

X-ray Analysis of Structural Changes in Photochromic Salicylideneaniline Crystals. Solid-State Reaction Induced by Two-Photon Excitation

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Light-induced reversible color change of substances is known as photochromism and has attracted considerable attention from various fields of chemistry.¹ Salicylideneanilines, which are the condensation products of salicylaldehydes and anilines, exhibit photochromism both in solutions and in the solid state.^{2,3} Photochromic salicylideneanilines are usually pale yellow and exist in the enol form in crystals. On irradiation with ultraviolet light, the proton bonded to the oxygen atom is translocated to the imine nitrogen atom. A subsequent geometrical rearrangement in the excited state forms a red photoproduct. The deepened color can be erased by irradiation with light absorbed in a newly developed band or by thermal fading in the dark. Over the past three decades many studies on the subject have been carried out. There is still a controversy about the structure of the colored species.⁴ In this paper we determined the structure of the photoinduced colored species of salicylideneanilines from X-ray diffraction analysis of *N*-3,5-di-*tert*-butylsalicylidene-3-nitroaniline (**1**).⁵ To our knowledge, this is the first crystallographic determination of the structural changes accompanying the reversible phototransformation of an organic photochromic crystal.

In this study all of the X-ray diffraction measurements were carried out at 90 K on a Siemens SMART CCD diffractometer. To compare the crystal structures before and after light irradiation, all of the data collections and the integrations were performed under the same conditions. The crystal structure of **1** before light irradiation was determined using a pale yellow crystal. The crystal belongs to the triclinic system and the space group is $P\bar{1}$. There is one molecule in an asymmetric unit.⁶ The molecular structure is shown in Figure 1a. The molecule **1** exists in an enol form in the crystal. The observed bond lengths of C2–O1, C1–C7, and C7–N1 were 1.361(1), 1.454(1), and 1.295(1) Å, respectively.

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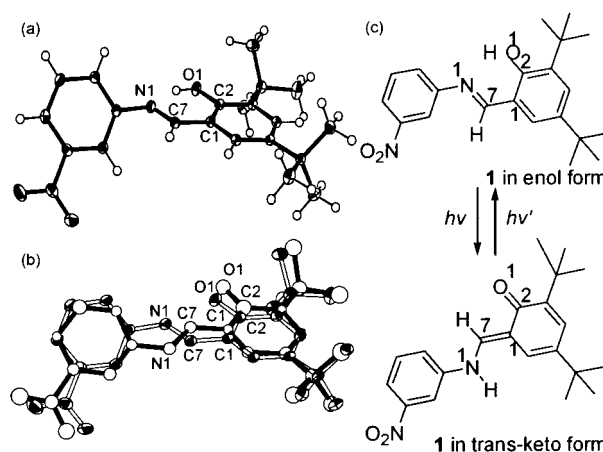


Figure 1. (a) Molecular structure of **1** before light irradiation (in pale yellow crystal). The thermal ellipsoids are drawn at 50% probability level. The circles of the hydrogen atoms are drawn in an arbitrary scale. (b) Disordered structure of **1** after laser irradiation (in red crystals). The bonds of the enol and trans-keto forms are drawn by open and filled lines, respectively. The thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. (c) The chemical structures of original enol and photoinduced trans-keto form of **1**.

The photoreaction of **1** was performed by irradiation with output pulses of an optical parametric oscillator with wavelength of 730 nm at room temperature.⁹ The pale yellow crystals turned dark red. Because the compound **1** has no absorption band at 730 nm, the reaction was induced by two-photon excitation. The two-photon excitation mentioned here is a concerted absorption of two photons by individual molecules and does not mean two sequential one-photon absorption events.¹⁰ The IR spectra of the crystals irradiated with the laser light showed that the photoproduct obtained by the two-photon excitation was identical with that obtained by one-photon excitation at 365 nm with a high-pressure mercury lamp.

Among the laser-irradiated dark-red crystals, a crystal whose quality did not deteriorate was selected and mounted on the goniometer. X-ray diffraction analysis of the crystal was then carried out. The space group was retained. The cell dimensions were changed, and the unit-cell volume was slightly increased.¹¹ The difference Fourier electron density map showed additional peaks around the original salicylideneaniline molecule. The peaks

(6) All of the diffraction measurements were carried out using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) ($2\theta_{\max} = 60.0^\circ$). The chemical formula and the molecular weight are $C_{21}H_{26}N_2O_3$ and 354.44, respectively. The cell dimensions: $a = 6.1043(1)$ Å, $b = 10.3155(2)$ Å, $c = 16.2882(2)$ Å, $\alpha = 102.1932(11)^\circ$, $\beta = 92.2811(11)^\circ$, $\gamma = 103.0796(11)^\circ$, $V = 972.36(3)$ Å³. A total of 19 223 reflections were collected, of which 5660 reflections were independent. The number of the parameters was 339. The structure was solved by the direct method using *SHELXS-97*⁷ and refined by the full-matrix least-squares on F^2 using *SHELXL-97*.⁸ All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located on the difference Fourier map and refined isotropically. The final R value calculated for 4817 reflections ($F_o > 4\sigma(F_o)$) was 0.035 and $wR2$ for all the reflections was 0.104. The value of GOF was 1.043.

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(9) The optical parametric oscillator (Spectra-Physics MOPO-730) was pumped with the third harmonic of a pulsed Nd:YAG laser (355 nm) at a repetition rate of 10 Hz. Output pulses were reduced by neutral density filter to 20 mJ at 730 nm (5 ns pulse width). The laser beam was depolarized to minimize the effects of optical anisotropy. The beam was focused on about 1.5 mm diameter at the crystal position. The crystal was irradiated for 4 h at room temperature. Review of optical parametric devices: Zhou, J. X.; Hou, X.; Yank, K. X.; Tsai, S.-J. J.; Michel, R. G. *Appl. Spectrosc.* **1998**, *52*, 176–189.

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were assigned and successfully refined as another molecule which coexists with the original enol form in the crystal (Figure 1b). The occupancy factor of the newly produced molecule was converged to 0.104(2). In this molecule, the oxygen atom (O1) and the nitrogen atom (N1) are in a trans position with regard to the C1–C7 bond. The observed bond lengths of C2–O1, C1–C7, and C7–N1 were 1.30(2), 1.42(1), and 1.35(1) Å, respectively. Although the small occupancy factor of the molecule prevented us from determining the accurate geometric parameters, the C2–O1, C1–C7, and C7–N1 bonds were significantly shorter, shorter, and longer than the corresponding ones of the enol form, respectively. On the basis of these structural features the newly produced molecule can be unambiguously interpreted as a trans-keto form of **1** (Figure 1c). The result revealed that the structure of the colored species is the trans-keto form.

After X-ray diffraction analysis of the laser-irradiated crystal, the same crystal was irradiated with a xenon lamp ($\lambda > 530$ nm, using a TOSHIBA O-55 filter) at room temperature. The dark-red crystal returned to the original pale yellow color. X-ray diffraction analysis of the crystal was then carried out. The space group was retained, and the cell dimensions returned to those of the original crystal.¹² The analyzed structure was the same as that of nonirradiated crystal. The peaks of the trans-keto form disappeared, and no significant residual peak was observed in the difference Fourier map. These results clearly show that the photoreversible color changes in crystals are caused by an interconversion between the enol and trans-keto forms. Thus, the first crystallographic determination of the structural changes accompanying the reversible phototransformation of an organic photochromic crystal was achieved.

The phototransformations demonstrated here involve large structural changes and are seemingly difficult to take place in crystals. Such molecular transformations, however, can easily occur through the motion of a pair of benzene rings which is analogous to the pedal motion of a bicycle. Azobenzenes, which have molecular skeletons similar to those of salicylideneanilines, undergo the pedal motion in crystals.¹³ This type of molecular motion is responsible for the phototransformation of salicylideneanilines in crystals.

It must be emphasized that the two-photon excitation is very important to observe the structure change accompanying photochromism of organic crystals. X-ray diffraction analysis is the most powerful method to determine the molecular structures in crystals. In disordered crystals, however, it is very difficult to determine the structure of the minor component whose occupancy factor is less than 10%. To produce enough of the colored species to be detected by X-ray diffraction analysis, the light for excitation must meet the following conditions. First, the absorbance of the crystal at the wavelength must be very small. Second, the light should not be strongly absorbed only by the colored species. An

(11) The cell dimensions: $a = 6.1295(3)$ Å, $b = 10.3683(5)$ Å, $c = 16.2420(7)$ Å, $\alpha = 101.9536(12)^\circ$, $\beta = 92.8584(9)^\circ$, $\gamma = 103.3458(12)^\circ$, $V = 977.38(8)$ Å³. A total of 19 172 reflections were collected, of which 5678 reflections were independent. The number of the parameters was 324. The 23 atoms of a total of 26 non-hydrogen atoms belonging to the trans-keto form were found in difference Fourier maps. The non-hydrogen atoms of the enol form were refined anisotropically, and the hydrogen atoms were refined isotropically. In the trans-keto form the non-hydrogen atoms were refined isotropically, and the hydrogen atoms were refined according to the riding model. Details of the structure refinement have been deposited with Supporting Information. The final R value calculated for 4997 reflections ($F_o > 4\sigma(F_o)$) was 0.045, and $wR2$ for all the reflections was 0.121. The value of GOF was 1.129.

(12) The cell dimensions: $a = 6.0956(1)$ Å, $b = 10.3034(2)$ Å, $c = 16.2777(2)$ Å, $\alpha = 102.1639(5)^\circ$, $\beta = 92.3604(10)^\circ$, $\gamma = 103.0128(5)^\circ$, $V = 969.49(3)$ Å³. A total of 19 104 reflections were collected, of which 5638 reflections were independent. The number of the parameters was 339. The final R value calculated for 4952 reflections ($F_o > 4\sigma(F_o)$) was 0.036, and $wR2$ for all the reflections was 0.106. The value of GOF was 1.045.

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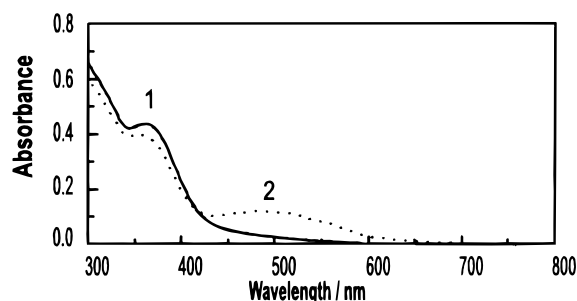


Figure 2. Absorption spectra of **1** and its photoproduct. The spectra were recorded on a JASCO V-560 at room temperature (KBr disk). Absorbance is taken in an arbitrary scale. 1 (full curve), original form; 2 (dotted curve), after irradiation with 365-nm light. Subsequent irradiation with wavelength shorter than 530 nm gave the same spectrum as 1.

inherent property of the photoreversible systems, however, makes it very difficult to meet both conditions at the same time. For example, irradiation with ultraviolet light (a high-pressure mercury lamp, 365 nm) of **1** (KBr disk) yielded a colored species which has an absorption band with a maximum at 480 nm (Figure 2). When the photoreaction is carried out by irradiation with strongly absorbed light, the light intensity drops off drastically in the bulk of the crystal, and the photoreaction takes place only near the surface of the crystal. Light with much longer wavelength than that of the absorption maximum readily penetrates into the crystals and meets the first condition.¹⁴ Light with such wavelength, however, lies within the newly developed absorption band and erases the color. Therefore, there is practically no suitable wavelength for an effective phototransformation in the bulk of the crystal. This is usually the case for other organic photochromic systems.

The difficulty is solved by using two-photon excitation. Two-photon excitation by 730 nm radiation gives molecules with the same energy as one-photon excitation at 365 nm, which is nearly at an absorption maximum of the lowest energy band of **1**. Because the probability of two-photon excitation is much smaller than that of one-photon excitation, the light intensity hardly decreases in the bulk of the crystal. Thus, the two-photon excitation makes it possible to excite the bulk of the crystal and to form enough of photoproduct for X-ray diffraction analysis.

In summary, we succeeded in the observation of the structural changes accompanying the photochromism of salicylideneanilines in crystals. It was revealed that an interconversion between the enol and trans-keto forms is responsible for the color changes. The phototransformation induced by two-photon excitation in crystals is essential to obtain enough of the photoinduced species for X-ray diffraction analysis. This method will be generally applicable and very useful for studies on many other solid-state photoreactions.

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Supporting Information Available: Tables of crystal data, structure refinement, atomic coordinates, anisotropic displacement parameters, details of the structure refinement on the disorder model (dark red crystal) and ORTEP diagrams for **1** (PDF). An X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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