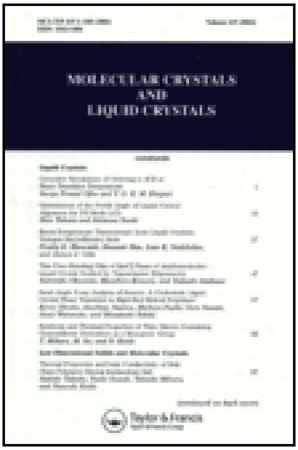

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Photochromism of Guest N-Salicylideneaniline in the Rooms of Host Bile Acid Derivatives

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Photochromism of Guest *N*-Salicylideneaniline in the Rooms of Host Bile Acid Derivatives

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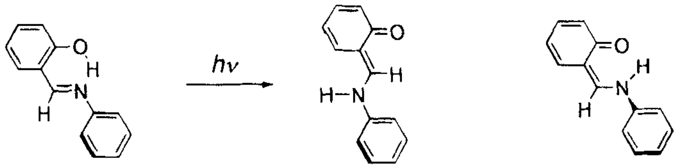
Definite clathrate crystals of deoxycholic acid and its amide and alcohol derivatives as host molecules with *N*-salicylideneaniline as a guest molecule were prepared to investigate their photochromic properties. The photocoloration study was done by irradiating the crystal powder with 365 nm light; the thermal fading reaction of the photocolored species was followed by reflectance spectrophotometry at 303 K. From the sharp difference in the first-order rate constants of the thermal bleaching of the photochromes, it was found that the thermal unimolecular motion of photo-colored species was strongly influenced by the neighboring environments in the crystal state.

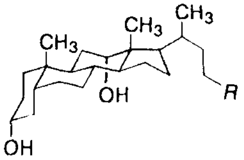
Keywords: salicylideneaniline; deoxycholic acid; deoxycholamide; clathrate crystal; Schiff base; photochromism

INTRODUCTION

Photochromic crystals have become the subject of very active research because of their potential usefulness as data storage devices and others.[1] The development of methodology for the selective formation of photochromic crystals is a first important step for the application of such a molecular device system. *N*-salicylideneaniline (**1**) and its derivatives are well-known to exhibit photochromism in the crystal state without any side-reactions.[2] Occurrence of the photochromic phenomenon does not depend on the electronic effects nor steric effects of the substituents. In the previous papers, we described that the existence of reaction field or room in which the photoisomerization occurred was of basic importance for the appearance of the phenomenon.[3]



1 *trans*-keto form keto-amine form



Host : Bile Acid Derivatives

DCA : R = COOH
DAA : CONH$_2$
DCO : CH$_2$OH

Recently, clear X-ray crystal structure of the photocolored species of *N*-(3,5-di-*tert*-butylsalicylidene)-3-nitroaniline was reported to be *trans*-keto form.[4] From kinetic studies on the phenomenon, however, more than two photocolored species have been considered;[3] thus, there is no cogent argument to exclude keto-amine form with sp^3-nitrogen atom as a photo-isomerized structure. In order to develop a better understanding of the mechanism of the photochromic process of Schiff bases, we examined the photochromic properties of inclusion crystals of three different host molecules with fundamental *N*-salicylideneaniline.

EXPERIMENTAL

Materials

N-salicylideneaniline(**1**) was prepared by ordinary condensation of salicylaldehyde and aniline. The amide (DAA) and alcohol (DCO) derivatives of deoxycholic acid (DCA) were prepared by the methods described in the literature.[5] Synthesis of clathrate crystals was accomplished by mixing **1** (1.0 mmol, 200 mg) with each bile acid derivative (4.0 mmol) in hot methanol (20 ml). Evaporation of the solvent gave the desired complex as pale-yellow crystals, which were recrystallized from methanol.

[**1**·4DCA]: Yield 1.4 g (79%); mp 182-183 °C. ^{1}H NMR (270 MHz, CD_3COCD_3): δ 0.70 ppm (s, 3H, 18-DCA-CH_3), δ 0.92 ppm (s, 3H, 19-DCA-CH_3), δ 1.02 ppm (d, *J*=6.7 Hz, 3H, 21-DCA-CH_3), δ 0.99 - 1.68 ppm (m, 18H, CH_2 in DCA), δ 1.73-1.95 ppm (m, 6H, CH in DCA), δ 2.15 - 2.40 ppm (m, 2H, 23-DCA-H_2), δ 3.43 - 3.58 ppm (m, 1H, 3-DCA-H), δ 3.97 ppm (bs, 1H, 12-DCA-H), δ 6.95 - 7.01 ppm (m, 0.5H, 3',5'-Ar-H), δ 7.29 - 7.35 ppm (m, 0.25H, 4-Ar-H), δ 7.39 - 7.50 ppm (m, 1.25H, Ar-H), δ 7.60 ppm (dd, *J*=7.9 and 1.8 Hz, 0.25H, 6'-Ar-H), δ 8.90 ppm (s, 0.25H, N=CH), δ 13.2 ppm (bs, 0.25H, OH). Anal. Calcd for $(C_{13}H_{11}NO)\cdot4(C_{24}H_{40}O_4)$: C, 74.16; H, 9.79; N, 0.79%. Found: C, 74.14; H, 9.79; N, 0.74%.

[**1**·4DAA]: Yield 980 mg (55%); mp 191-192 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.68 ppm (s, 3H, 18-DAA-CH_3), δ 0.91 ppm (s, 3H, 19-DAA-CH_3), δ 0.98 - 1.01 ppm (d, *J*=6.7 Hz, 3H, 21-DAA-CH_3), δ 1.03 - 1.89 ppm (m, 24H, CH_2 and CH in DAA), δ 2.10 - 2.34 ppm (m, 2H, 23-DAA-H_2), δ 3.61 ppm (bs, 1H, 3-DAA-H), δ 3.98 ppm (bs, 1H, 12-DAA-H), δ 5.28 - 5.39 ppm (m, 2H, NH_2), δ 6.95 ppm (dt, *J*=8.2 and 1.5 Hz, 0.25H, 5'-Ar-H), δ 7.03 ppm (bd, *J*=8 Hz, 0.25H, 3'-Ar-H), δ 7.26 - 7.47 ppm (m, 1.75H, Ar-H), δ 8.63 ppm (s, 0.25H, N=CH), δ 13.3 ppm (s, 0.25H, OH). Anal. Calcd for $(C_{13}H_{11}NO)\cdot 4(C_{24}H_{41}NO_3)$: C, 74.10; H, 10.04; N, 3.91%. Found: C, 74.23; H, 10.00; N, 3.97%.

[**1**·4DCO]: Yield 700 mg (40%); mp 143-144 °C. ^1H NMR (270 MHz, $CDCl_3$): δ 0.69 ppm (s, 3H, 18-DCO-CH_3), δ 0.91 ppm (s, 3H, 19-DCO-CH_3), δ 0.99 ppm (d, J=6.7 Hz, 3H, 21-DCO-CH_3), δ 1.03 - 1.85 ppm (m, 26H, CH_2 and CH in DCO), δ 3.60 - 3.65 ppm (m, 3H, 3- and 24-DCO-H), δ 4.0 ppm (m, 1H, 12-DCO-H), δ 6.95 ppm (dt, J=8.2 and 1.5 Hz, 0.25H, 5'-Ar-H), δ 7.03 ppm (bd, J=8 Hz, 0.25H, 3'-Ar-H), δ 7.26 - 7.47 ppm (m, 1.75H, Ar-H), δ 8.63 ppm (s, 0.25H, N=CH), δ 13.3 ppm (bs, 0.25H, OH). Anal. Calcd for $(C_{13}H_{11}NO)\cdot 4(C_{24}H_{42}O_3)$: C, 76.13; H, 10.50; N, 0.83%. Found: C, 76.49; H, 10.54; N, 0.82%.

Crystal data

Single crystals of inclusion compounds for X-ray analysis were obtained by slow evaporation of solvent from a 4:1 mixture of each bile acid derivative and **1** in ethanol. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation (λ=0.71069 Å) and a rotating anode generator.

[**1**·4DCA]: Pale-yellow needles 0.20 x 0.15 x 0.30 mm; $C_{13}H_{11}NO\cdot 4C_{24}H_{40}O_4$, FW = 1767.55. Orthorhombic, space group $P2_12_12_1$ (#19), a=13.287(4), b=26.886(4), c=7.023(4) Å, V=2509(.1) Å^3, Z=1, D_{calc}=1.17 g·cm^{-3}, μ(Mo-Kα)=0.77 cm^{-1}.

[**1**·4DAA]: Pale-yellow needles 0.10 x 0.10 x 0.10 mm; $C_{13}H_{11}NO\cdot 4C_{24}H_{41}NO_3$, FW = 1763.61. Orthorhombic, space group $P2_12_12_1$ (#19), a=13.073(5), b=27.157(4), c=7.094(4) Å, V=2518(.1) Å^3, Z =1, D_{calc}=1.16 g·cm^{-3}, μ(Mo-Kα)=0.75 cm^{-1}.

Kinetic measurement.

Thermal fading reaction of the photochrome, which went on in two steps (rate constants: k_1 and k_2), was followed by reflectance spectrophotometry at 303 K by measuring the optical density (A_t) at 482 nm for [**1**·4(DCA)], 507 nm for [**1**·4(DAA)], and 484 nm for [**1**·4(DCO)], at which a maximal decrease occurred in the dark. The final optical density (A_∞) was taken after 10 half-lives. The experimental optical density *vs.* time (t) data were treated with the standard integrated expression, $kt = \ln\{(A_o - A_\infty) / (A_t - A_\infty)\}$, for a first-order process using linear least-squares analysis.[3]

RESULTS AND DISCUSSION

Yielded clathrate compounds showed reasonable ^{1}H NMR spectra and correct elemental analyses consistent with the definite complexes (host/guest molar ratio = 4). Melting points of the clathrate crystals were sharp; they are much higher than that of pure **1** crystals (51-52 °C). The fact that the size of unit cells of [**1**·4(DCA)] and [**1**·4(DAA)] was similar to that of [(*N*,*N*-dimethyl-4-aminoazobenzene)·4(DCA)] (Orthorhombic; space group $P2_12_12_1$ (#19); a=13.76, b=25.68, c=7.16 Å)[6] and the inspection of the reported structure[7] of related clathrate compounds of DAA and DCO suggested the similarity of the structure of the obtained clathrate crystals in this study.

All these clathrate crystals exhibited photochromism by irradiating the crystal powder with 365 nm light. Rate constants (k) of the thermal fading of the photochromes were measured to be distinct in the different clathrate environments: k_1 = 1.4×10^{-3} s^{-1} and k_2 = 9.3×10^{-5} s^{-1} for [**1**·4(DCA)], k_1 =1.0×10^{-4} s^{-1} and k_2 =4.8×10^{-6} s^{-1} for [**1**·4(DAA)], and k_1 = 1.0 x 10^{-3} s^{-1} and k_2 = 7.2 x 10^{-6} s^{-1} for [**1**·4(DCO)], respectively.

These results demonstrate that the photochromic process of Schiff bases is delicate and a small change of neighboring molecular environment influences strongly the photochromic properties in the crystal state.

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