

## Novel Photochromic Dye Based on Hydrogen Bonding

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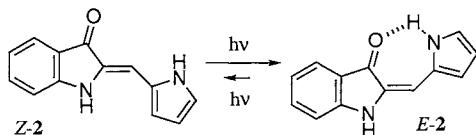
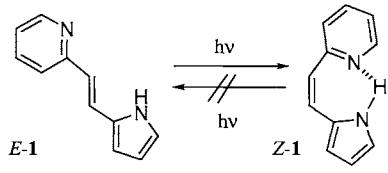
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2-(2-Pyrrolylmethylidene)indolin-3-one (**2**) exhibited color change from reddish orange to greenish yellow giving the *E* isomer composition from 99% to 15% on irradiation at 366 nm and 546 nm, respectively.

Photochromic compounds having absorption band at visible region have been received considerable attention from the view point of development of photochromic memory or switching devices in recent years.<sup>1,2</sup> For example, Irie et al. reported a series of diarylethenes, exhibiting photochromic properties based on photochemical cyclization reaction.<sup>3</sup>

We are interested in the photochromism based on intramolecular hydrogen bonding. For example, an olefin with a pyrrole ring and a pyridine ring (**1**) exhibited the one-way *E*→*Z* isomerization due to the presence of an intramolecular hydrogen bonding.<sup>4</sup> The *Z*-isomer in benzene exhibited an absorption maximum at longer wavelength region ( $\lambda_{\text{max}} = 372$  nm) than the *E*-isomer ( $\lambda_{\text{max}} = 347$  nm).<sup>4</sup>

In the course of our study about the effect of intramolecular hydrogen bonding on photochemical behavior of olefins, we came to find a compound **2** capable of forming an intramolecular hydrogen bonding and of exhibiting the absorption spectrum at considerably longer wavelength region.<sup>5</sup>



The absorption maximum of *E*-**2** appeared at longer wavelength ( $\lambda_{\text{max}} = 524$  nm) than that of *Z*-**2** ( $\lambda_{\text{max}} = 470$  nm) in benzene probably due to the presence of intramolecular hydrogen bonding in *E*-**2**. With irradiation at 366 nm light, **2** gave a photostationary isomer mixture ( $[E] / [Z]_{\text{pss}}$ ) with a very high composition of *E*-form to give ( $[E] / [Z]_{\text{pss}}$ ) = 99 / 1 in benzene. The time development of the absorption spectrum of *Z*-**2** on irradiation at 366 nm is shown in Figure 1. The ( $[E] / [Z]_{\text{pss}}$ ) value decreased in polar and protic solvent and is 95 / 5 and 90 / 10 in acetonitrile and methanol, respectively.

Quantum yields of *Z*-to-*E* isomerization were 0.3 in all the solvents examined, whereas those of *E*-to-*Z* isomerization were ~0.003, 0.02 and 0.05 in benzene, acetonitrile and methanol, respectively. The fluorescence emission in benzene was

observed at the normal region for *Z*-**2** ( $\lambda_{\text{max}} = 500$  nm) and *E*-**2** ( $\lambda_{\text{max}} = 554$  nm) with the quantum yield of 0.023 and 0.006, respectively. In addition, the fluorescence lifetime of *E*-**2** ( $\tau_s = 210$  ps) is shorter than that of *Z*-**2** ( $\tau_s = 350$  ps). An intramolecular hydrogen bonding in *E*-**2** plays an important role in the deactivation from the excited singlet state; the effect of an intramolecular hydrogen bonding decreased in polar solvent. However, the *E*-isomer composition is still dominant even in methanol.

On irradiation at 546 nm in benzene *E*-**2** underwent isomerization to *Z*-**2** to give the *Z*-isomer composition as high as 85%. The isosbestic points appeared at 366, 408 and 483 nm as depicted in Figure 2. Therefore, the irradiation wavelength affected the photostationary state isomer composition to give

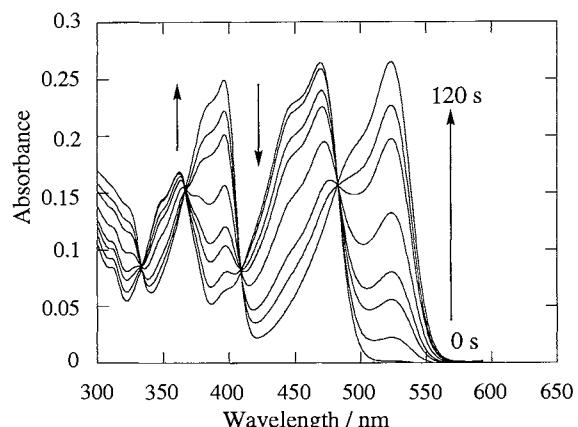


Figure 1. Change of absorption spectrum of *Z*-**2** on irradiation at 366 nm in benzene under argon.

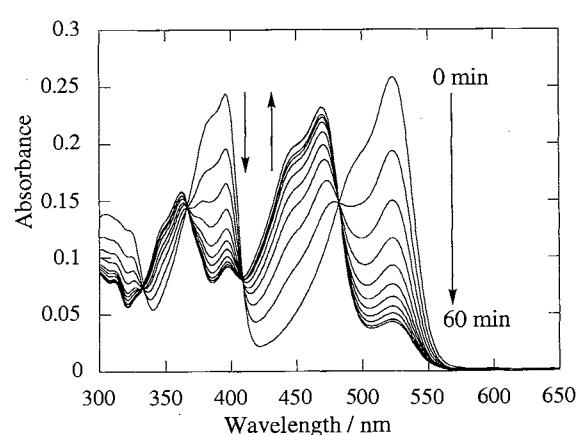
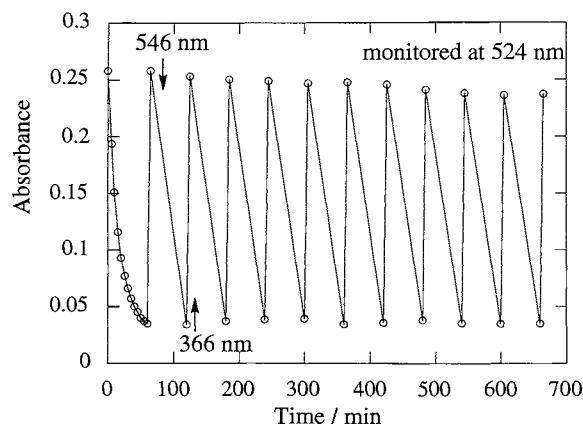


Figure 2. Change of absorption spectrum of *E*-**2** on irradiation at 546 nm of high pressure mercury lamp in benzene under argon.

~99% of the *E*-isomer and ~85% of the *Z*-isomer with irradiation at 366 nm and 546 nm, respectively. The change of the absorbance at 524 nm with irradiation at 366 nm and 546 nm is shown in Figure 3.



**Figure 3.** Repetition characteristics of **2** by alternate irradiation at 366 and 546 nm of high pressure mercury lamp in benzene under argon monitored at 524 nm.

As to the absorption maximum, the photochromic compounds based on *Z*-*E* isomerization have scarcely been studied probably because of the difficulty of constructing molecules with absorption maximum at longer wavelength region as well as with moderate photochemical response. The difference of absorption maximum between *E*-**2** and *Z*-**2** is ~50 nm and is not very large, but is considerably larger than those of usual olefins, such as stilbene or stylylanthracene. In addition, *E*- and *Z*-**2** are stable at room temperature in benzene.

In conclusion, **2** exhibited almost one-way *Z*→*E* isomerization on irradiation with 366 nm light, where both *Z*- and *E*-**2** have similar absorption coefficient, due to the considerably large difference of  $\Phi_{Z \rightarrow E}$  and  $\Phi_{E \rightarrow Z}$ . However, **2** gives a photostationary mixture with a very high ratio of *Z*-**2** to *E*-**2** as 85:15 on irradiation at 546 nm where the *E*-**2** has much higher absorption coefficient than *Z*-**2**. Thus, the intramolecular

hydrogen bonding could play an important role for constructing photochromic compounds having absorption at longer wavelength region and necessary photostability of the isomer.

To the best of our knowledge, **2** exhibited interesting photochromic properties exhibiting the absorption at longer wavelength region and the considerable photostability of *E*-isomer.

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- Z-2:**  $^1\text{H-NMR}$ (DMSO-d<sub>6</sub>, 200 MHz)  $\delta$  6.31 (1H, m; pyrrole-H), 6.71 (1H, s; olefinic-H), 6.87 (2H, m; aromatic-H), 7.07 (1H, m; pyrrole-H), 7.13 (1H, d,  $J$  = 8.2 Hz; indolin-H), 7.50 (2H, m; indolin-H), 9.30 (1H, s; NH), 11.40 (1H, s; NH). mp 200-202 °C. **E-2:**  $\delta$  6.34 (1H, m; pyrrole-H), 6.71 (1H, m; pyrrole-H), 6.81 (1H, s; olefinic-H), 6.87 (1H, m; indolin-H), 7.06 (1H, d,  $J$  = 8.4 Hz; indolin-H), 7.25 (1H, m; pyrrole-H), 7.47 (1H, m; pyrrole-H), 7.63 (1H, d,  $J$  = 8.4 Hz; indolin-H), 9.78 (1H, s; NH), 13.35 (1H, s; NH). mp 191-193 °C. Anal. Calcd for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O: C, 74.27; H, 4.79; N, 13.32%. Found: C, 74.04; H, 4.74; N, 13.19%.
- Irradiation was performed in the quartz cell at room temperature with 400 W high pressure mercury lamp. 366 nm light was obtained with UV-35 cutfilter and U-360 bandpass filter. L-39 and Y-50 cutfilters were used for the purpose of irradiation at 546 nm.