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Photoactivity within Cyclodextrin Cavities: Inclusion Complexes of Anils with Cyclodextrins

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PHOTOACTIVITY WITHIN CYCLODEXTRIN CAVITIES: INCLUSION COMPLEXES OF ANILS WITH CYCLODEXTRINS.

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Abstract

Complexation of the thermochromic compounds N-5- chloro-salicylideneaniline and N-salicylidene-2-aminopyridine with cyclodextrins results in disappearance of thermochromic properties and appearance of photochromism. From uv, visible and fluorescence spectra in the crystalline state and supporting evidence from NMR spectra in solution the structure of the complexes is proposed.

INTRODUCTION

The formation of supramolecular entities perturbs the photophysical and photochemical properties of the component species. It may allow to control their reactivity and induce novel effects. If the components are photoactive, their organization into supramolecular architecture may be expected to perturb the ground and/or excited state properties of the individual species giving rise to novel properties which define supramolecular photochemistry¹.

EXPERIMENTAL

The compounds (anils) employed in the present work are N-5-chlorosalicylideneaniline (1), N-salicylidene-2-amino-pyridine (2). They were synthesized by direct condensation of the appropriate salicylaldehyde with aniline or 2-aminopyridine. The β -, permethyl- β -, γ - and permethyl- γ -cyclodextrins used were commercially available. NMR spectra were obtained in an FT-NMR BRUCKER AC 250. The UV-visible low temperature studies for the thin polycrystalline films were performed on a VARIAN TECHRON 635 spectrophotometer and the fluorescence spectra were recorded with a PERKIN-ELMER LS-5B luminescence spectrophotometer.

RESULTS

UV-VISIBLE. The effect of the complexation of the strongly thermochromic anil(1)² in γ -cyclodextrin is shown in Figure 1. The spectra of the complexes of (1) in β -CD, permethyl- β -CD and permethyl- γ -CD as well as of anil (2) in all the above mentioned cyclodextrins is similar. In all cases the anils have lost the thermochromic property and appear to be photochromic under ultraviolet irradiation. The upper limit of temperature where the photocolor is stable is -65°C with the most intense spectrum in the range -100 to -120°C . The photocolor of complex (1) in γ -CD and β -CD is formed more rapidly than that of (2) under the same experimental conditions.

A different behaviour is observed in the case of methylated β and γ -cyclodextrins. The rate of appearance of photocolor does not depend on the anil but it is affected by the size of the macrocycle cavity. Thus, the photocolor is formed faster in the methylated- γ -cyclodextrin which has a wider cavity.

FLUORESCENCE. The emission spectra of the crystalline complexes indicate the presence of the "enol" form only (Figure 2) because no emission was detected under excitation at the long wavelength region where the keto form absorbs. On the other hand, by lowering the temperature a blue shift of the maximum of the fluorescence band is not observed, a fact that provides further evidence for the absence of reabsorption effect from the keto form.

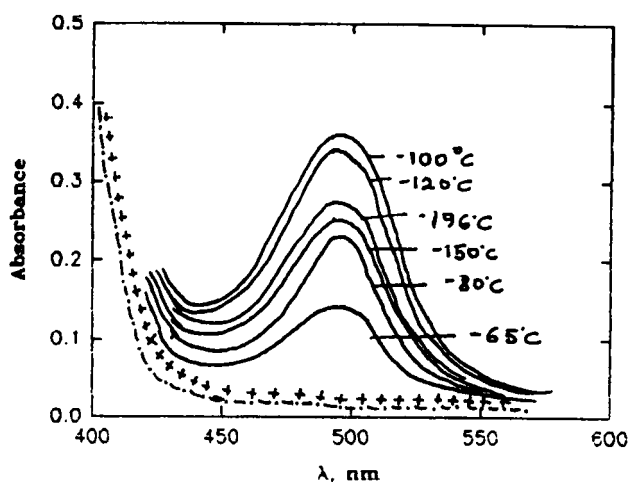


FIGURE 1 The absorption spectrum of the complex of (1) with γ -CD at RT (---).

The absorption spectrum of the complex of (1) with γ -CD at 77K (++++).

The absorption spectrum of the photocolour after 1h irradiation with 365nm light, 200 Watt high pressure mercury lamp at the indicated temperatures (solid lines).

DISCUSSION

From H-NMR, uv-visible and fluorescence studies in DMF solutions, it is found that β - and γ -cyclodextrins bind the more thermodynamically stable enol form of anils (1) and (2). Moreover, the perturbations of protons at the positions 3 of cyclodextrin glycoses located at the secondary rim of the macrocycle shows that the anils are complexed at the secondary rim in a equatorial or lid type disposition. In addition, a significant perturbation of the hydrogen atoms around the aldimino bridge is observed, a fact indicating that the binding site of anil in the CD occurs in that part of the structure. This part is exactly the one that dictates the *enol-keto* equilibrium. The slower appearance of the photoproduct of the complexes of anil (2) with β - and γ -CD from that of (1) is

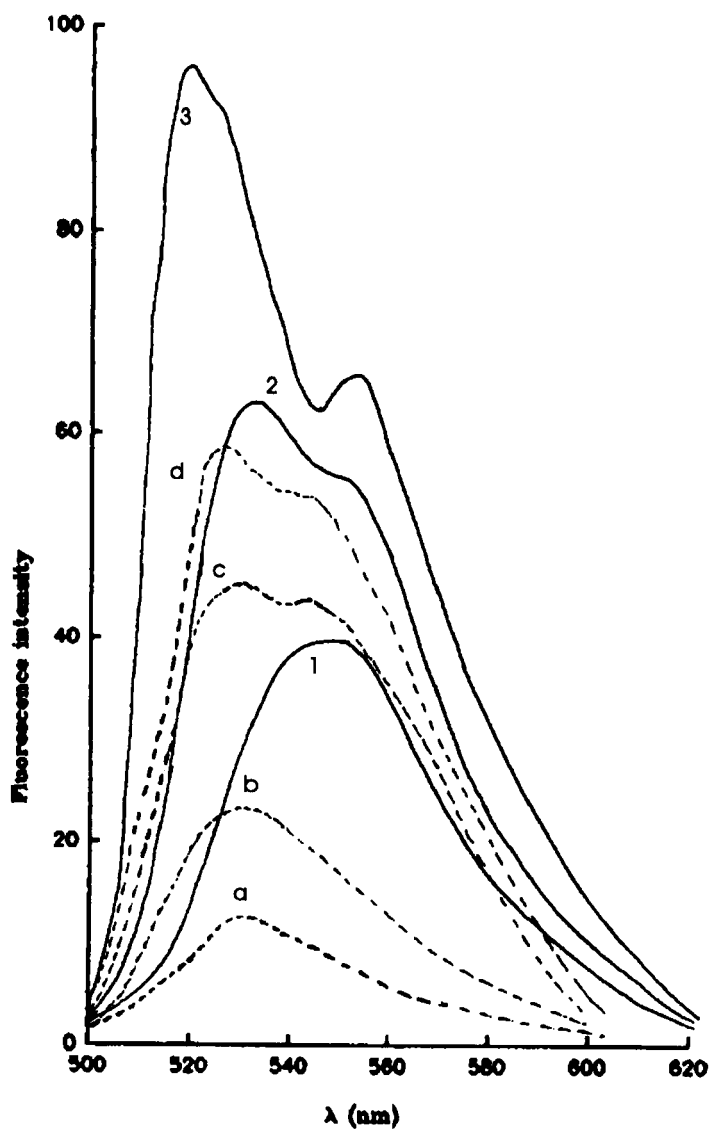


FIGURE 2. Full lines 1, 2, 3 : the emission spectra of anil (2) at RT, -70°C , -170°C . Excitation at 365nm or 470 nm. Dashed lines a, b, c and d : the emission spectra of complex of (2) with γ -cyclodextrin at RT, -70°C , -130°C and -170°C . Excitation at 365nm. No fluorescence occurs with excitation at 470nm.

attributed to an interaction of the N atom of the pyridine ring with a hydroxyl group of the rim, giving rise to an additional energy barrier for the cis-trans isomerization. On the other hand, in methylated β - and γ -CD the NMR studies in cyclohexane solutions indicate that an axial and more deep inclusion of the anils takes place in the cavity.

The absence of hydroxyl groups in the rims of methylated CDs has no effect on the rate of appearance of photocolour between (1) and (2) in the same cyclodextrin. However, it appears that there is a size dependence in this case since the rate of appearance of the photocolour in the methylated γ -CD which is wider, is higher than that of the permethylated β -CD.

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