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Photoactivation of the thermochromic solid di-anil of 2-hydroxy-5-methyl-isophthalaldehyde in β-cyclodextrin

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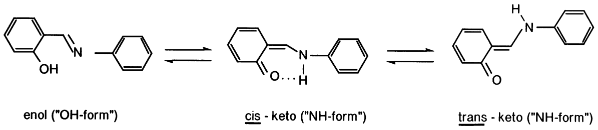
Abstract

The dual phenomenon of photo/thermochromism has been observed for the first time in inclusion complexes of anils with β-cyclodextrin. Thus, the solid inclusion complex of the strongly thermochromic di-anil of 2-hydroxy-5-methyl-isophthalaldehyde with β-cyclodextrin has been found to be both photochromic and thermochromic contrary to other anils which, either photochromic or thermochromic, when complexed with β-cyclodextrin turn out to be only photochromic. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Anils; β-Cyclodextrin; Inclusion complex; Photochromism; Thermochromism

1. Introduction

In studies of solid-state photochemistry, it has been recognized that the topochemical relations among neighboring molecules and atoms dictate the outcome of photochemical excitation [1]. Thus, the crystalline anils (salicylideneanilines) are classified as photochromic or thermochromic [2]. The photochromic compounds, 'open' non planar structures, develop an absorption band near 480 nm upon irradiation with UV light, while the thermochromic, 'close packed' planar structures, exhibit an absorption band at room temperature in the same spectral region which diminishes with decreasing temperature. Both processes are reversible and mutually exclusive. Since the same compound may occur in dimorphs of which one is thermochromic and the other photochromic it seems that the crystal structure determines the above behaviour, rather than the molecule as such [3]. Thus, in the planar molecules the lone pair of the nitrogen does not overlap with the π electrons of the aniline ring whereas in the non planar structure such overlap is possible and consequently the basicity of the nitrogen and hence the strength of the H–N bond is higher in the planar, i.e. thermochromic form (*cis*-keto form); the photochromic species is associated with the *trans*-keto form [4]. The required *cis*–*trans* conversion is improbable in the plane-to-plane packing type of the thermochromic crystals but possible in the 'open structure' of the photochromic ones (Scheme 1).



Scheme 1.

Since photochromism in this class of compounds is attributed to geometrical isomerization, then must be sensitive to molecular environment. Indeed, a number of thermochromic anils investigated, lose this property and become photochromic in the environment of cyclodextrins (CDs) as it was shown by the absorption spectra of the inclusion complexes formed [5,6]. In our search on the relation between geometry in the crystalline state and the properties of photochromism and thermochromism [4], we decided to prepare an inclusion complex of the di-anil of 2-hydroxy-5-methyl-isophthalaldehyde (**1**) which exhibits, as other members of the di-anil series [7], remarkable thermochromic characteristics with strong contribution of the cis-keto form (**2**) in the ground state at room temperature [8] with β-cyclodextrin (β-CD) (**3**) creating thus a new supramolecular entity (**4**) (Schemes 2 and 3) ruled by new topochemical factors for the purpose of continuing our efforts to find new ways to improve the photochromic systems, the interest of which arises from their many potential applications [4].

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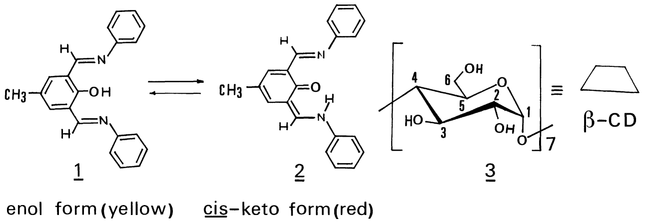
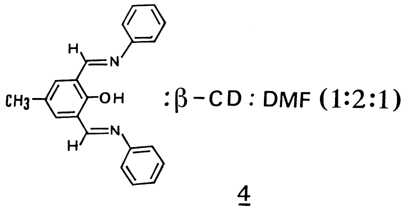


Scheme 2.



Scheme 3.

2. Experimental details

2.1. Materials

The di-anil (**1**) was synthesized by direct condensation of 2-hydroxy-5-methyl-isophthalaldehyde with aniline in ethanol, followed by repeated recrystallization from the same solvent. The inclusion complex (**4**) was obtained from concentrated solutions of di-anil (**1**) and of β-cyclodextrin (**3**) in *N*,*N*-dimethylformamide (DFM) which was left to evaporate slowly in a vacuum desiccator. The formation of the complex has been established by FT–IR spectra in KBr pellets. The crystalline substance was examined also by ^{1}H NMR spectroscopy in dimethyl sulfoxide (DMSO-d_6). The signals of the di-anil due to the aromatic ring protons (7.75 and 7.25 ppm) were integrated against the signals of β-cyclodextrin (H1, OH-2, OH-3 and OH-6) and the ratio was found 1 : 2. In addition, peaks due to DMF were observed, integration of which showed that one molecule of this solvent co-exists in the complex. The observed ratio, di-anil 1 : β-CD : DMF of 1 : 2 : 1 was not altered after repeated washing of the crystalline substance with absolute ethanol (Scheme 3).

2.2. Thin films

The polycrystalline film of the di-anil was obtained by slow cooling from the melt between two optical quartz plates under pressure. The corresponding film of the complex was obtained by slow evaporation of a concentrated solution of the complex in DMF, placed in a Petri dish containing an optical quartz plate, in a vacuum desiccator. After completion of the evaporation, the plate was covered by another quartz plate. The quality of the films was examined under a polarizing microscope.

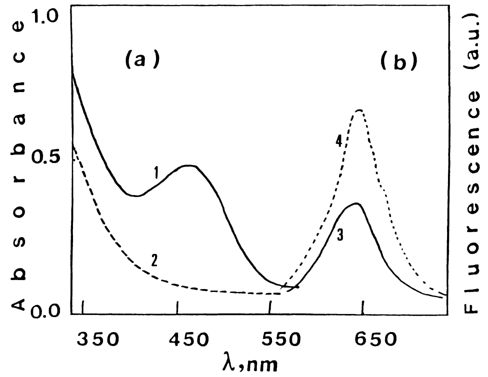


Fig. 1. (a) Absorption spectra of a thin polycrystalline film of the di-anil of 2-hydroxy-5-methyl-isophthalaldehyde at room temperature (1) and at liquid nitrogen temperature (2); (b) fluorescence spectra of the same film at room temperature (3) and at liquid nitrogen temperature (4).

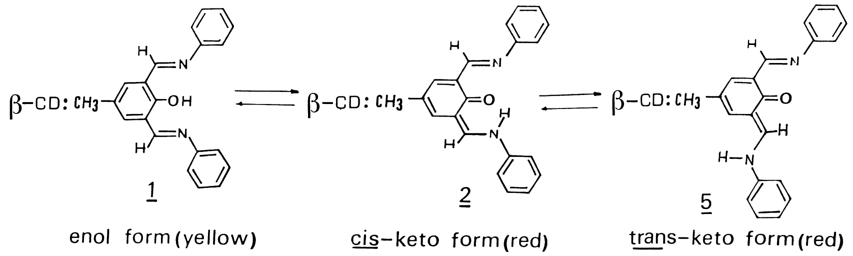
2.3. Instrumentation

The absorption and fluorescence spectra were obtained on a Perkin-Elmer Lamda 16 spectrophotometer and a Perkin-Elmer LS-5B spectrofluorimeter. The infra-red spectra were obtained on a Magna 550 Nicolet FT-IR spectrometer. NMR spectra were recorded on a Bruker AC 250 spectrometer. Steady-state photochemical experiments employed a 200 W high pressure Hg lamp with Corning glass filters.

3. Results and discussion

The results obtained, using polycrystalline thin films are as follows: The strong red colour of de-anil (**1**) at room temperature changes to yellow at liquid nitrogen temperature. The colour turns back to the original red when the temperature is raised to room temperature. By irradiating the crystals with ultraviolet light (365 nm) at room temperature or at liquid nitrogen temperature a red emission is produced with no colour change, i.e. no photochromism. Thus, the strongly red crystalline di-anil (**1**) is thermochromic. Fig. 1 shows the effect of temperature along with the fluorescence spectra at the corresponding temperatures which are typical (mirror image of the long wavelength absorption band) of a thermochromic crystalline anil [9].

The crystal structure in connection with the chromobehaviour of this compound has been examined elsewhere [8]. The results, using polycrystalline thin films of the inclusion complex **4** indicate that the di-anil is not totally in the enol form **1** as we have noticed in previous cases of inclusion complexes of anils with β-cyclodextrin [5]. In the present case the guest molecule continues to have a considerable contribution of the quinoid form **2** at room temperature (curve 1 of Fig. 2) while the enol form **1** is achieved at lower temperatures (curve 2 of Fig. 2) and therefore, the supramolecule **4** presents thermochromism. The



Scheme 4.

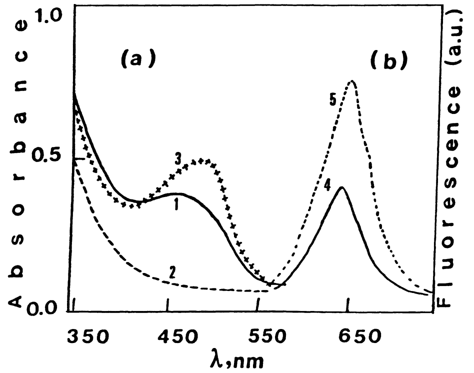


Fig. 2. (a) Absorption spectra of a thin polycrystalline film of the inclusion complex of the di-anil of 2-hydroxy-5-methyl-isophthalaldehyde with β-cyclodextrin: (curve 1) at room temperature, (curve 2) at liquid nitrogen temperature and (curve 3) after irradiation with 365 nm light at liquid nitrogen temperature; (b) (curves 4 and 5) fluorescence spectra at room temperature and liquid nitrogen temperature correspondingly.

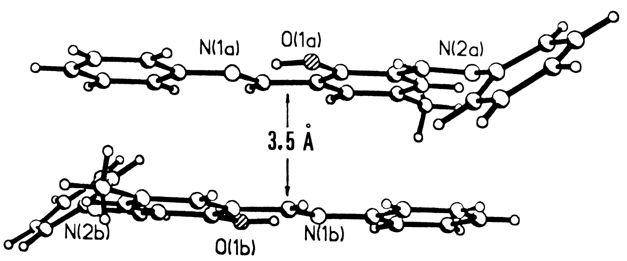


Fig. 3. Adjacent molecules of di-anil of 2-hydroxy-5-methyl-isophthalaldehyde. The close contacts — 3.5 Å apart — between molecules cease to exist in the inclusion complex with β-cyclodextrin.

fluorescence of the guest di-anil is enhanced as a result of the reduction of some degrees of freedom of its molecular motion as it has been observed also with other inclusion complexes of cyclodextrins [10,11]. From the other side photochromism is observed also at low temperatures (curve 3 of Fig. 2) indicating that the intramolecular hydrogen bond of the thermochromic form (*cis*-keto, **2**) is broken in the inclusion complex, most probably because the close contacts — 3.5 Å apart — between the planes of the planar parts of the molecule (Fig. 3) cease to exist [8,12] and therefore enough space is provided for photo-isomerization, the prerequisit for photochromism [4,9], to take place and the photo-product *trans*-keto form **5** to be formed (Scheme 4).

This dual phenomenon of photo/thermochromism is observed for the first time in inclusion complexes of anils with β-cyclodextrin and suggests that, on complexation, the topochemical factors have been greatly differentiated. However, the structural configuration of the supramolecule **4** is not known and therefore, an X-ray analysis is needed in order to elucidate the observed interesting phenomena, a physical feature which is absent when considering the molecular components in the solid phase or in a 'homogeneous' solvent, thus indicating the exciting opportunities that supramolecular photochemistry provides in investigating important exemplar reactions in novel ways [13].

Acknowledgements

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