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Two-Photon Photochromism of a Naphthopyran Derivative

Manabu Uchida[1] and Masahiro Irie*

Institute of Advanced Material Study
Kyushu University, Kasuga-Koen 6-1
Kasuga, Fukuoka 816, Japan

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Photochemical reactions, in general, proceed in proportion to the number of photons absorbed by the molecules. Such a single-photon photochemistry cannot be used as the basis of optical recording or imaging,[2] because the memories or images are destroyed during storage under room light or after many readout operations. When photochromic compounds are intended to be applied to rewritable optical memory media, the compounds are required to have gated photochemical reactivities[2–4] or two-step two-photon reaction mechanisms[5] to avoid such inconvenience.

During the course of a study on the photoisomerization of naphthopyran derivatives,[6,7] we found that the photodecoloration quantum yield of a naphthopyran derivative **1** depends on the light intensity. The yellow naphthopyran **1** isomerized to a colorless bicyclohexene isomer **2** via an unstable intermediate by a *two*-photon process ($\lambda = 405$ nm), and the bicyclohexene isomer again returned to the original naphthopyran by irradiation with 334-nm light. When the light intensity is weak, the bleaching scarcely occurs even after prolonged irradiation, while the yellow color disappears immediately by illumination with high intensity light.

The above naphthopyran was synthesized by dehydration of the diol, which was prepared by the reaction of 1-lithio-2-methylnaphthalene with 2-hydroxy-1-naphthaldehyde.[7] Figure 1 illustrates the change in spectral absorption of a hexane solution of **1** (λ_{max} 396 nm, ϵ 1.4×10^4 dm^3 mol^{-1} cm^{-1}) by photoirradiation in the presence of air. Upon irradiation with 405-nm light (intensity = 3.9 mW/cm^2), the visible absorption decreased by as much as 20% in 5 min and converted to a new spectrum (λ_{max} 348, ϵ 5.4×10^3 dm^3 mol^{-1} cm^{-1}). The photogenerated isomer, which gives the above spectrum, was thermally stable (>10 days at room temperature) and could be isolated by a column chromatographic technique (hexane/ethyl acetate = 5/1). The structure was examined by ^{1}H and ^{13}C NMR and mass spectroscopy. The methyl and methine protons were observed at 0.9 and 2.2 ppm, respectively. The high field signals suggested the formation of a cyclopropane ring. In the ^{13}C NMR spectrum four peaks were observed at 12.5, 24.6, 28.4, and 29.7 ppm in addition to the peaks due to aromatic carbons. The large J_{CH} (= 177 Hz) of the peak at 28.4 ppm also supports the cyclopropane structure. The parent peak of the mass spectrum was the same as compound **1**. These results indicate that the photogenerated isomer has a cyclopropane ring in the structure. It has been reported that 1,2-dihydro-1,2-dimethylnaphthalene undergoes a photoreaction to produce bicyclohexene.[8–10] The reaction observed for compound **1** is considered to be similar to the reaction, as shown in Scheme I.

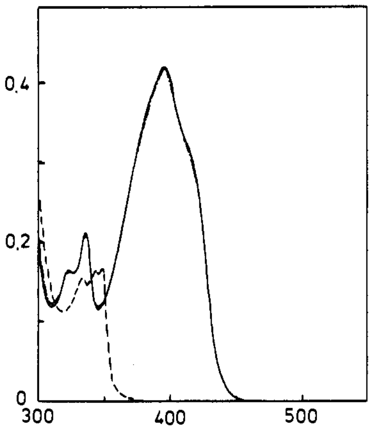


Figure 1. Absorption spectral change of compound **1** (3×10^{-5} dm^3 mol^{-1} cm^{-1}) in hexane in the presence of air: (—) original sample; (– –) after irradiation with 405-nm light; (– • –) after irradiation of the preirradiated sample with 334-nm light.

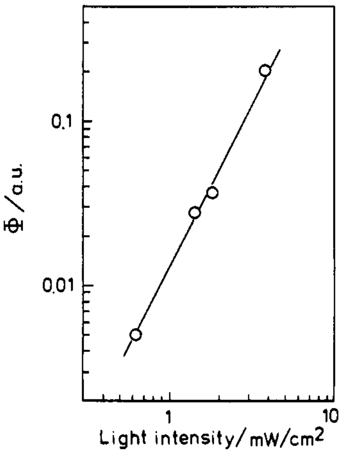
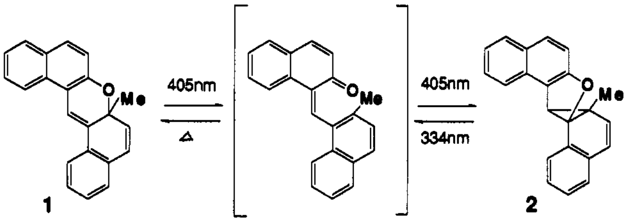


Figure 2. Light intensity dependence of relative decoloration quantum yields of compound **1** in hexane. Irradiation wavelength was 405 nm.

Scheme I



The bicyclohexene isomer **2** returned almost completely to the original isomer **1** by irradiation with 334-nm light, as shown in Figure 1. The decoloration/coloration cycle could be repeated many times. Although a similar two-step photoisomerization to produce a three-membered ring (ethylene oxide) was mentioned in the photoreaction of isochromenes,[11] attention was not paid to the reverse process (or the photochromic reactivity).

When the light intensity was decreased to 0.039 mW/cm^2, the photobleaching was scarcely observed even after 7-h irradiation. The decoloration quantum yield was strongly suppressed. Figure 2 shows the light intensity dependence of the relative quantum

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(1) Present address: Chisso Corporation, Kanazawaku, Yokohama, Japan.

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yield. The yield changes in proportion to the square of the light intensity. This result indicates that two photons are required for the isomerization. A photon produces a reaction intermediate, possibly an open-ring keto form as shown in Scheme I, and the second photon converts the keto form to the bicyclohexene isomer **2**. The good reversibility of the spectrum shown in Figure 1 suggests that microscopic reversibility is well-retained, i.e., photoexcited bicyclohexene isomer **2** converts to the unstable keto form, and the keto form thermally returns to the naphthopyran isomer **1**.

The steady-state concentration of the intermediate depends on its lifetime. When the lifetime is long, the steady-state concentration increases. Then, the reaction probability by the second photon is considered to increase. This was confirmed by decreasing the reaction temperature. The decoloration rate increased by as much as eight times when the reaction temperature was decreased from 0 to −70 °C at constant light intensity of 0.52 mW/cm^2.

In conclusion, compound **1** underwent an unusual two-step two-photon photochromic reaction to produce a bicyclohexene isomer **2** through a thermally unstable intermediate.

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