Enclathrated Solvent Effects on the Photochromic Process of *N*-Salicylideneaniline in the Crystal State

Toshio Kawato,* Hajime Kanatomi, Kiichi Amimoto, Hiroyuki Koyama, and Hideki Shigemizu
Department of Chemistry, Faculty of Science, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810-8560

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N-{3,5-bis(1-methyl-1-phenylethyl)salicylidene}-4-tritylaniline and its clathrate crystals with methanol and acetone were prepared. Solvent effects were observed on the solid-phase photoisomerization of the Schiff base.

Photochromism of organic crystals has been a subject of increasing interest in materials science due to their potential for various applications.[1] Salicylideneamines are well-known examples to exhibit either photochromism or thermochromism in the crystal state.[2-4] Recently, we found that the introduction of bulky *t*-butyl substituents to the aromatic rings of salicylideneanilines provided a general method to prepare photochromic Schiff base crystals.[4] The bulky groups are assumed to space out the molecules in the crystal lattice and allow photo-induced motion of the Schiff bases in the solid state. For such a bulky substituent, we planned to use 1-methyl-1-phenylethyl group and trityl group to check the steric influence of such a large group on the photochromicity of salicylideneanilines. During the course of the syntheses of *N*-salicylideneaniline derivatives with those bulky substituents, we found that small solvent molecules were captured easily in the crystals of *N*-{3,5-bis(1-methyl-1-phenylethyl)salicylidene}-4-tritylaniline(**1**) in a definite stoichiometry and influenced photochromic properties of the crystals.

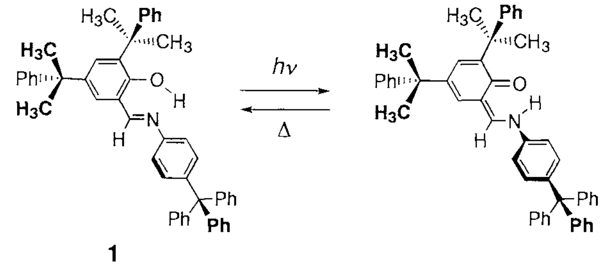

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Figure 1. Photochromism of *N*-{3,5-bis(1-methyl-1-phenylethyl)salicylidene}-4-tritylaniline(**1**).

Photo-coloration of salicylideneamines involves an intramolecular proton transfer from the *o*-hydroxyl group to the imine nitrogen atom in the excited state followed by the intramolecular framework alteration: the resultant photochrome fades thermally in the ground state when they are kept in the dark.[2-6] By measuring the first-order rate constant (*k*) of the thermal bleaching reaction of the photochrome derived from salicylideneamine, one can estimate the rate of the intramolecular framework change or unimolecular motion of the compound in the ground state.[4-6] Since neither photochromism nor thermochromism is observed in a regular solution of salicylideneamines, it has been difficult to discuss the solvent effect on the phenomena. In relation to the topochemical interest in solid-state reactions and crystal habits,[7] we will report herewith the novel solvent effects on the photo-induced isomerization of salicylideneaniline in the crystal state.

Starting 3,5-bis(1-methyl-1-phenylethyl)salicylaldehyde was prepared from 2,4-bis(1-methyl-1-phenylethyl)phenol under standard Reimer-Tiemann conditions.[8] The parent Schiff base **1** (mp 107-109 °C) was obtained as yellow crystals by the condensation of the aldehyde and 4-tritylaniline in ethanol.[9] When the synthesis of the desired **1** was carried out in acetone or methanol in place of ethanol, the solvent molecules were easily incorporated in the crystal lattice to give 1:1 definite clathrate compounds as yellow crystals, which were pure by ^{1}H NMR and were further purified by recrystallization from the same solvent used in the synthesis. The host : guest ratios of the adducts, [$\mathbf{1}\cdot CH_3OH$] and [$\mathbf{1}\cdot CH_3COCH_3$] were determined by satisfactory elemental analyses and reasonable intensity ratios of the ^{1}H NMR peaks. These solvent clathrate compounds could be also obtained by recrystallization of **1** with acetone or methanol, and returned to the parent **1** crystals by recrystallization of the adducts with ethanol. The enclathrated solvent molecules could not be removed by heating the crystals at 50 °C *in vacuo* for 12 h. Upon being heated to 106-110 °C, these solvent clathrate compounds acquired a somber color without melt. It was found that propanol, 3-pentanone, and cyclopentanone as well as ethanol were not incorporated in the crystal lattice when they were used as reaction and recrystallization solvents. Infrared spectra of pure **1** and its solvent adducts were almost superimposable except for some peaks due to the included solvents (*e.g.*, 1712 cm^{-1} for the acetone). The characteristic IR bands at 1614 cm^{-1} for **1**, 1617 cm^{-1} for [$\mathbf{1}\cdot CH_3OH$], and 1616 cm^{-1} for [$\mathbf{1}\cdot CH_3COCH_3$] were assigned to the C=N stretching vibration peaks, suggesting the presence of strong intramolecular hydrogen bond in the Schiff base in each crystal. Hydrogen bonding interaction between the Schiff base and the solvent in the crystals is not clear but there is no valid reason to be excluded. Reflectance spectra of the solvent clathrate compounds were strikingly similar to that of the parent **1**, the electronic state and conformation of the Schiff base is supposed to be closely similar in these crystals.[10] Thus, the Schiff base with bulky phenylethyl substituents as picket fences at both ends of the molecule was suggested to act as a host compound and offer a guest room at the center part of the molecule to receive just a small solvent molecule fit for a limited size of the cavity.

The yielded crystals were photochromic; each photo-colored species was obtained by irradiating crystalline powder with 365 nm light. The large substituents on both aromatic rings were found not to disturb the occurrence of photochromism of salicylideneaniline. Difference reflectance spectra obtained from **1**, [$\mathbf{1}\cdot CH_3OH$], and [$\mathbf{1}\cdot CH_3COCH_3$] before and after UV irradiation are shown in Figure 2. The degrees of the spectral changes after UV irradiation for the solvent clathrate compounds were much smaller than that of pure host Schiff base crystals.

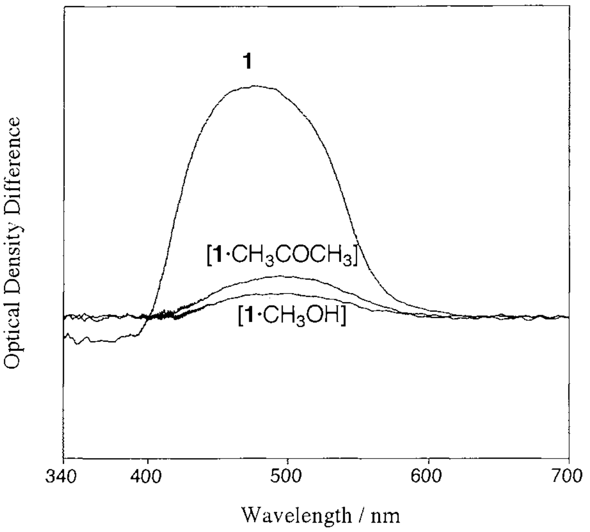

Figure 2. Difference reflectance spectra of **1**, [**1**·CH_3OH], and [**1**·CH_3COCH_3] before and after UV irradiation.

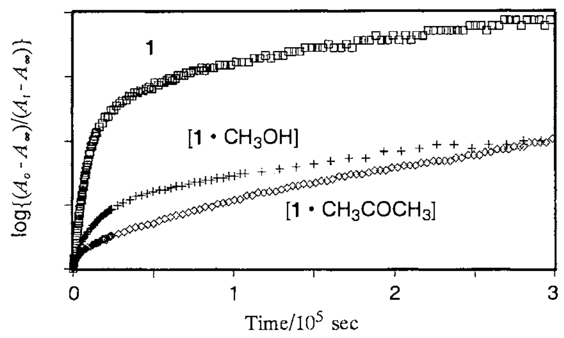

Figure 3. Kinetic plots of optical density decrease for the photochromes derived from **1**, [**1**·CH_3OH], and [**1**·CH_3COCH_3].

The maximum changes in optical density were observed at 481 nm for **1** and 499 nm for both solvent adducts.

The thermal fading reaction of the photochrome was then followed by reflectance spectrophotometry at 30 °C by measuring the optical density (A_t) at the wavelength 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.[5] The thermal decoloration of the photochrome from **1** went on in two steps and the rate constants were measured to be $k_1 = 2.6 \times 10^{-4}$ s^{-1} and $k_2 = 3.5 \times 10^{-6}$ s^{-1}. Although the degrees of photo-induced molecular alteration of the solvent clathrate compounds were similar, the rate constants of the thermal back reaction were different each other ($k_1 = 1.1 \times 10^{-4}$ s^{-1} and $k_2 = 4.0 \times 10^{-6}$ s^{-1} for [**1**·CH_3OH] and $k_1 = 2.2 \times 10^{-3}$ s^{-1} and $k_2 = 4.5 \times 10^{-6}$ s^{-1} for [**1**·CH_3COCH_3], respectively) (Figure 3). Methanol and acetone are polar solvents and make hydrogen bonds in a different way depending on whether it is protic or aprotic. The difference of the kinetic data might be ascribed to the intermolecular hydrogen bonding of the solvent to the photochromic center of the Schiff base.

In conclusion, this study demonstrates clearly that the photo-induced framework alteration of salicylideneaniline is influenced by the neighboring solvent molecules; thus, it is suggested that unimolecular motion in the crystals depends on both free room size for the molecular mobility and intermolecular interaction with the neighboring molecules. Further studies on the scope of the solid state isomerization of related Schiff bases are in progress and will be reported in due course.

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References and Notes

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