Another Photochromism of a Spironaphtoxazine Due to the Geometric Isomerization of the Open-Form

Toyokazu Horii,* Yoshinobu Miyake, Ren Nakao, and Yasuo Abe
Research Institute for Advanced Science and Technology, Osaka Prefecture University, 1-2 Gakuen-cho, Sakai 593

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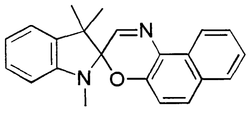
The photodecoloration rate of colored spironaphtho[1,2-b]oxazine **2** was much slower than the corresponding [2,1-b]oxazine **1**. Existence of another photochromic system between two of the open-form isomers of **2**, in addition to the well-known one for **1** between the closed and the open forms, was proved.

Spironaphthoxazine is one of the typical photochromic compounds, and many interesting studies have already been reported.[1] The geometric structures of the colored forms, however, were not fully established because of their thermally unstable characters. Recently, several studies by transient spectroscopy showed the presence of a series of colored open-form isomers,[2-4] and NOE experiments of ^{1}H NMR spectroscopy determined the structure of the most stable isomer.[5] These studies, however, always dealt with spironaphtho[2,1-b]oxazine **1**, derived from 1-nitroso-2-naphthol.



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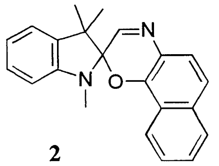

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In the present work, we prepared spironaphtho[1,2-b]oxazine **2**[6] from 2-nitroso-1-naphthol, and examined its photochromism. We here show that the photodecoloration rate of colored **2** is much slower than that of **1** and there is another photochromic system between two of the open forms of **2**, in addition to that between the closed and open forms.

The photochromic character of **2** at room temperature was similar to that of **1**, that is, dilute solutions of **2** in organic solvents became blue upon exposure to UV-light and the blue color disappeared rapidly when UV-irradiation was ceased. Figure 1(A) shows the change of absorption spectra of **1** (dashed lines) and **2** (solid lines) in hexane (each 1.68×10^{-5} mol dm^{-3}) at 183 K, from the maximum coloration by UV-light irradiation (xenon lamp with Toshiba UV-D33S and IRA-25S as filters). The absorption spectrum of colored **1** has one maximum and a shoulder while that of colored **2** has absorption maxima at 615 and 579 nm, and shoulders at 545 and about 510 nm in the visible region. For photodecoloration, the light from the xenon lamp passed through a Toshiba R-60 glass filter was used. The shapes of the spectra of vis-irradiated **2** varied as described below and steady states were reached in 2 h, therefore, the spectra measured after 2 h of irradiation were shown in Figure 1(A). The rate of photodecoloration of **2** was much slower than **1**.

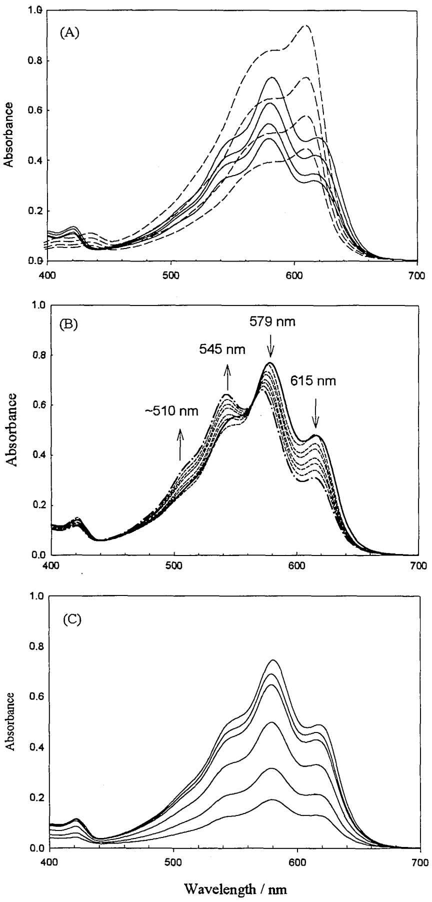
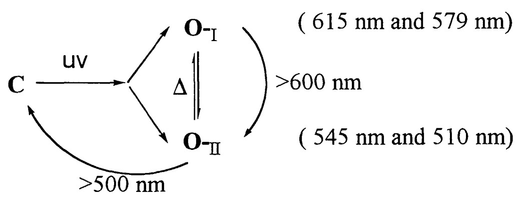


Figure 1. Visible absorption spectral changes of spironaphtoxazines in hexane colored by irradiation with UV-light for 5 min at 183 K. All photo-irradiations were carried out with a 500 W xenon lamp. (A) Absorption spectra of colored **1** (dashed lines) decolored by irradiation with light of >600 nm for 0, 1, 2, 3 min, and those of colored **2** (solid lines) for 0, 2, 4, 6 h. (B) Absorption spectra of colored **2** (solid line) irradiated with >600 nm for 30 min (chain line), and allowed to stand at 2, 6, 10, 20, 30, and 120 min (dashed lines). (C) Absorption spectra of colored **2** irradiated with light of >500 nm for 0 min, 10 min, 20 min, 1 h, 2 h, and 3 h.

The solid line in Figure 1(B) shows the absorption spectrum of colored **2** in hexane at 185 K. To study the early stage of decoloration, the absorption spectrum of the colored solution was measured after the irradiation of vis-light (>600 nm) for 30 min. After the irradiation, the absorption spectrum changed to the chain line, in which the intensities of the bands at 615 and 579 nm decreased and those at 545 and 510 nm increased. When the irradiation was stopped, the spectrum changed gradually. The dashed lines showed the time course of the absorption spectral change when the colored solution was left at that temperature in the dark, and the spectrum before vis-light irradiation was almost restored after 2 h. This means that the decoloration due to the ring-closure hardly occurred with >600-nm light irradiation for 30 min.[7] Therefore, the spectral change mentioned above implies that, together with the fact that an isosbestic point appeared at 564.5 nm in Figure 1(B), there is a photochromic process between two of the geometric isomers of the colored species. This is different from the well-known open-form—closed-form photochromism.

Figure 1(C) shows the spectral change of colored **2** by photoirradiation (>500 nm) onto the whole absorption band of the visible region of colored **2**. This procedure decreased the whole absorption band in the visible region with keeping the proportion of the band. This means that the ring closing reaction occurred by >500-nm light irradiation. It took, however, a long time for **2** (the half-life was about 1.5 h) compared to **1** (2.5 min).

Above observations allowed us to postulate a conceptual reaction mechanism shown in Scheme 1. The closed form (**C**) changes to the open form (**O**) by UV-light irradiation, which consists of **O**-$_{\mathrm{I}}$ (λmax =615 and 579 nm) and **O**-$_{\mathrm{II}}$ (λmax=545 and 510 nm). With >600 nm light, **O**-$_{\mathrm{I}}$ changes to **O**-$_{\mathrm{II}}$, which then returned gradually to the thermal equilibrium between these two. Irradiation of >500-nm light to the equilibrium mixture causes ring closure of **O**-$_{\mathrm{II}}$ to form **C**. Although the photoinduced isomerization of **O**-$_{\mathrm{II}}$ to **O**-$_{\mathrm{I}}$ was not observed, the photochemical back-and-forth reaction between them might be one of the reasons of the low reaction rate of decoloration of **2**.



Scheme 1.

The differences in the spectra of colored **1** and **2** may be attributed to the number of their stable geometric isomers. *Ab initio* molecular orbital calculations showed that EZ and ZZ isomers of **1** are much more stable than the EE and ZE isomers.[5] This result is agreeable from the viewpoint of the steric hindrance. The instability of the latter ones was due to the repulsion of the proximate hydrogen atoms shown in Figure 2. On the other hand, because this kind of repulsion is absent in any isomers for **2**, all of the geometric isomers may be comparably stable. This might be the reason of the complex spectrum and the complex photochemical and thermal behavior of colored **2**. Although it is interesting to correlate the structure of the isomers with the absorption bands, it has not yet been done.

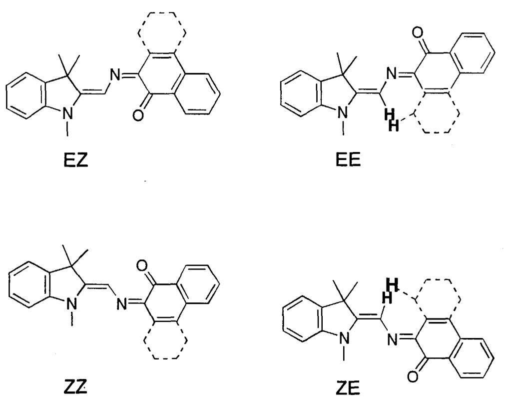


Figure 2. Possible open-formed isomers of **2**. Dashed lines indicate parts of naphthalene rings in **1**.

In summary, the selective transformation of one geometric isomer of the colored forms of **2** to another was achieved by selective visible-light irradiation. As these two isomers are in a thermal equilibrium, this is a thermally reversible photochromic system of a spironaphthoxazine.

References and Notes

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6 Compound **2** was prepared by a modification of the literature procedure: Yamamoto and T. Taniguchi, Jap. Patent 62-33184(1987). **2** (pale green semisolid): ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.35 (s, C-Me, 6H), 2.75 (s, N-Me, 3H), 6.57 (d, J=8.0 Hz, 1H), 6.90 (t, J=7.0 Hz, 1H), 7.08 (d, J=7.0 Hz, 1H), 7.21 (t, J=7.0 Hz, 1H), 7.32 (t, J=8.0, 1H), 7.40 (d, J=8 Hz, 1H), 7.41 (t, J=7 Hz, 1H), 7.53 (d, J=8 Hz, 1H), 7.69 (s, 1H), 7.73 (d, J=8.5, 1H), and 7.98 (d, J=8.5Hz, 1H). Found: m/z 328.1551. Calcd for $C_{22}H_{20}N_2O$: 328.1576.

7 By photoirradiation over 30 min, the whole absorption in the visible region decreased gradually under an isosbestic point.