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# Photoisomerization of 2-(2-Hydroxyphenyl)benzothiazole Derivatives as an Adequate Model to Reveal Photochromism of Schiff Bases in the Solid State

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Photochromic behavior of 2-(2-hydroxyphenyl)benzothiazole derivatives, whose photoinduced deformation was restricted by the cyclic structure, was first observed to suggest the existence of a *cis*-keto form as a certain structure for the photochrome of *N*-salicylideneanilines in the crystal state.

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Photochromism of organic molecules has been the subject of a number of previous investigations owing to its scientific interest as well as technical applications.[1] The crystalline photochromism of *N*-salicylideneaniline (**1**) and its analogues is of interest owing to the usefulness for a model system to elucidate molecular tautomerism in the solid state (Figure 1).[2,3] There is general agreement that the coloration processes involve excited-state intramolecular proton transfer (ESIPT) from the *o*-hydroxy group to the imine nitrogen atom followed by framework changes in the molecule.[3] However, the mechanistic diversity has not completely been solved yet. An unambiguous mechanistic study, made by Ohashi et al. using X-ray diffraction analysis, shed light on a *trans*-keto form as the photocolored species of *N*-(3,5-di-*tert*-butylsalicylidene)-3-nitroaniline (**2**).[4] Considering from the result, the photochromism is caused by pedal motion of two phenyl rings of the molecule. This suggests that the interatomic distances at the peripheral part of the molecule may not be so important for the photochromism. In contrast with these aspects, we have reported that the stability of the photochrome depends on the circumstances of molecules in the crystal lattice. Furthermore, our previous communication described the coexistence of another type of isomer, which was tentatively assigned to a *cis*-keto form, in the photocolored crystals.[5] Even if a small amount of a *cis*-keto species is present in the crystal, its structural resemblance to the original enol–imine form can lead to serious difficulties in solving the X-ray diffraction data with satisfactory accuracy. The clarification of the mechanism of color change processes of Schiff bases and the development of new compounds with photochromic properties continue to be of interest in the search for practical utilization of ESIPT.[6] In order to be able to tackle this problem we needed additional reliable or preparative information on the structure of the photochrome. In this study, we employed cyclic Schiff bases to prove that the pedal motion of the molecule is not always necessary for the occurrence of photocoloration of Schiff bases, whose photochrome is ascribed to the formation of a *cis*-keto isomer.

2-(2-Hydroxyphenyl)benzothiazole derivatives used in this study are shown in Figure 2. Compounds **3**, **4**, and **5** were prepared by condensation of 2-aminobenzenethiol with salicylaldehyde, 3,5-di-*tert*-butylsalicylaldehyde, or 3,5-bis(1-methyl-1-phenylethyl)salicylaldehyde[7] in dimethyl sulfoxide, respectively.[8] The resultant products were purified by recrystallization from methanol to yield fine crystals, which were not suited for X-ray analysis but were identified by satisfactory elemental analytical data and spectral data.[9] Crystals of **5** included a small amount of water molecules, which could not be removed completely by heating at 50 °C in vacuo. Although **3** can be regarded as an analogue of **1**, whose aniline ring carbon and azomethine carbon are connected by a sulfur atom, crystals of **3** did not show any color change on irradiation with UV light. The ESIPT of 2-(2-hydroxyphenyl)benzothiazoles has been extensively investigated.[10] After the photo-excitation of an enol conformer, ESIPT from the hydroxy group to the ring nitrogen atom occurs to give a keto form, which returns to the original enol form in the electronic ground state. The lifetime of the keto form is known to be very short in gas phase or in solution.[11] Thus far the lifetime of such a keto form in the crystal state has not been reported. Crystal structure of **3** was analyzed by Stenson,[12] who reported that **3** was planar and packed face to face with short intermolecular contacts in the crystal. The most important condition for exhibiting crystalline photochromism of Schiff bases is to secure reaction room for the photoinduced isomerization in the crystal lattice.[13] Thus, **3** undergoes ESIPT in crystals; however, a little more room in the crystal is needed for **3** to form distorted *cis*-keto form that is different from the form derived from a fast equilibrium between the OH form and the NH form in the electronic ground state. On the other hand, color of crystals of **4** and **5** with bulky substituents in the molecules changed from light yellow to deeper color on UV light irradiation and returned to the starting yellow after placing them in the dark. The bulky substituents were effective to act as a space opener, which maintained room for the molecular deformation of a keto form after ESIPT to stabilize the photochrome in the excited state as observed

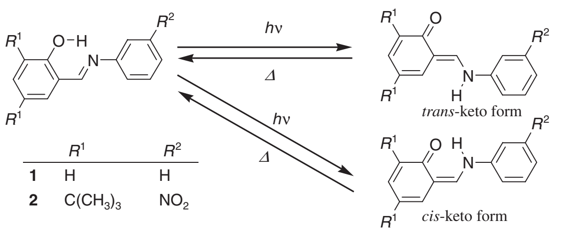

**Figure 1.** Photochromism of *N*-salicylideneanilines.

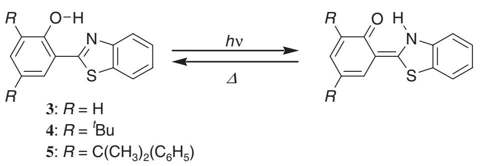

**Figure 2.** Photochromism of 2-(2-hydroxyphenyl)benzothiazoles.

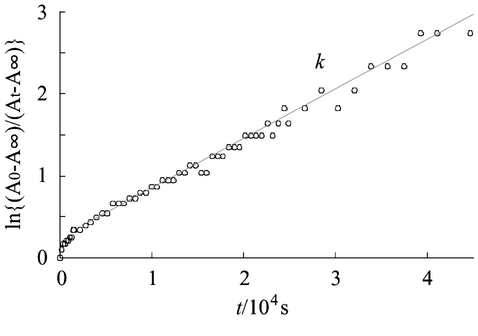

**Figure 3.** Kinetic plots of optical density decrease for the photo-colored species derived from **5**.

for crystals of derivatives of **1** with *tert*-butyl substituents.[14] The maximum changes in optical density after photo-irradiation were observed at 440 nm for **4** and 480 nm for **5**, respectively. It is worthwhile to note that the isomerization from a *cis*-keto form to a *trans*-keto form cannot occur through the pedal motion of phenyl rings for **4** and **5** since the pivotal C=N bond is incorporated into the cyclic structure. Furthermore, the benzothiazole ring cannot turn over reversely to achieve axial rotation of the two rings in the crystal lattice cavity. Consequently, photo-colored species of **4** and **5** are reasonably assigned to a *cis*-keto isomer with some distortion.

The thermal bleaching reaction of the resultant photochrome was followed by reflectance spectrophotometry at 30 °C by measuring the optical density at a proper wavelength where the maximum change of the optical density was observed at regular intervals. Kinetic analysis exhibited a good fit to a first-order equation for both **4** and **5**.[9,14,15] The constructed first-order plots for **4** showed a single straight line and the rate constant $k$ was measured to be $2.0 \times 10^{-3}\,\mathrm{s}^{-1}$. Kinetic plots of the thermal back reaction for photocolored species of **5** are illustrated in Figure 3. Thermal fading of the photochrome of **5** was analyzed by sum of two relaxation passes and the rate constants $(k' + k)$ and $k$ were observed to be $2.0 \times 10^{-4}\,\mathrm{s}^{-1}$ and $5.8 \times 10^{-5}\,\mathrm{s}^{-1}$, respectively. The $k$ values are now assigned to the rate constant of thermal isomerization of photocolored *cis*-keto species. The lifetime of photocolored species of **5**, which has larger substitutions in the aromatic ring, was longer. In our previous study, the stability of *cis*-keto isomer of related Schiff base was correlated to the size of cavity, which was maintained by bulky substituents in the crystal.[16] The fast fading $(k' = 1.4 \times 10^{-4}\,\mathrm{s}^{-1})$ for **5** is responsible for the coexisting pseudopolymorphic structure due to a small amount of enclathrated water molecules in the crystal.[7,9,16]

In conclusion, we could prepare the first photochromic crystals of 2-(2-hydroxyphenyl)benzothiazoles with bulky substituents at the aromatic ring. The structure of photocolored species was reasonably assigned to a *cis*-keto form and thermal fading process of photochrome was observed. From the inspection of similarity and difference of structure between 2-(2-hydroxyphenyl)benzothiazoles and *N*-salicylideneanilines, which exhibit crystalline photochromism, the existence of *cis*-keto forms in photocolored crystals of *N*-salicylideneanilines was confirmed. The result also suggests that the deformation of planar molecular shape should be considered in case of discussion on ESIPT process of 2-(2-hydroxyphenyl)benzothiazole analogues with bulky substituents.[10]

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