A strategy for the photoisomerization of aromatic norbornadienes in aqueous media, based on β-cyclodextrin inclusion complexes

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Abstract. The formation of 1:1 inclusion complexes between norbornadiene aromatic derivatives and β-cyclodextrin was investigated spectrofluorometrically, in aqueous media. Photophysical properties, thermodynamic constants, and photoisomerization kinetics of these complexes were determined.

Keywords. Norbornadiene derivatives; inclusion complexes; β-cyclodextrin; photoisomerization; spectrofluorimetry; spectrophotometry; kinetics.

1. Introduction

Among the valence photoisomerization reactions, the phototransformation of norbornadiene (NBD) into quadricyclane (QC) has received particular attention [1-3]. Notably, in the late seventies and eighties, this photochemical system has been widely investigated as an efficient means for solar energy storage [4]. Indeed, its high quantum yield, long-time storage capacity and cheapness are major advantages [5]. However, this system also presents serious drawbacks such as the existence of side-reactions competitive with photoisomerization, the location of the electronic absorption spectrum of NBD in the low UV region which is far from the solar spectrum, and the toxicity and inflammability of the reagents and solvents used, which impede real applications of this reversible system [5].

Different approaches have been proposed in order to solve these problems. The structure of NBD has been modified by introducing chromophores and/or substituents able to lower the absorption energy of the molecule and/or to increase its solubilization in water [6,7]. Recently, chemically and electrochemically synthesized polymers bearing NBD moieties have been studied to avoid side reactions and/or to use these systems in the solid state [8-10].

In this work, we have investigated the photoisomerization of four new hydrophobic NBD derivatives (figure 1) in aqueous medium by using β-cyclodextrin (β-CD) as a complexing agent. Cyclodextrins (CD) are doughnut-shaped molecules able to include organic molecules of smaller geometric dimensions in their cavity. Generally, inclusion complexes formed with CD are more hydrosoluble than the free molecules. We have determined fluorimetrically the stoichiometry and association constant of such NBD:β-CD complexes. Several reports [11-14] have shown that the photoisomerization reactivities of various organic compounds, including substituted NBD [11] and azobenzene [12] are significantly changed upon inclusion in β-CD.

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*For correspondence

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a: -H
b: -CH$_2$-pC$_6$H$_5$
c: -CH$_2$-pC$_6$H$_4$-O-CH$_3$
d: -(CH$_2$)$_6$-O-pC$_6$H$_4$-O-CH$_3$
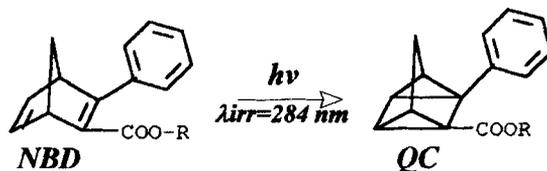
Figure 1. Structures of the aromatic NBD and QC derivatives (*a-d*).

Table 1. Absorption and fluorescence spectral properties of the NBDs (a–d) in the studied media^a.

N°	Medium	λ_{abs},(nm)^b, (log ε)^c	λ_{exc} (nm)^b	λ_{emi} (nm)^b	$I_F{}^d$
a	Ethanol	288(3·85), 205(4·55)	NF^e	NF	NF
	Eau/Ethanol	292(4·04), 222(3·81)	—	—	—
	Eau/Ethanol/β-CD	285(3·85), 225(4·13)	—	—	—
b	Ethanol	293(3·74), 205(4·35)	284	332, 350	1
	Eau/Ethanol	284(3·95), 230(4·01)	283	334	1·2
	Eau/Ethanol/β-CD	292(3·84), 227(4·03)	282	334	1·6
c	Ethanol	298(3·84), 276(3·95), 224(4·33), 203(4·39)	274	298	1
	Eau/Ethanol	322(3·93), 286(3·92), 241(4·04)	275	302	1·3
	Eau/Ethanol/β-CD	294(3·68), 277(3·74), 224(4·19)	276	306	2
d	Ethanol	290(3·40), 224(3·79), 203(4·11)	291	326	1
	Eau/Ethanol	295(4·02), 228(4·20)	282	328	1·2
	Eau/Ethanol/β-CD	287(3·88), 231(4·24)	278	328	3

a: NBD derivative concentrations: 5×10^{-5} M. **b**: λ_{abs}, λ_{exc}, λ_{em} = absorption and fluorescence excitation and emission wavelengths, respectively. The main absorption peak is underlined. Précision ± 1 nm. **c**: molar absorption coefficient. **d**: relative fluorescence intensity, calculated by the ratio: $\dfrac{F(medium)}{F(ethanol)}$. **e**: compound not fluorescent.

2. Results and discussion

Since NBD aromatic derivatives (*a–d*) are very slightly soluble in water, the NBD stock solutions (10^{-3} M) were prepared in ethanol, and were diluted with water. Working solutions (5×10^{-5} M) were prepared in ethanol (EtOH), water/ethanol mixture (v/v, 99/1) (WE), and WE in the presence of 0·01 M β-CD (WECD).

The electronic absorption, excitation and emission fluorescence spectra of compounds *a–d* (5×10^{-5} M) were performed in EtOH, WE and WECD (table 1). The absorption spectra were found to be similar in EtOH and WECD, whereas in WE there

was no well-resolved band. This indicates that specific interactions occur between the NBD derivatives and the β-CD molecules. Moreover, the existence of solvation microheterogeneities and/or autoassociations, is suggested by the spectral characteristics of the NBD derivatives in aqueous solution.

Fluorescence emission spectra were recorded in the same experimental conditions as above; the excitation (λ_{ex}) and emission (λ_{em}) wavelengths are reported in table 1. The fluorescence intensity increased considerably when β-CD was added to the aqueous medium, while only small spectral shifts were noticed in the emission band. These results and similar spectral features previously reported for β-CD complexes [15,16] suggest that the NBD derivatives are included in the β-CD cavity, forming host-guest complexes.

We evaluated the thermodynamic properties of the complexes, by studying the β-CD concentration effect on the fluorescence intensity of 5×10^{-5} M NBD derivative aqueous solutions. The analytical treatment was based on the mathematical models (1, 2 and 3) proposed by Scatchard and Benesi–Hildebrand [15,17]. Assuming that β-CD forms a 1:1 stoichiometry inclusion complex with NBD, the relationship between the observed fluorescence intensity enhancement $(F - F_0)$ and the β-CD concentration is given by

$$(F - F_0)/[\beta - CD] = (F_\infty - F_0)K_f - (F - F_0)K_f \tag{1}$$

where F_0 and F_∞ denote the fluorescence intensity of the NBD derivative under study, in the absence and in the presence of 0·01 M β-CD respectively, and F is the observed fluorescence at each β-CD concentration under study; and K_f is the formation constant of the binary complex. For a 1:1 complex, a plot of $(F - F_0)/[\beta - CD]$ versus $(F - F_0)$ should give a straight line. In figure 2, such a representation is shown and a linear relationship is obtained. This suggests that the stoichiometry of the complex is 1:1.

The same conclusion is reached when applying the Benesi–Hildebrand equation (2),

$$1/(F - F_0) = 1/(F_\infty - F_0)K_f(\beta - CD) + 1/(F_\infty - F_0). \tag{2}$$

Using (3), which is a rearrangement of equation 2, we calculated the formation constant of these (1:1) host-guest complexes by a nonlinear regression. K_f values ranged between 310 and 350 M^{-1} (table 2). These relatively low K_f values indicate that
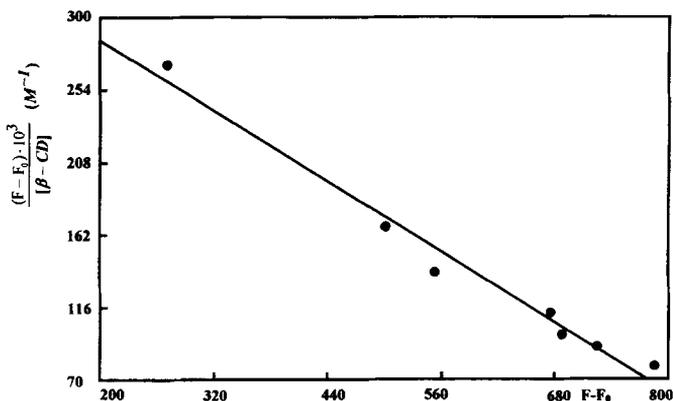

Figure 2. Scatchard plot for the NBD derivative **d**: β-CD complex.

Table 2. Formation constants (K_f) of the 1:1 complexes and observed photoisomerization rate constants $(k_{obs})^a$ of the four aromatic NBD derivatives $(5 \times 10^{-5}$ M) in EtOH and WECD media

		$k_{obs}/s^{-1 b}$	
Compound	K_f^b	*EtOH*	*WECD*
a	$-^c$	0·18	0·15
b	310	0·15	0·12
c	390	0·28	0·25
d	330	0·19	0·14

a: Relative values, measured spectrophotometrically and depending on the incident light intensity, b: relative error $\leqslant 10\%$. c: compound not fluorescent
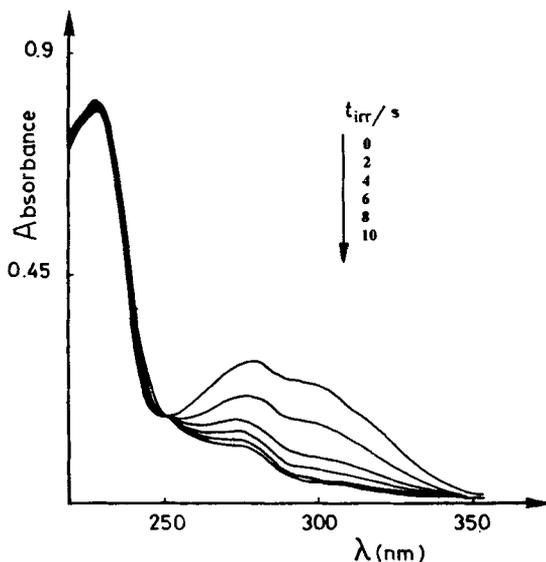
Figure 3. Evolution of the absorption spectrum of compound $\underline{c}$ with irradiation time in WECD ($[\beta$-CD$] = 0\cdot01$ M).

NBDs are partially included. On the other hand, it can be assumed that complexation with β-CD is a prior step to photoisomerization[18].

$$F = F_0 + (F_\infty - F_0) \cdot K_f \cdot [\beta\text{-CD}]/1 + K_f \cdot [\beta - CD]. \tag{3}$$

Photoisomerization reactions were performed in the three media under study, at room temperature (25°C) using a quartz cuvette (optical path: 1 cm). We used an interferential filter, allowing an excitation light (200 W high-pressure mercury lamp), centred around 284 nm ($\pm$ 37 nm).

In ethanol, as well as in WECD, the photoreaction progress is characterized by a decrease of absorbance and an increase of fluorescence intensity occurring simultaneously with the irradiation time, as observed previously for the photoreaction in

several organic solvents [19]. The absorption spectra show an isosbestic point in both media, indicating that the photoisomerization proceeds without side reaction (figure 3). The treatment of kinetic data, using the Guggenheim method [19], indicates that the NBD derivative photoisomerization obeys an overall first order kinetic in these media.

In contrast, an erratic kinetic behaviour was observed in the absence of β-CD (WE medium). These kinetic differences, according to the medium, confirm that the NBD:β-CD complexation occurs before the photoisomerization reaction [18].

The observed photoisomerization rate constants (k_{obs}) determined in ethanol [18] and in WECD under identical irradiation conditions (see above), were of the same order of magnitude (table 2), suggesting that the microenvironment polarities are analogous in both media.

3. Conclusion

Our approach demonstrates that the complexation of hydrophobic aromatic NBD derivatives by β-CD, allows these NBDs to become hydrosoluble and photoisomerize in non-toxic and inexpensive aqueous media.

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