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N-Salicylidene-2-aminopyridine as a Photochromic Guest for Deoxycholic Acid Crystal Lattice Cavities

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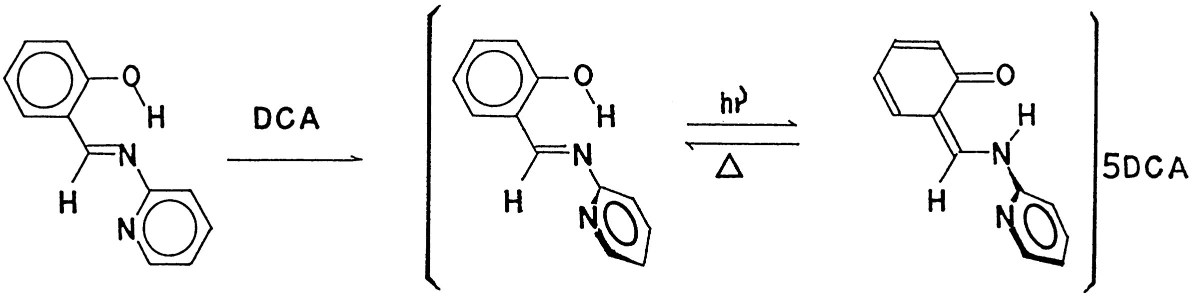
Deoxycholic acid formed a definite inclusion compound with non-photochromic *N*-salicylidene-2-aminopyridine. The guest Schiff base exhibited photochromism within the clathrate cavities. First-order rate constants for the thermal bleaching reaction of the photochrome were measured by reflectance spectrophotometry.

Crystalline *N*-salicylideneanilines (SAs) have long been known to exhibit either photochromism or thermochromism irrespective of the chemical properties of their ring substituents;1) thus, topochemical problems exist in the phenomena. Although introduction of *tert*-butyl substituents into SAs was successful in preparing a large number of photochromic Schiff bases,2) the *tert*-butyl method was ineffective in producing a photosensitive Schiff base from *N*-salicylidene-2-aminopyridine (**1a**). The thermochromic characteristic of **1a** has been significantly investigated on the "crystal engineering" concept.3) Recently, we found that deoxycholic acid (DCA) formed definite clathrate compounds with SAs.4) The crystal lattice cavities of DCA were suggested to be utilized for an alternative preparation of photochromic Schiff base crystals. We now report the photochemical properties of **1a** within the DCA inclusion environment.

An inclusion compound was prepared by mixing **1a** (0.5 mmol) with DCA (3 mmol) in hot methanol (25 ml) for 15 min. After concentration of the reaction mixture by evaporation, the desired inclusion complex was obtained in 40% yield as pale yellow crystals, which were purified by recrystallization from ethanol. The host/guest ratio of the product$^{5)}$ was determined by satisfactory elemental analysis and reasonable intensity ratios of the ^1H NMR peaks to be 5. The ratio, which was not changed by recrystallization from ethanol, is larger than the value 4 measured for an SA-DCA complex.$^{4)}$



1a 1b 1c

By irradiating the crystalline inclusion complex with 365 nm light, its yellowish color was altered to somewhat deeper one and the color faded with time in the dark. The maximum change in optical density in the reflectance spectrum was observed at 480 nm, which was adopted to obtain a first-order rate constant for the thermal back reaction of photocoloration at 30 °C. A good linear fit was found in the standard kinetic plots$^{2)}$ from which the rate constant was measured to be 6.0×10^{-3} s^{-1}.

It is of general acceptance that the photochromism of SAs is associated with an open crystal structure, in which the aminoaromatic ring is out of the plane of the *N*-salicylideneamine moiety, whereas thermochromism is associated with a planar structure for each starting molecule.$^{6,7)}$ The non-photochromicity of **1a** has been ascribed to its preferable planar conformation in the crystal state.$^{3,7)}$ A guest molecule within the DCA crystal lattice cavity must be appropriately oriented to be stabilized primarily by hydrophobic forces.[8] Thus, the shape of the guest might be different to that in the pure crystal state. The cavity of DCA may be of good size to accommodate the non-planar **1b** and to allow the guest a certain extent of conformational change after an intramolecular proton transfer from the hydroxyl group to the imine nitrogen atom induced by photo-irradiation. The photochromic property of **1a** was revealed for the first time by this inclusion method.

When the clathrate compound was crystallized from acetone, the solvent molecules were comprised as an alternate for the guest Schiff base. A ratio of DCA : **1b** : acetone in the resultant complex was observed to be 25 : 1 : 12. Since the DCA/acetone ratio in an acetone-DCA clathrate compound has been reported to be 5/3,[9] the **1b**-acetone-DCA complex may be expressed by the rational formula $[(\mathbf{1b})(\mathrm{DCA})_5]\cdot4[(\mathrm{acetone})_3(\mathrm{DCA})_5]$.[10] In an acetone solution of **1b** and DCA (1 : 5), DCA is considered, therefore, to enclathrate acetone molecules in 4 times preference to **1b** in a first stage to form stable crystals. The rate constant of the thermal bleaching for the acetone adduct was measured to be $1.0 \times 10^{-2}\ \mathrm{s}^{-1}$. Since the stability of the photocolored species **1c** is slightly decreased by the coexisting polar acetone molecules, the $[(\mathbf{1b})(\mathrm{DCA})_5]$ moiety is not entirely independent from the $[(\mathrm{acetone})_3(\mathrm{DCA})_5]$ moiety in the crystal.

Development of methodology for the selective formation of photochromic crystals is a first important step for a better understanding of solid state photochromism. In order to change topochemical relations among neighboring molecules, DCA may be replaced by other proper host substances;[11] the preparation of such an inclusion compound is now under investigation.

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10) Mp 168 - 170 °C. Anal. Found: C, 72.75; H, 10.17; N, 0.26%. Calcd for $C_{12}H_{10}N_2O \cdot 12(C_3H_6O) \cdot 25(C_{24}H_{40}O_4)$: C, 72.67; H, 10.18; N, 0.26%.

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