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LETTERS

Complexation Properties of a new Photosensitive Calix[4]arene Crown Ether Containing Azo Unit in the Lower Rim towards alkali cations.

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Abstract : A new photosensitive calix[4]arene crown ether with azo unit (1) is studied. *Trans*-**1** was isomerized by UV light to *cis*-**1** which in turn was isomerized thermally to *trans*-**1**. Reversible isomerizations have been observed and the cis isomer extracts cesium and rubidium better than the trans isomer.

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. The partitioning of toxic radioelements is obtained by specific complexation through liquid-liquid extraction.[1] Nevertheless, decomplexation of some special cations sometimes becomes difficult with very strong ligands.[2]

One solution could be to induce a structural modification of the cavity of the extracting ligand between the complexation and decomplexation steps of the cation, thanks to the introduction of a light-isomerizable chromophoric group in the frame of the molecule. First of all, many examples of photosensitive extracting agents containing azo units allowing modifications of the complexing cavities through cis and trans isomerizations are reported in literature[3] ; and furthermore, calixarenes have shown very high extraction selectivities towards cesium when bridged with crown ethers.[4] That is why we have decided to introduce an azo unit in the crown ether bridge of a 1,3 alternate calix[4]arene. Although the crown ether bridge is modified by the introduction of an azobenzene unit in its frame, the synthesized photosensitive calixarene should not only combine the properties of preorganized calixarenes with the complementarity properties of classical crown ethers,[5] but should also benefit from the properties of the azobenzene function which changes its conformational configuration through Ultra Violet irradiation or thermic isomerization.[6]

In this paper, we report the complexation properties of a mono-crown-6-azobenzo-calix[4]arene **1** synthesized by Vicens and Asfari.[7] Figure 1 shows the cis-trans isomerization of **1**.

Photoisomerization of 1. The photosensitive calixarene tested is a mixture of trans and cis forms at equilibrium. The *Trans*-**1** is the major form of the mixture, because it is the most thermodynamically stable. The azobenzene unit possesses a low level energy absorption band in the visible spectrum and a high level energy absorption band in the UV spectrum.[6] In the case of **1**, the absorption maximum of *trans*-**1** appears at 360 nm (π-π* transition), whereas that of *cis*-**1**, of much lower intensity, appears at 460 nm (n-π* transition). The cis isomer also absorbs at 360 nm, but its molar extinction coefficient is much lower in comparison to that of the trans isomer at the same radiation. 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 **1** at equilibrium and under the photostationary state. The composition of the mixture was determined by NMR studies : 82% *trans*-**1** + 18% *cis*-**1**.[8] This composition allowed us to calculate the molar extinction coefficients of trans-**1** and

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of cis-**1** at 360 nm thanks to the Beer-Lambert equation, assuming that : $\varepsilon_{trans} = 7.4.\varepsilon_{cis}$, as referred to reported studies performed on azobenzo-bis-crowns.[9] We thus obtained : $\varepsilon_{trans} = 11900$ and $\varepsilon_{cis} = 1600$ at 360 nm. We then estimated the composition under the photostationary state to be 55/45 ([*cis*-**1**]/[*trans*-**1**]) similar to published data on azobenzobiscrown[9].

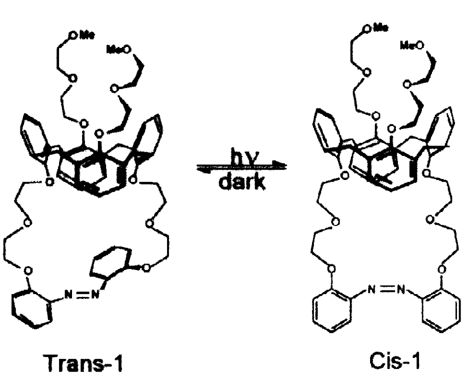

Figure 1. Cis-Trans Isomerization of **1**.

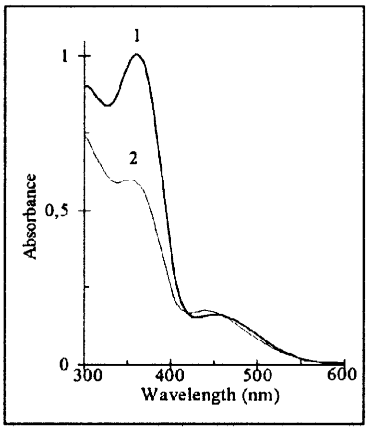

Figure 2. Absorption spectra of **1** : (1) cis/trans mixture at equilibrium ; (2) cis/trans mixture under the photostationary state; [**1**] = 10^{-4} M in 1,2-dichlorobenzene.

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 their two isomers. The reported experiment allowed us to define the affinities of cis and trans isomers towards alkali cations : Na^+, K^+, Rb^+ and Cs^+. By observing the reversibility of the photoisomerization, it was possible to determine the stability of the complexes formed with the different isomers. Figure 3 shows the percentage of *cis*-**1** under photostationary state plotted as a function of added metal cations. The compositions of cis/trans mixture at photostationary state and after thermal isomerization are listed in Table I for [cation]/[**1**] = 1.

In the presence of alkali cations the percentage of the cis form increased in the following order: $Na^+ < K^+ < Rb^+ < Cs^+$. Na^+ and K^+ only slightly increase the percentage of the cis isomer under photostationary state, which suggests that these cations are moderately complexed by *cis*-**1**. Nevertheless, the complexation constant of K^+ by *cis*-**1** should be greater than that of Na^+.

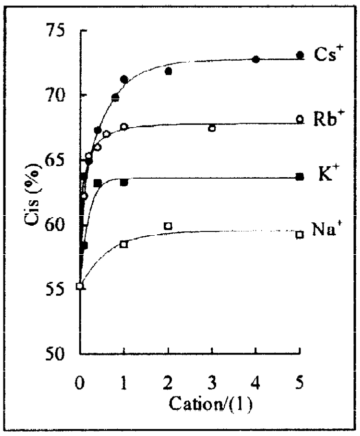

Figure 3. Composition of *cis*-**1** under photostationary state plotted as a function of added metal cations.
[**1**] = 10^{-4} M, 1,2-dichlorobenzene:*n*-butyl alcohol = 86.8:13.2 by volume.

Table I. Influence of Added Alkali Metal Ions on the Cis/Trans Ratio under Photostationary State[a] and after thermal isomerization [b]

cation	*cis/trans* [a]	*cis/trans* [b]
none	55/45	18/82 after 80 min
Na^+	58/42	58/42 after 100 h
K^+	63/37	63/31 after 100 h
Rb^+	68/32	68/32 after 100 h
Cs^+	71/29	71/29 after 100 h

1,2-dichlorobenzene/*n*-butanol 86.8/13.2 by volume, [cation]/[1] = 1

On the other hand Rb^+ and Cs^+, which usually show very similar physical structures, drastically increase the percentage of the cis isomer. This allowed us to assume that these two cations are strongly complexed by the *cis*-**1** isomer and that both complexes are very stable. In any case, the presence of alkali cations completely prevent thermal isomerization, which implies strong thermodynamise stability of complexes.

Solvent Extraction of Alkali Metal Cations with 1. The study of the loading capacity of compound **1** has revealed that both isomers *cis*-**1** and *trans*-**1** extracted Cs^+ and Rb^+.[10] Table II sums up the observed distribution coefficients of Na^+, Rb^+ and Cs^+ with compound **1** at equilibrium and under photostationary state (photoirradiation time = 5 min). For Na^+, the multiplicative factor (MF) of distribution coefficient between equilibrium and photostationary state is less than one, which implies that Na^+ is preferentially extracted by *trans*-**1** isomer ; whereas for Rb^+ and Cs^+ MF is greater than one indicating that the latter two cations are better extracted by *cis*-**1** isomer. The extraction constants of Rb^+ and Cs^+ are higher in the case of the *cis*-**1** isomer than in the case of the *trans*-**1** isomer. It is difficult to make any assumption in the case of Na^+ because the distribution coefficients are too low.

Table II. Extraction of Alkali Metals Cations with 1.

	Equilibrium	PSS [c]	MF [d]
D_{Na}[a]	$4.4.10^{-4}$	$2.7.10^{-4}$	0.6
D_{Rb}[a]	1.8	5.1	2.8
D_{Cs}[a]	2.2	6.6	3.0
Cis-**1**[b]	18	55	
Trans-**1**[b]	82	45	

[a] distribution coefficients ; [b] composition of the cis/trans mixture of the free ligand in percentage ; [c] PSS photostationary state ; [d] MF multiplicative factor between equilibrium and photostationary state

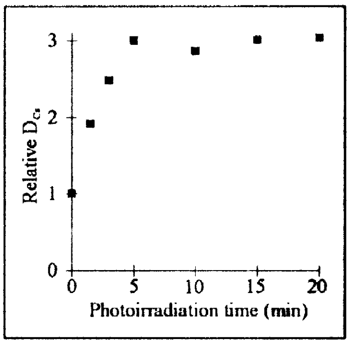

Figure 4. Cesium distribution coefficient relative plotted as a function of photoirradiation time.

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

Adding an aryl group (in the 1,2 position) in the frame of the crown of a calix[4]arene-crown-6 not only modifies the size of its cavity but also increases the number of its coordination sites, which favors the complexation of cesium more than the complexation of sodium (cesium beeing a voluminous polarizable cation, "softer" and less hydrated than sodium, a small dense and "hard" cation).[11] Therefore both phenyl rings of the *cis*-**1** isomer should take part in the complexation of cesium. Whereas in the case of the *trans*-**1** isomer, the crown shrinks owing to the opposite positions of the phenyl rings (on both sides of the N=N bond). The *trans*-**1** isomer thus lacks two sites of coordination as regard to *cis*-**1** isomer, because all free electron doublets of the oxygen atoms attached to the azobenzene function on the one hand and of the nitrogen atoms on the other hand are pointed outside the cavity of the calixarene.

In figure 4 the cesium relative distribution coefficient 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*-**1** proportion, which confirms the results reported in table II.

Our investigations show that isomerization mechanisms of **1** are totally reversible. Extraction of Cs^+ and Rb^+ prove that *cis*-**1** exhibits the greater binding ability than *trans*-**1**. Extraction properties of **1** may be controlled with UV-isomerization. It would be very interesting to develop this process in the case of very strong ligands.

EXPERIMENTAL SECTION

Photoisomerization of 1. The spectrophotometric tube was irradiated with a 500 W high-pressure Hg lamp. The absorption band of *trans*-**1** in 1,2-dichlorobenzene (λ_{max} = 360 nm, ε_{trans} = 11900) rapidly decreased with photoirradiation time and finally reached a constant intensity after 5 min : the photostationary state. All experiments were recorded on a Varian spectrophotometer (Cary13E). The distance between the lamp and the sample tube was 12 cm.

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

Photoisomerizations and Thermal Isomerizations in Presence of Alkali Metal Cations. Alkali cations were introduced in the organic phase as carboxylate salts of dodecanoïc acid. The diluent used was a mixture of 1,2-dichlorobenzene and *n*-butanol (86.8/13.2 vol.), *n*-butanol favoring the dissolution of the salts in the organic phase. Each organic solution were prepared with a constant concentration of calixarene (10^{-4} M) and a various concentration of one and only one alkali cation. Each organic solution was irradiated during 5 min to attempt the photostationary state.

Solvent Extraction Procedure. Prior to extraction, organic solutions were irradiated if necessary. Equal volumes of organic solutions containing **1** (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 lithium nitrate 1 M, pH = 3.4) were mixed for 20 min (25 +/- 2 °C) in centrifugal dark polypropylene stopped tubes on a rotative agitation device (60 rd.min^{-1}). After centrifugation, both phases were separated and aliquots were analysed by gamma spectrometry. Distribution coefficients were directly calculated as the ratios of the organic phase activities and aqueous phase activities at equilibrium.[1] Total activity balance allowed estimation of an experimental error of 5 - 10 %.

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