

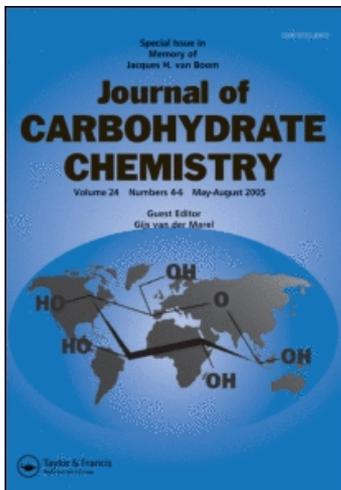
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**PHOTOACTIVITY WITHIN CYCLODEXTRIN CAVITIES:  
INCLUSION COMPLEXES OF ANILS<sup>1</sup>**

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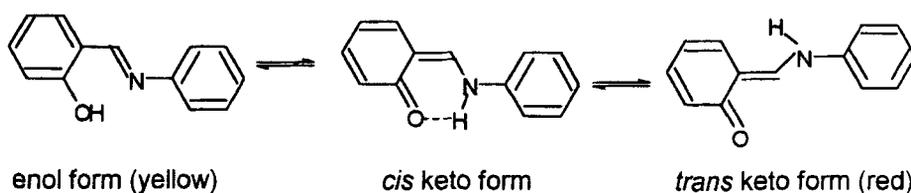
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**ABSTRACT**

Photochromic percinnamoylated cyclomaltoheptaose ( $\beta$ -cyclodextrin) solid inclusion complexes with guests *N*-salicylideneaniline and *N*-5-chlorosalicylideneaniline were prepared and characterized. The guests of these inclusion complexes can be easily "locked" with UV irradiation in the solid state by formation of cyclobutane bridges among the percinnamate residues rendering them more stable than before and stronger in fluorescence. The reverse reaction, rupture of the cyclobutane bridges, has not been achieved in the solid state and more work toward this goal is in progress.

**INTRODUCTION**

Solid aromatic anils present the phenomena of photochromism and thermochromism according to their crystalline structure: non-planar molecules photochromic, planar molecules thermochromic.<sup>2</sup> The phenomenon of photochromism in this class of compounds is attributed to hydrogen transfer from the *ortho* OH-group to the imino nitrogen and a subsequent *cis-trans* geometrical isomerization leading to the photo-product, the *trans*-keto form (Scheme 1). If this hypothesis is correct, then the whole mechanism, its formation



Scheme 1

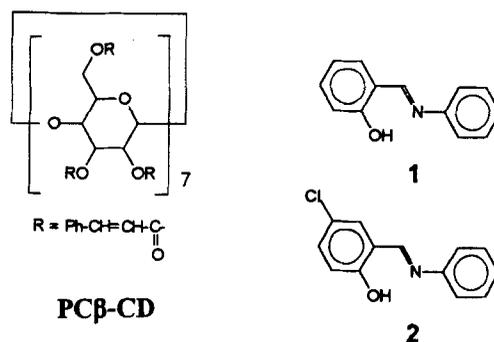
and rate of coloration and decoloration must be sensitive to molecular environment as it was found with  $\beta$ -cyclodextrin.<sup>3,4</sup>

In the present work the environmental effect of percinamoylated  $\beta$ -cyclodextrin (pc $\beta$ CD) on the photochromic *N*-salicylideneaniline (anil 1) and on the thermochromic *N*-5-chlorosalicylideneaniline (anil 2) has been investigated (Scheme 2) in order to find new ways to improve supramolecular photochromic systems. Such systems present considerable interest both from a fundamental and a technical viewpoint.<sup>5</sup>

Percinamoylated  $\beta$ -cyclodextrin was chosen because irradiation in solution is known to lead to the formation of intramolecular cyclobutane bridges<sup>6</sup> and it was our interest to use such a photoreaction in the solid state in conjunction with the environmental effect on photochromic and thermochromic anils.

## RESULTS AND DISCUSSION

**Characterization of the complex in the solid state.** The solid complex was prepared from DMF solutions as described in the experimental section. The host/guest (pc $\beta$ CD/anil) ratio was determined with dissolution of the complex in DMSO- $d_6$  and integration of the respective  $^1\text{H}$  NMR signals. The stoichiometry was found to be 1:1, while from the NMR spectrum it was verified that no chemical modification occurred during preparation of the complex. The complex formation was supported also by Differential Scanning Calorimetry. Thus in the thermogram of the complex, in contrast to the mechanical mixture with a similar composition, the peaks corresponding to melting points of 1 and 2 (52 °C and 110 °C) did not appear. An X-ray diffraction pattern showed that



Scheme 2

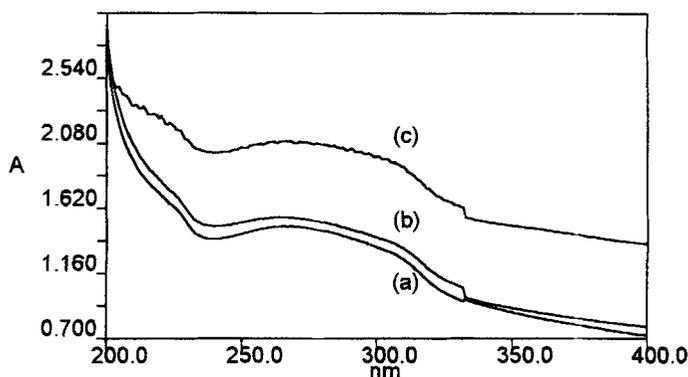
pcβCD and its complexes were in an amorphous state. Finally, the UV spectrum of the complex (KBr pellets) differs slightly at 230 nm from that of a mechanical mixture, which in turn is the same as that of pcβCD. Figure 1 shows the case of pcβCD/2 complex.

**Characterisation of the complex in solution.** The complexation of **2** with pcβCD was studied in solution by NMR, UV-Vis and fluorescence spectroscopy. The <sup>1</sup>H NMR spectra of pcβCD in DMSO, CDCl<sub>3</sub> and acetonitrile were assigned. Then the NMR signals of CD protons were observed in the presence of **2**. No spectral variations were observed in the spectrum of pcβCD in DMSO and CDCl<sub>3</sub>, even when the anil was in a large excess (15:1), indicating the absence of complex in solution. The solubility of pcβCD in acetonitrile is lower compared to the above solvents and is about 2 mM. Addition of **2** to a solution of pcβCD in acetonitrile, resulted in very small modification of the NMR frequencies of the signals. When **2** was in fifteen fold excess, the observed chemical shift changes Δδ were up to 0.012 ppm, indicating very weak complexation in this solvent.

Consequently, dissolution of the complex in above solvents, results in complete dissociation to the free components, that is:



where *s* and *l* correspond to the solid state and in solution correspondingly. Similar conclusions were drawn from UV-Vis and fluorescence experiments. The spectra of the complex diluted in CHCl<sub>3</sub> were exactly the same with those of the mechanical mixture. The

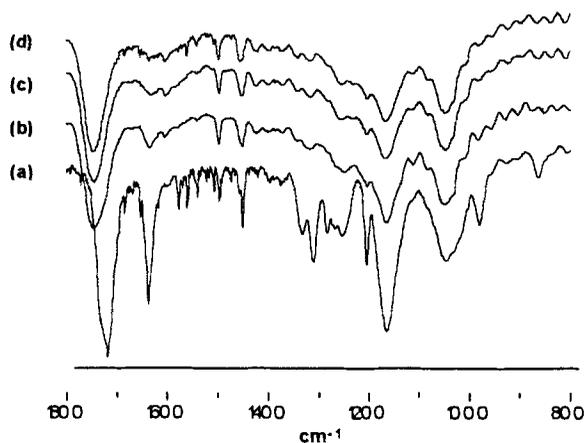


**Figure 1.** Absorption spectra of pc $\beta$ CD (a), pc $\beta$ CD/2 mixture (b) and pc $\beta$ CD/2 complex (c) in KBr pellets.

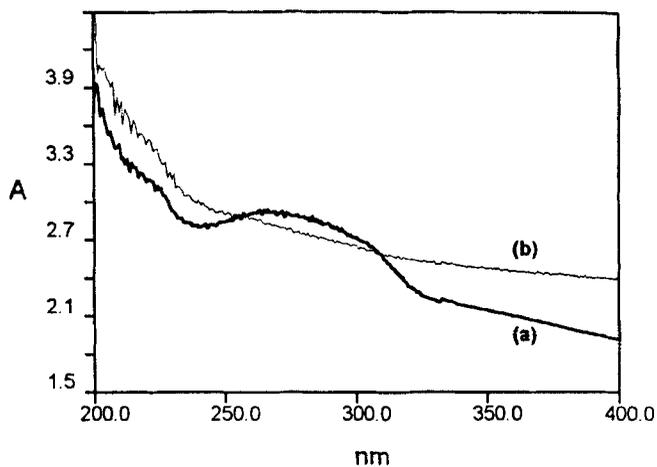
above results indicate that the complex practically does not exist in  $\text{CHCl}_3$ , DMSO and acetonitrile solutions in the usual working range of concentrations.

**UV-irradiation of solid pc $\beta$ CD.** Whitish pc $\beta$ CD powder was irradiated with 365 nm light and the photochemical reaction was followed by recording FT-IR spectra. Upon irradiation the colour of the powder turned lighter. After one hour irradiation, the reaction was completed. The absorption band at  $1640\text{ cm}^{-1}$  ( $-\text{CH}=\text{CH}-$ ) practically disappeared while the band at  $1719\text{ cm}^{-1}$  ( $-\text{CO}-$ ) was shifted to  $1750\text{ cm}^{-1}$ . It is worth noting that the reaction proceeded significantly during the first 30 minutes of irradiation (Figure 2).

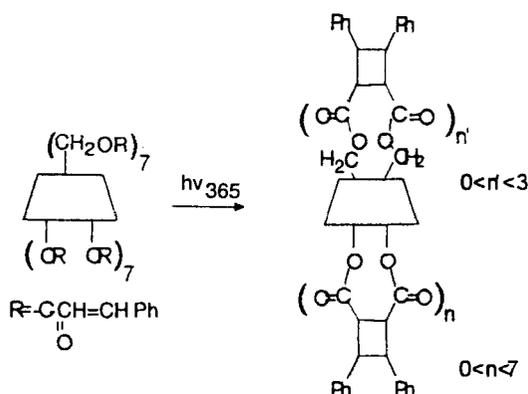
The change in the colour of the irradiated pc $\beta$ CD is shown in the absorption spectra of Figure 3 in which, after irradiation, the absorption due to the cinnamoyl chromophore at 275 nm is not observed. Further irradiation of the solid pc $\beta$ CD resulted in no difference in the FT-IR and UV spectra showing that the unsaturated esters became aliphatic by double bond (2+2) photocycloaddition forming cyclobutane rings (Scheme 3). Thus this  $\beta$ -CD derivative is "open" before irradiation and "closed" after irradiation as it has been reported with prolonged irradiation in solution.<sup>6</sup> The solubility of the "closed" pc $\beta$ CD is largely reduced in  $\text{CHCl}_3$ , DMSO and acetonitrile, indicating that the photochemical reaction is not only intramolecular but, most probably, across different



**Figure 2.** FT-IR spectra of pc $\beta$ CD before irradiation (a) and after irradiation for 30 min (b), 60 min (c), 120 min (d) in KBr pellets.



**Figure 3.** Absorption spectra of pc $\beta$ CD in KBr pellet before (a) and after 1 hour UV-irradiation (b).



Scheme 3

cyclodextrin molecules forming oligomers and/or polymers rendering their NMR study difficult.

**UV irradiation of the solid pc $\beta$ CD/anil complex.** The solid complex of pc $\beta$ CD with anil **2** was irradiated with 365 nm light for two hours. The FT-IR spectra recorded after irradiation were similar to those of irradiated solid pc $\beta$ CD (Fig. 2), showing that bridging units have been formed across the cavity openings. Therefore, it is expected that the bound molecules of the anil have been trapped in the cyclodextrin cages during the closure reaction. This was confirmed, in the case of anil **2**, by the NMR spectrum of a suspension of this complex in CDCl<sub>3</sub>. In contrast to the non-irradiated complex, which dissociates completely upon dissolution, the irradiated complex exists in solution having a solubility of about 10<sup>-5</sup> M. Furthermore, the solvent did not extract the anil from the insoluble complex. In conclusion, irradiation of the solid complex “locks” the anil in the cyclodextrin cages formed by the bridging units across the cavity openings of one or several cyclodextrins. As a result, the irradiated complex does not dissociate upon dissolution, and remains stable due to anil entrapment (“locking”). The same is true for the anil **1** complex.

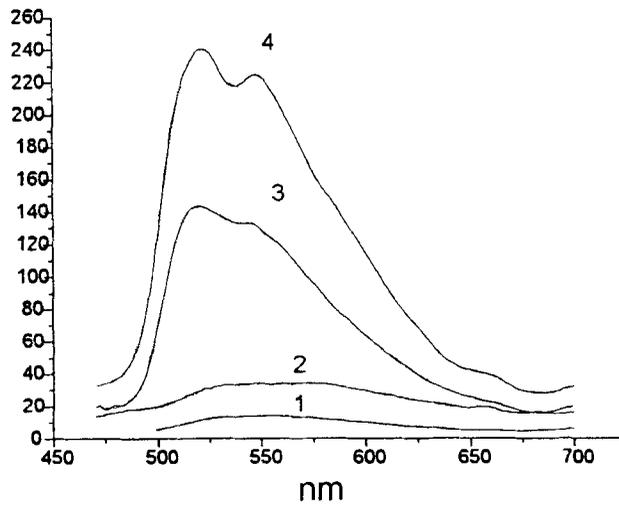
**Photochromism and Thermochromism.** Solid *N*-salicylideneaniline (anil **1**) at room temperature (rt) is non-fluorescent but, under UV-irradiation (365 nm light), changes its colour from yellow to red; the red colour turns to yellow on standing in the dark

(photochromism). At liquid nitrogen temperature (LN) the anil **1** is fluorescent but very fast develops the red colour and the fluorescence drops until disappearance (the red photoproduct is not fluorescent).<sup>2,5</sup> In contrast to anil **1** its solid complex with pc $\beta$ CD at rt is not photochromic (practically speaking a red colour is not observed with the naked eye) and fluorescent. At LN temperature the complex is strongly fluorescent but slowly develops colour with parallel decrease of the fluorescence. When the temperature is raised up, the colour disappears much faster (seconds versus hours) than in the case of the free solid anil **1** under the same conditions. It should be noted that after irradiation of the complex with 365 nm light ("locked" inclusion complex) the fluorescence intensity increases significantly (see Figure 4). This is in agreement with spectroscopic investigations of CD inclusion complexes which have shown that CDs offer a protective, more constrained microenvironment to an electronically excited lumiphor such that the resulting fluorescence is enhanced.<sup>7</sup>

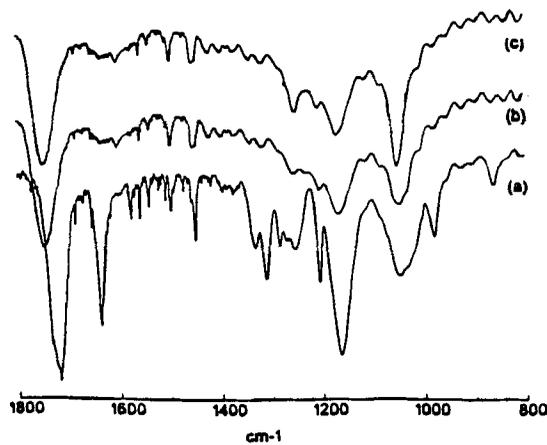
Solid *N*-5-Cl-salicylideneaniline (anil **2**) is fluorescent at rt and no change of colour is observed under UV irradiation (365 nm light). Instead, its red-orange colour at rt turns to light yellow at LN temperature; the light yellow colour turns to red-orange when the temperature is raised up to rt (thermochromism). In contrast to anil **2**, its complex with pc $\beta$ CD presents the same features with the pc $\beta$ CD/anil **1** complex, thus under UV irradiation is fluorescent at rt and practically nonphotochromic, but at LN temperature is much more photochromic than the pc $\beta$ CD/anil **1** complex.

**The Reverse Solid State Photochemical Reactions.** The "locked" pc $\beta$ CD was irradiated in the solid for two hours with 254 nm light since it is known that this wavelength splits aryl cyclobutane rings and therefore the reverse reaction could be anticipated.<sup>8</sup> However this was not the case. Instead, further infrared spectral changes have been observed but not reappearance of the 1640 cm<sup>-1</sup> (-CH=CH-) band. Figure 5 shows the results with pc $\beta$ CD. The results are similar with the pc $\beta$ CD/anil **1** and pc $\beta$ CD/anil **2** complexes.

Experiments with different conditions are under the way in order to achieve this reaction because of the interest in applications depending upon reversibility, particularly by photochemical means.<sup>9</sup>



**Figure 4.** Fluorescence spectra of anil **1** at 77 K (1), complex pc $\beta$ CD/anil **1** at 298 K (2) and 77 K (3) and of the irradiated complex at 77 K (4) in the solid state. Excitation wavelength 365 nm.



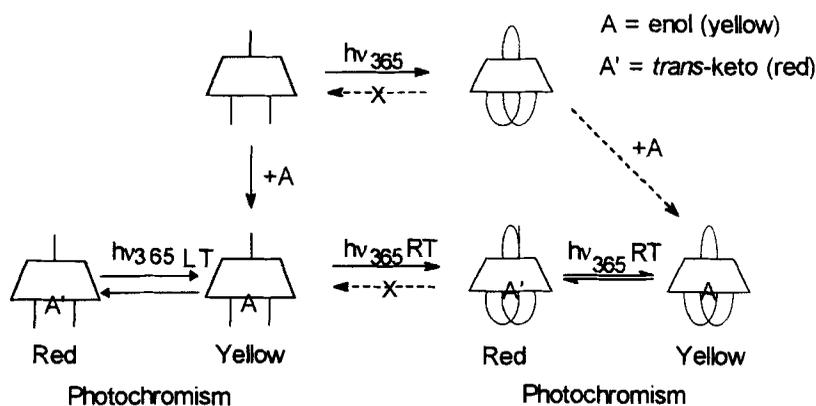
**Figure 5.** FT-IR spectra of pc $\beta$ CD before irradiation (a), after irradiation with 365 nm light for 2 hours (b) and after irradiation of b with 254 nm light for 2 hours (c).

## CONCLUSION

Percinnamoylated  $\beta$ -cyclodextrin forms solid inclusion complexes with photochromic and thermochromic anils. These complexes, independently of the property of the free guest (photochromic or thermochromic anil), are all photochromic as it was the case with  $\beta$ -CD, most probably because the complex formation breaks down the close packing of the planar molecules which is responsible for the lack of photochromic properties.<sup>3,4</sup> The anil is involved in the “caging” process, as in the case of  $\beta$ -CD,  $\gamma$ -CD and their permethylated derivatives,<sup>4</sup> in that its intramolecular hydrogen bond O-H...N is broken in the inclusion complexes. The interruption of the intramolecular bond is probably due to a deviation of the guest from planarity and/or to the intramolecular bonds formed between the anil and pc $\beta$ CD. The main difference, however, in the present case lies in the fact that percinnamoylated  $\beta$ -cyclodextrin is light active as well. Thus UV irradiation leads easily to the formation of intramolecular and/or intermolecular cyclobutane bridges. When the UV irradiation is applied after the formation of the complex, the guest molecule is “locked”, because of the cyclobutane bridges, and the complex becomes more stable. The reverse solid state photochemical reaction (photocleavage with 254 nm light), at least under the described experimental conditions, has not been observed. If we denote with a trapezoid the pc $\beta$ CD and A the anil, then the complex formation and its solid state photophysical interconversions may be represented as in Scheme 4.

The photocleavage with 254 nm light and the complex formation between the already “closed” pc $\beta$ CD and anil A (dotted arrows in Scheme 4) are currently under study.

The described system defines an assembly of molecular components (i.e., a supramolecular structure) in which, each molecular component performs and/or is involved, in one or more single acts (bond forming, hydrogen transfer, fluorescence enhancement) while the entire supramolecular device performs one or more complex functions, characteristic of the assembly (photochromism in this case). These simple acts may find useful applications in the field of photochromism, photoluminescence, photochemical synthesis, etc.<sup>10</sup>



Scheme 4

## EXPERIMENTAL

**General methods.** NMR spectra were recorded on a Bruker AC 250 spectrometer. Thermograms were obtained using a Perkin-Elmer DSC 7 Differential Scanning Calorimeter, using vented Al pans. X-ray powder diffraction diagrams were taken on a Debye-Scherrer camera with  $\text{CuK}_\alpha$  radiation. FT-IR Nicolet 550 instrument was used to record FT-IR spectra of the compounds in the form of KBr pellets. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer, using solutions in  $\text{CHCl}_3$  ( $10^{-5}$  M) or KBr transparent pellets. Fluorescence spectra were obtained on a Perkin-Elmer LS-5B spectrofluorometer. Steady state photochemical experiments employed a 200 W high pressure mercury lamp with appropriate filters and a 254 nm Mineralight Lamp Model UV S-54.

**Percinnamoylated  $\beta$ -cyclodextrin** was prepared according to the literature<sup>11</sup> and further purified by silica gel column chromatography first, using cyclohexane ethyl acetate 9:1 as eluent followed by a second column using ethanol 100% as eluent. The purified product was isolated as polycrystalline powder showing  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra corresponding to three non-equivalent cinnamate signals.

***N*-Salicylideneaniline** and ***N*-5-Chlorosalicylideneaniline** were synthesized by direct condensation of the appropriate salicylaldehyde with aniline in ethanol, followed by

repeated recrystallization from the same solvent.<sup>12</sup> The purity of the compounds was established by NMR, IR spectra and melting points: anil **1**, 51-52 °C (lit.<sup>13</sup> 51 °C); anil **2**, 110 °C (lit.<sup>13</sup> 110 °C).

**Preparation of the complexes.** To a solution of 0.03 mmol pc $\beta$ CD in 2 mL of dimethylformamide was added 0.15 mmol **1** (yellow solid) or **2** (orange solid) and the mixture was left to stir under an air current at room temperature. After 2 h the solvent was evaporated and the resulting brown powder was washed with ethanol until the washings were colorless. The solid was air dried for 1 day and then further dried in a desiccator, under vacuum; yield 90%.

## ACKNOWLEDGMENTS

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