbs at 360 nm, but its molar extinction coefficient is much lower than that of the *trans* isomer at the same wavelength. For a better interpretation of the absorption spectra it is therefore easier to work at 360 nm.

Figure 2 shows the absorption spectra of the *cis-trans* mixture of **5** at equilibrium and under the photostationary state. The *cis-trans* ratio of **5** was determined by ^{1}H-NMR studies: 82% *trans*-**5** + 18% *cis*-**5**. Figure 3 shows the ^{1}H-NMR (400 MHz, $CDCl_3$) of the aromatic region of mixture **5**. The *trans-cis* ratio was evaluated by calculating the ratio between the integration of the triplet at 6.32 ppm (J = 7.5 Hz) corresponding to two *para* protons, $H_{p,p'}$ of the calix unit of *trans*-**5** and the integration doublet at 7.15 ppm (J = 8.2 Hz) corresponding to the two protons $H_{3,3'}$ (numbering of the azobenzene unit) of *cis*-**5**. This value allowed us to calculate the molar extinction coefficients of *trans*-**5** and of *cis*-**5** at 360 nm by using the Beer–Lambert equation and assuming that: ϵ_{trans} = 7.4 × ε_{cis}, as referred to reported studies performed on azo benzo-bis-crowns [12]. We thus obtained: ε_{trans} = 11 900 and ε_{cis} = 1600 at 360 nm from which we have estimated the *cis-trans* composition under the photostationary state to be 55/45 ([*cis*-**5**]/[*trans*-**5**]).

3.3. INFLUENCE OF ALKALI METAL CATIONS ON THE PHOTOISOMERIZATIONS AND THERMAL ISOMERIZATIONS

The presence of alkali cations in the organic phase can directly influence the photostationary state of the photosensitive ligand if the cations are selectively complexed by one of the two isomers. From the reported experiments we evaluated the affinities of *cis*-**5** and *trans*-**5** towards alkali cations: Na^+, K^+, Rb^+ and Cs^+, by observing the reversibility of the photoisomerization. It was also possible to determine the stability of the complexes formed with the different isomers. Figure 4 shows the percentage of *cis*-**5** under photostationary state plotted as a function of the added cations. The compositions of *cis-trans* mixtures at the photostationary state are listed in Table I for [cation]/[**5**] = 1.

In the presence of alkali cations, there is a steady increase of the percentage of the *cis*-**5** in the following order: $Na^+ < K^+ < Rb^+ < Cs^+$. The presence of any of these cations suppressed the thermal isomerization, indicative of a thermodynamic stability. Na^+ and K^+ only slightly increased the percentage of the *cis* isomer in the photostationary state, which suggests that these cations are moderately complexed

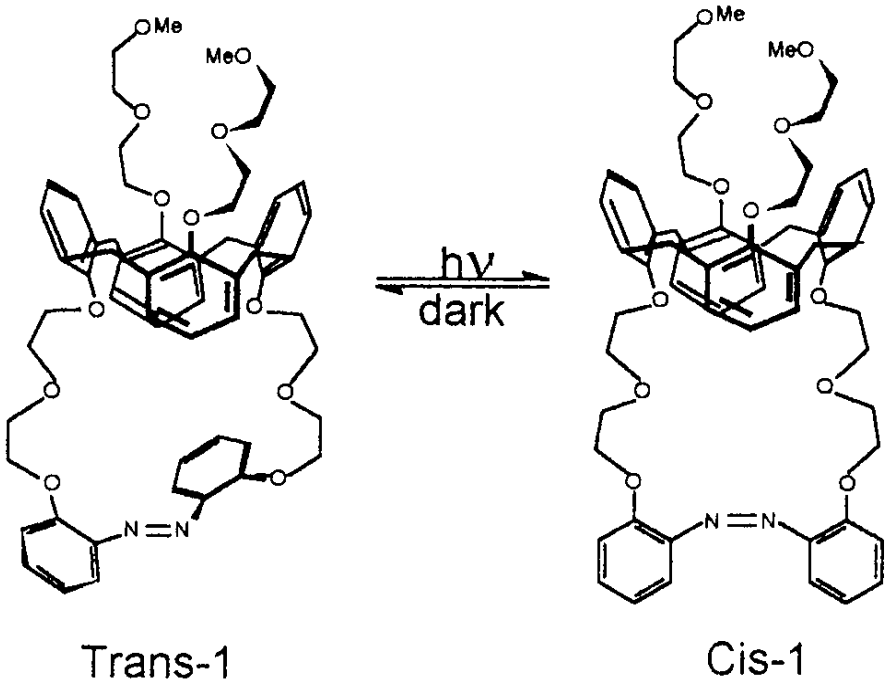


Figure 1. *Cis-trans* isomerization of **5**.

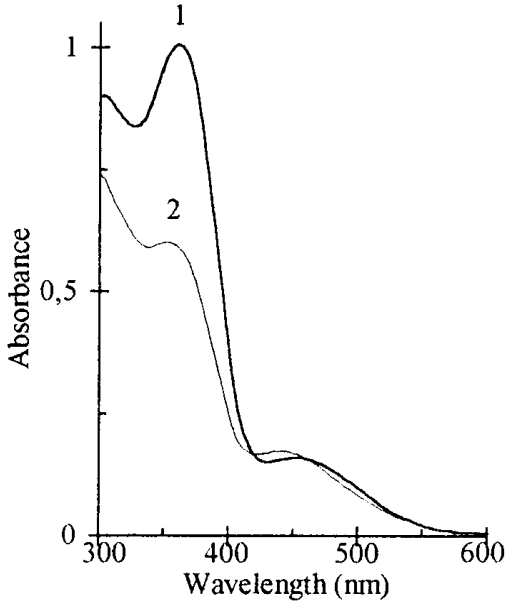


Figure 2. Absorption spectra of **5**: (1) *cis-trans* mixture at equilibrium; (2) *cis-trans* mixture in the photostationary state; [**5**] = 10^{-4} M in 1,2-dichlorobenzene.

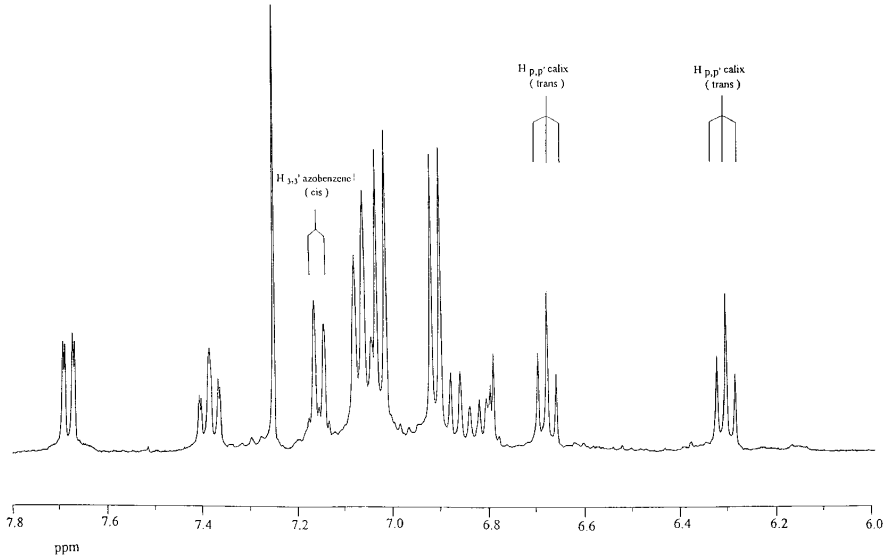


Figure 3. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$, r. t.) of the aromatic region of mixture **5**.

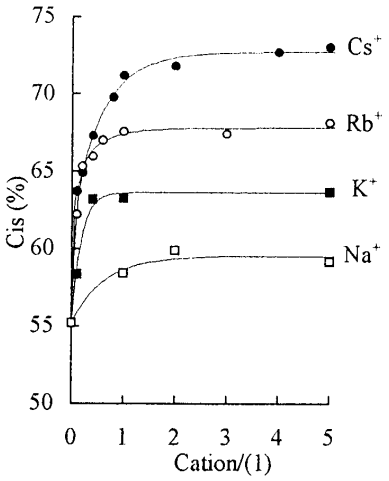


Figure 4. Composition of *cis*-**5** in photostationary state plotted as a function of added metal cations. [**5**] = 10^{-4} M, 1,2-dichlorobenzene/*n*-butanol = 87/13 by volume. The counter ion is dodecanoate (see Experimental).

by *cis*-**5**. Nevertheless, one can assume that the constant of complexation of K^+ by *cis*-**5** should be greater than that of Na^+.

Rb^+ and Cs^+ increased the percentage of the *cis*-**5** and prevented thermal isomerization. This allowed us to assume that these two cations are strongly complexed by *cis*-**5** and that both complexes are highly stable.

Table I. Influence of added alkali metal ions on the *cis-trans* ratio in photostationary state[a].

Cation	*cis/trans*
None	55/45
Na^+	58/42
K^+	63/37
Rb^+	68/32
Cs^+	71/29

[a] 1,2-dichlorobenzene/*n*-butanol = 87/13 by volume, [cation]/[**5**] = 1.

Table II. Extraction of alkali metal cations with **5**.

	Equilibrium	PSS[c]	MF[d]
D^a_{Na}	4.4.10-4	2.7.10-4	0.6
D^a_{Rb}	1.8	5.1	2.8
D^a_{Cs}	2.2	6.6	3.0
Cis-**5**[b]	18	55	
Trans-**5**[b]	82	45	

[a] Distribution coefficients; [b] % composition of the *cis*/*trans* mixture; [c] PSS photostationary state; [d] MF multiplicative factor between equilibrium and photostationary states.

3.4. SOLVENT EXTRACTION OF ALKALI METAL CATIONS WITH **5**

The study of the loading capacity of compound **5** revealed that both *cis*-**5** and *trans*-**5** extracted Cs^+ and Rb^+. Table II summarises the distribution coefficients [13] of Na^+, Rb^+ and Cs^+ with ligand **5** at equilibrium and in the photostationary state (photoirradiation time = 5 min). For Na^+, the multiplicative factor (MF) of the distribution coefficient between the equilibrium and photostationary states is less than one, which implies that Na^+ is preferentially extracted by *trans*-**5**, whereas for Rb^+ and Cs^+ the MF is greater than one indicating that these two cations are better extracted by *cis*-**5**. The extraction constants of Rb^+ and Cs^+ are higher in the case of the *cis*-**5** than in those of the *trans*-**5**. It is difficult to make any assumption for Na^+ because the distribution coefficients are too low.

We have shown in preceding papers [6] that introduction of a 1,2-phenylene residue in the middle of the crown of calix[4]-*bis*-crown-6 favored the complexation of cesium as compared to sodium. This could be attributed to the replacement of sp^3 oxygens by sp^2 ones leading to a 'flattening' of the glycolic chain. By a

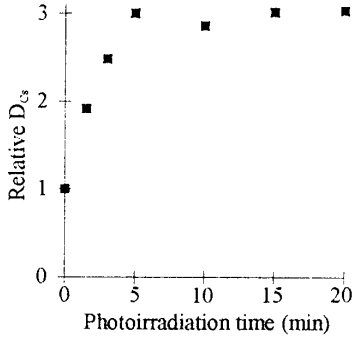


Figure 5. Relative cesium distribution coefficient plotted as a function of photoirradiation time. Aqueous phase: picric acid 7.10^{-3} M, $LiNO_3$ 1 M, pH = 3,4 and ^{137}Cs at trace level; Organic phase: [1] = 10^{-2} M in 1,2-dichlorobenzene. Relative D_{Cs} = 1 corresponding to D_{Cs} = 2,2.

similar 'flattening effect' one can assume that the phenyl rings of *cis*-**5** organize the polyether loop like tweezers for complexing the cesium, whereas in *trans*-**5**, the crown shrinks because of the opposite positions of the phenyl rings on both sides of the *trans* —N=N— bond. *Trans*-**5** thus lacks two or more sites of coordination as compared to the *cis*-**5** isomer, because all lone pairs of the oxygen atoms attached to the azobenzene function are pointing outside of the central point of the cavity of the loop (see Figure 1).

This was confirmed by the following observations: in Figure 5 the relative distribution coefficient of cesium is plotted as a function of the photoirradiation time. D_{Cs} first increases with the irradiation time and then reaches a 'plateau' corresponding to the photostationary state: Cs^+ extraction actually increases with the *cis*-**5** proportion, which confirms the results reported in Table II.

To conclude, our investigations show that the isomerization mechanism of **5** is totally reversible. Extraction of Cs^+ and Rb^+ proved that *cis*-**5** exibits a greater binding ability than *trans*-**5**. Extraction properties of **5** may be controlled with UV-isomerization. It would be very interesting to develop this process in the case of very strong ligands.

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