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Photodegradation of Calixarenes*

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ABSTRACT

Calixarenes are interesting compounds with respect to their high melting points and complexing properties. Spectroscopic characteristics and photochemical stability data are reported in these present studies of quantum yield of fluorescence, phosphorescence and photodegradation. The photodegradation occurs from the triplet state. The addition of a chromophore into the molecule, and the presence of a triplet inhibitor, are necessary for any potential use of these compounds in the colour industry. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The increasing number of patents on calixarenes attests to the interest of industry in these compounds[1] and many reports have been published on their syntheses and characterization.[2,3]

It is known that calixarenes can be used as complexes[4] and as catalysts,[5] and that these molecules are also capable of 'mimicking various aspects of natural systems'.[1]

In this paper we are concerned with calixarenes which could be used as supports for dyes after addition of chromophores on the phenolic nucleus.[6] In this perspective, spectroscopic and photochemical properties were studied. The calixarenes used were:

p-isopropylcalix [*n*] arene : $n = 4, 6, 8$ (4–<, 6–<, 8–<).

p-tert-butylcalix [*n*] arene : $n = 4, 6, 8$ (4+, 6+, 8+).

*In memory of Professor Robert Perrin.

They were synthesized according to the method previously reported by Gutsche *et al.*[7–10]

EXPERIMENTAL

UV absorption spectra were recorded on a Perkin Elmer 554 and emission spectra on a Jobin-Yvon JY 3D fluorimeter-phosphorimeter.

Irradiations were carried out with a low-pressure mercury-vapour lamp emitting mainly at 254 nm. The amount of radiation entering the reaction vessel was 9×10^{-7} Einstein s^{-1}.

The photodegradation of the calixarenes was carried out in ethanol and their concentration measured by HPLC with a C18 reversed phase column (25 cm, 10 μ). The solvent used was a mixture of acetonitrile (85%), chloroform (4·5%), tetrabutylmethylether (9%) and acetic acid (1·5%).

Spectroscopic and photochemical properties

The absorption spectra are approximately the same for all the compounds;[11] data are shown in Table 1 (solvent:chloroform).

The emission spectra are also very similar, with the same values for the singlet state, the triplet state, the quantum yield of fluorescence and phosphorescence.

TABLE 1
UV Spectra of Calixarenes and Initial Monomers (in Chloroform)

Calixarene		*4 –<*	*4 +*	*6 –<*	*6+*	*8–<*	*8+*
Absorption	(1)	280	278	280	278	280	281
Maxima	(2)	286	284	287	286	286	288
Molecular	ϵ_1	13460	13900	16300	16480	25460	23040
Absorption	ϵ_2	10900	10800	17000	17400	28000	26900
Coefficients	$\epsilon_1\epsilon_2$	1·23	1·28	0·96	0·94	0·90	0·86

and for the initial monomers:

	λ *max*	ϵ *max*	ϵ_1/ϵ_2
Iso-propylphenol	274	1860	1·15
	280	1620	
tert-Butylphenol	273	1830	1·14
	280	1600	

λ = absorption wavelength (nm).
ϵ = molar extinction coefficient (litre mol^{-1} cm^{-1}).

TABLE 2
Emission Spectra of Calixarenes

Calixarene	*4–<*	*4 +*	*6–<*	*6 +*	*8–<*	*8 +*
λ_f (nm)	318	315	340	306	310	307
S_1 (kJ)	397	401	389	409	409	409
ϕ_f	0·10	0·09	0·05	0·07	0·08	0·10
λ_p (nm)	420	413	425	395	382	390
T_1 (kJ)	284	288	280	300	309	305
ϕ_p	0·17	0·14	0·14	0·16	0·10	0·05

λ_f = fluorescence maximum wavelength.
ϕ_f = fluorescence quantum yield.
λ_p = phosphorescence maximum wavelength.
ϕ_p = phosphorescence quantum yield.
S_1 = singlet state level.
T_1 = triplet state level.

TABLE 3
Emission Spectra of Initial Monomers

Phenol	*Iso-propylphenol*	tert-*Butylphenol*
λ_f	310	307
ϕ_f	0·045	0·09
λ_p	395	395
T_1	305	305
ϕ_P	0·25	0·15

For explanations see Table 2.

Comparing the properties of calixarenes with those of phenols, the main difference is in the quantum yield of phosphorescence (Tables 2 and 3). This result is interesting, since it is known that the photodegradation of phenols occurs from their triplet state.[12]

PHOTODEGRADATION

The photodegradation of the calixarenes was monitored in ethanol, using HPLC for the concentration measurements. For all compounds, first-order kinetics were observed and the values of the rate constants are shown in Table 4.

Under equivalent conditions of irradiation, the *p*-isopropylcalix [8] arene was the most photodegradable. To ascertain the photostability of the products

TABLE 4
Kinetic Constants and Quantum Yields of Photodegradation

Calixarene	*4* –<	*4* +	*6* –<	*6* +	*8* –<	*8* +
$k.10^5$ s	21	49	76	46	96	62,5
ϕ_d	0·4	0·7	0·6	0·9	0·5	0·2

ϕ_d iso-propylphenol = 0·11.
ϕ_d *tert*-butylphenol = 0·12.

it is necessary to calculate their quantum yield of photodegradation using the relationship:-

$$\phi_D = \frac{kV}{2{\cdot}3\ \epsilon\ l\ I_0}$$

in which

ϕ_D = quantum yield of photodegradation.
k = rate constant.
V = volume of irradiated solution.
ϵ = molecular extinction coefficient at 254 nm.
l = optical path in the solution.
I_0 = intensity of the reactor lamp.

Our experiments showed that the quantum yield was always higher for calixarenes than for the initial monomer (Table 4).

To confirm the nature of the excited state, the photodegradation of the *p-tert*-butylcalix [6] arene in presence of a triplet state inhibitor (biphenyl) was studied. The energy of the biphenyl triplet state is 274 kJ.

Using these conditions, the photodegradation quantum yield was calculated as a function of the inhibitor concentration using the Stern–Volmer relation :

$\phi°/\phi = 1 + k.\ \tau.$ [inhibitor]
k = diffusion constant in ethanol = 10^{10} s^{-1}
τ = life time of the triplet state = $7{\cdot}5 \times 10^{-7}$ s

The linear relationship between $\phi°/\phi$ and the concentration of the inhibitor confirms that the studied excited state is really the first step of the photodegradation.

CONCLUSION

The objective of the study was to evaluate spectroscopic and photochemical properties of the calixarenes. Where absorption data had already been

determined for any of the derivatives, no information pertaining to their emission properties and their photostability was available.

The low quantum yield of fluorescence and the high quantum yield of photodegradation are parameters which are not compatible with the use of the compounds in colour industry. In this context, it would be of interest to synthesize calixarenes containing chromophores and to use them in solution with an inhibitor of the triplet state. On this basis, there should result a red shift of the absorption and emission range, and a stabilization of the molecule.

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