Novel Photoisomerization of *N*-(2-Nitrobenzylidene)-3-amino-5-methylpyrazole Triggered by Intramolecular Proton Transfer from Azomethine Group to Nitro Group in the Crystal State

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Excited-state intramolecular proton transfer from the azomethine group to the nitro group of *N*-(2-nitrobenzylidene)-3-amino-5-methylpyrazole induced the formation of 2-nitrosobenzamide attended by vivid color change from yellow to reddish brown in the crystal state.

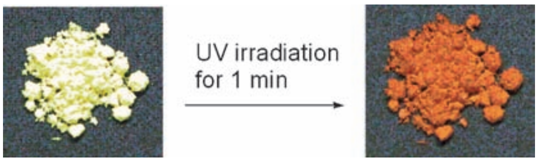
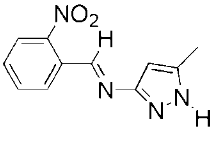


Figure 1. Photographs of crystals of **1** and **1P**.

Excited-state intramolecular proton transfer (ESIPT) phenomena continue to receive significant attention because of various applications to materials design and processes in the fields of chemistry and biology.[1] Certain organic molecules exhibit color changes through ESIPT in the crystal state.[2] A great deal of chemistry on such photosensitive crystals is now progressing because of their potential usefulness for photoelectron systems.[3] In the most accessible compounds of this type are included *N*-salicylideneanilines,[2,4] whose coloration process involves ESIPT from the phenolic hydroxy group to the imino nitrogen atom, and 2-(2,4-dinitrobenzyl)pyridine, whose photocoloration originates from a nitro group-assisted ESIPT from the methylene group to the nitrogen atom of the pyridine ring.[5] As for the practical usefulness, the resultant photochromes are thermally unstable and the colored species can return easily to the original form in the dark. Accordingly, it is required to develop a new ESIPT system that produces stable photochrome. Now we report that Schiff base **1** (Scheme 1) bearing a nitro group and a pyrazole ring is very sensible to light to yield a highly stable photochrome in the crystal state.

Schiff base **1** was prepared by condensation of 2-nitrobenzaldehyde with 3-amino-5-methylpyrazole in ethanol. The product was purified carefully by recrystallization from ethanol in the dark to yield pale yellow fibers, whose structure was identified as **1** by satisfactory elemental analysis and ^{1}H NMR spectral data.[6] Upon exposure of crystals of **1** to room light, the color of the crystals turned to bright brown, whose tone became much deeper with time. Photographs of the powdered crystals of **1** before and after irradiation with 365-nm light at room temperature are shown in Figure 1.



Scheme 1. Schiff base **1**.

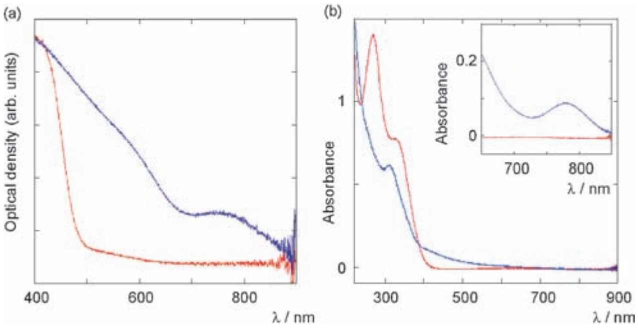


Figure 2. UV–vis spectra of **1** before (red line) and after 365-nm light irradiation for 1 h (blue line); (a) solid-state reflectance spectra and (b) absorption spectra in CH_3CN ([**1**] = 1.0×10^{-4} mol dm^{-3}). Inset in (b) shows absorption spectra in the case of a 50-fold concentrated solution.

Photocolored species **1P** was so stable in the crystal state that neither heating it on a hot plate nor irradiation with an incandescent light above 500 nm returned it to **1**. The photoreaction of **1** to **1P** proceeded in CH_3CN smoothly. UV–vis spectra of **1** before and after irradiation with 365-nm light in the crystal state and in CH_3CN solution are shown in Figure 2, which exhibits that **1P** absorbs a wide range of visible light around 400–650 nm and has a broad absorption maximized at around 760 nm, which is suggestive of formation of an aromatic nitroso compound by the photoreaction.

Direct information from the photochemical transformation of the nitro group in **1** to the nitroso group in **1P** was obtained from ATR-FTIR spectroscopy (Figure 3). The intense absorption bands at 1530 and 1340 cm^{-1} for **1** were indexed to the asymmetric and symmetric stretching vibration of the nitro group, respectively. As the photoreaction of **1** proceeded, these characteristic bands of **1** became weaker and new bands appeared at 1668 and 3280 cm^{-1}. The former is reasonably assigned to the characteristic N=O stretching band of a nitroso group, while the latter is ascribed to the N–H stretching vibration of amide. Promising clues to explain the photoreactivity of **1** and to imply the structure of **1P** were obtained through NMR analysis (Figure 4).[7] Judging from ^{1}H NMR spectral change due to the conversion of **1** to **1P** by UV irradiation in CD_3CN, the signal at 9.10 ppm for the azomethine proton of **1** disappeared and the new broad resonance appeared at 9.73 ppm. This observation implicates proton abstraction from the azomethine group and formation of an amide-like group. Remarkable changes of chemical shifts for aromatic protons were also observed concurrently.

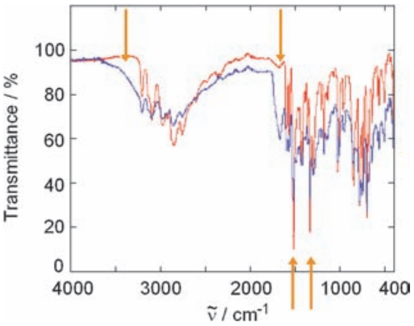


Figure 3. ATR-FTIR crystal surface transmittance spectra of **1** before (red line) and after (blue line) 365-nm light irradiation. Arrows indicate direction of change of intensity by photoreaction.

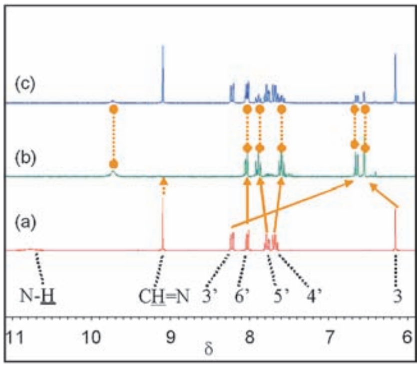
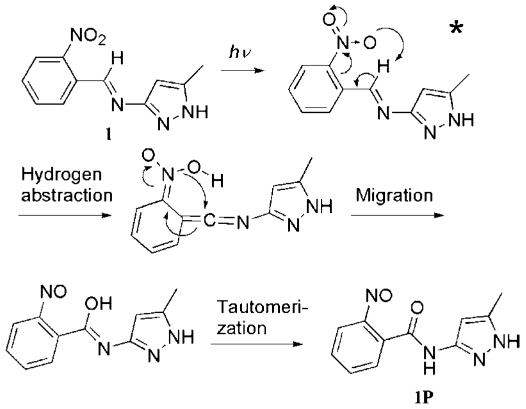


Figure 4. Low-field region ^{1}H NMR spectra of (a) **1**, (b) **1P**, and (c) photocolored crystals in CD_3CN. Arrows indicate direction of change of chemical shifts by photoreaction. Signals marked by ● with broken lines show the resonances for **1P**.

The signal due to the 3′-proton of **1P** was shifted upfield by 1.6 ppm compared to that for **1**, while other protons showed only slight shifts after the photoreaction. The significant shift for the proton adjacent to the nitro substituent supports the conversion of the nitro group into the nitroso group whose inductive effect falls markedly. These spectral observations are in accord with the formation of 2-nitrosobenzamide. The photoreaction in CD_3CN solution proceeded almost quantitatively for 1 h at room temperature. Because of the lability of nitroso group, neither recrystallization nor chromatography was effective for further purification of **1P**. As for the solid-state reaction, the NMR spectrum of the resultant reddish brown solid in CD_3CN was composed of two sets of signals attributed to **1** and **1P**. The yield of **1P** in the solid-state reaction was calculated to be 30% from the intensity ratio of the signals.

A plausible mechanism for the photoreaction of **1** to give **1P** is explained by an ESIPT process involving the nitro group (Scheme 2), in analogy with the photoinduced rearrangement of 2-nitrobenzaldehyde to 2-nitrosobenzoic acid.[8] An oxygen atom of the nitro group initially abstracts the azomethine hydrogen atom in the excited state to form *aci*-nitro-quinoid structure. The resultant OH group is then migrated to the electropositive quinoidal carbon atom to afford hydroxymethylideneamine, which isomerizes to amide tautomer **1P**.



Scheme 2.

In conclusion, we found a new photosensitive crystalline 2-nitrobenzylidene Schiff base, whose photochrome was extremely stable. Our success in creating a long-lived photocolored species is attributable to the employment of a conjugated system with nitrophenyl and pyrazole heteroaromatics. The mechanism of coloration process was explained on the basis of ESIPT to nitro group. Thus 2-nitrobenzylideneamine derivatives seem feasible for construction of a model system with opto-electronic properties. A remaining problem is to actualize reversibility of color change. Efforts to prepare such a photochromic system are currently underway.

References and Notes

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6 Experimental data for **1**: mp: 123–125 °C. Anal. Found: C, 57.38; H, 4.45; N, 24.29%. $C_{11}H_{10}N_4O_2$ requires C, 57.39; H, 4.38; N, 24.34%. δ_H (270 MHz, CD_3CN): 2.28 (3H, s, 5-CH_3), 6.16 (1H, s, Ar–H(3)), 7.65–7.71 (1H, dt, Ar–H(4′)), 7.76–7.82 (1H, dt, Ar–H(5′)), 8.01–8.05 (1H, dd, Ar–H(6′)), 8.21–8.24 (1H, dd, Ar–H(3′)), 9.10 (1H, s, CH=N), 10.79 (1H, brs, NH).

7 Experimental data for **1P**: δ_H (270 MHz, CD_3CN): 2.31 (3H, s, 5-CH_3), 6.55 (1H, s, Ar–H(3)), 6.63–6.66 (1H, dd, Ar–H(3′)), 7.57–7.63 (1H, dt, Ar–H(4′)), 7.86–7.92 (1H, dt, Ar–H(5′)), 8.03–8.06 (1H, dd, Ar–H(6′)), 9.73 (1H, s, CONH).

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