Structural Properties Required for Two-photon Photochromism of Pyran Derivatives

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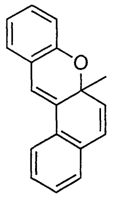
The photochromism of two new photochromic quinone monomethide derivatives was examined. While the 12aH-12a-methylnaphtho[3,2]chromene underwent a two-photon photochromic reaction, only a single-photon photochromic reaction between a keto form and an oxabicylcohexene form was observed for the phenanthrene analog.

Photochromic reactions, in general, proceed in proportion to the number of photons absorbed by the molecules. If the photochromic reactions are thermally irreversible, they can potentially be applied to photon mode erasable optical memory.[1] The single-photon photochromic reactions, however, cannot easily be applied to optical memory because the memory is destroyed after many readout operations. Some methods of non-destructive readout have been reported.[2] Recently we found that a naphthopyran derivative **1** undergoes a photochromic reaction with the absorption of two photons via an unstable intermediate **2** as shown in Scheme 1.[3] The two-photon photochromic reaction has advantageous in optical memory or image applications because the memory remains unchanged under low-intensity light, while it is readily erased upon irradiation with high-intensity light. In this letter we report on the photochromic properties of two new pyran derivatives **4** and **5**, and discuss the structural requirement for the two-photon photochromism.

The benzopyran derivative **4** was prepared by the same method as that of **1**.[3] Compound **5E** was synthesized by a Wittig reaction of phenanthrenequinone with a phosphorane derived from 1-chloromethyl-2-methylnaphthalene.[4] Compound **5Z** which is a geometric isomer of **5E** was obtained only in trace amounts.



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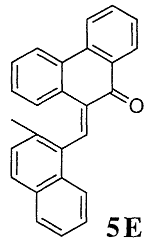


5E

The hexane solution of **4** was pale yellow and had an absorption maximum at 363 nm. When the solution was irradiated with light (λ > 365 nm), the color was bleached and a new absorption band appeared at 287 nm (Fig.1). The colorless form again returned to the colored form upon irradiation with 313 nm light. The bleaching rate increased by lowering the reaction temperature at a constant light intensity (0.32 mW cm^{-2}) as shown in Fig.2. The rate increased as much as 5.6 times when the temperature was lowered from 0 to -50 °C. The result indicates that the lifetime of the unstable intermediate increases at lower temperatures and the probability of absorbing the second photon by the intermediate increases concomitantly. The benzopyran derivative undergoes a two-step two-photon reaction similar to the naphthopyran derivative, **1**.

Figure 3 shows the spectral change of **5** in hexane by photoirradiation. The yellow color disappeared upon irradiation with visible light (λ>405 nm). The yellow color reappeared upon UV irradiation. As shown in Fig. 3, the absorption spectra of the yellow solutions before and after the light exposure differ. The spectral change between the dotted and the dashed lines was repeated many times. The structure of the colorless form which gave the dotted line spectrum was examined by ^{1}H NMR and was

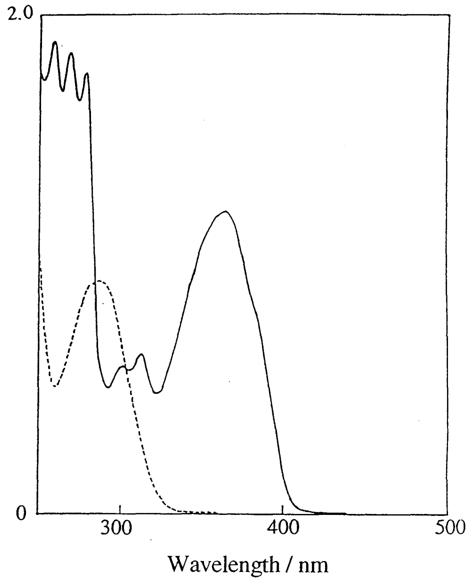
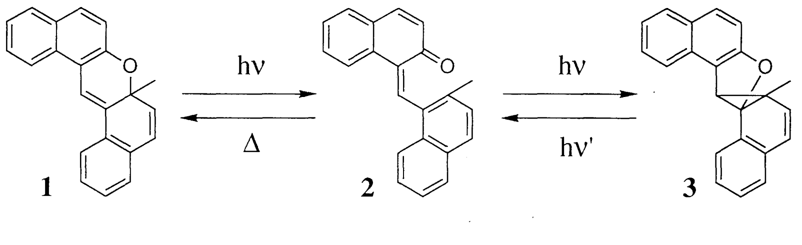


Figure 1. Absorption spectral change of compound **4** (1.0X10^{-4} moldm^{-3}) in hexane under the aerial atmosphere: (–) original sample; (--) after irradiation with light (λ>365–nm light)

Scheme 1.



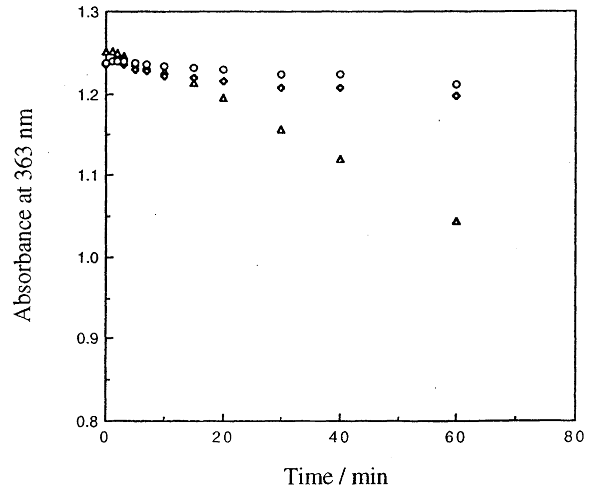


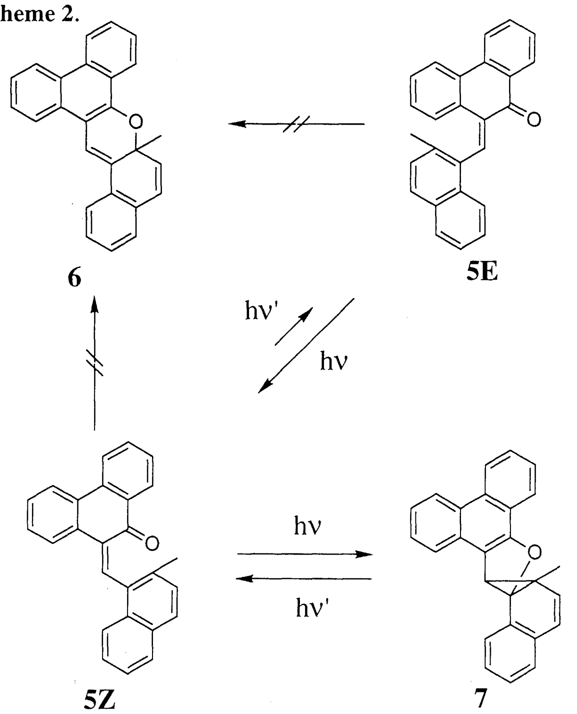
Figure 2. Temperature dependence of the photoreaction of **4** in hexane: (Δ)-50°C; (◇)0°C; (o)20°C.

identified as being an oxabicyclohexene isomer **7**.[4]

The photoproducts after UV irradiation (313 nm) which gave the dashed line spectrum were found by NMR spectroscopic and HPLC analysis, to be a mixture of the keto isomer **5E** and a geometric keto isomer of **5Z** (1 : 12).[4] The pyran isomer **6** was not produced from **5** either by irradiation with 313 nm light or even by being kept at 80°C in tridecane. The photochromic reaction occured between the oxabicyclohexene isomer **7** and the keto isomer **5Z**.

It is therefore concluded that the phenanthroquinone monomethide derivative which condenses a benzene ring to naphthopyran **1** looses the two-photon reactivity because of the increased thermal stability of the keto isomers, while the benzopyran derivative which substracts a benzene ring from the naphthopyran keeps the reactivity.

Scheme 2.



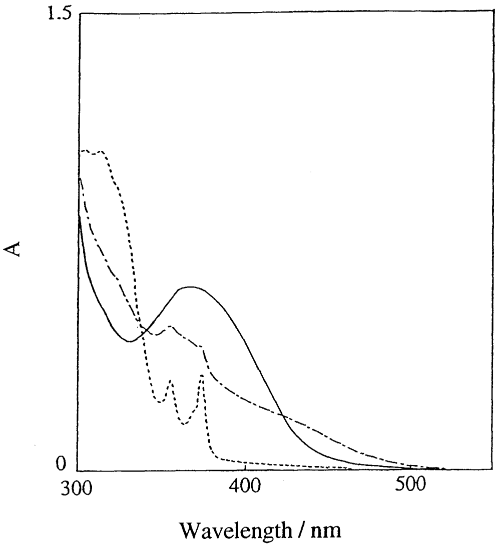


Figure 3. Absorption spectral change of compound **5** (1.0X10^{-4} mol dm^{-3}) in hexane under the aerial atmosphere: (–) original sample; (--) after irradiation with visible light (λ>405–nm light); (-··-) after irradiation of the preirradiated sample with 313-nm light.

References and Notes

1 M.Irie, *Jpn. J. Appl. Phys.*, **28**,215(1989).

2 F.Matsui, H.Taniguchi, Y.Yokoyama, K.Sugiyama, and Y.Kurita, *Chem. Lett.*, **1994**,1869; M.Irie, O.Miyatake, K.Uchida, and T.Eriguchi, *J. Am. Chem. Soc.*, **116**,9894(1994).

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4 Spectral data of **4**, **5E**, **5Z** and **7**. **4**: ^{1}H NMR δ 1.30(s,3H), 6.13(d,1H), 6.47(d,1H), 6.93(m,3H), 7.10-7.30(m, 5H), 7.73(m,1H). IR ν_{max} 1486 1474 1457 1266 1061 781 760 752 cm^{-1}. Anal. Found: C, 87.72; H, 5.97%. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73%. The synthetic sample **5E**: ^{1}H NMR δ 2.21(s,3H), 6.74(m,1H), 6.97(q,1H), 7.20(m,1H), 7.31(d,1H), 7.35–7.50(m,3H), 7.67(m,1H), 7.75(d,1H), 7.82(q,1H), 7.88(q,1H), 7.94(q,1H), 8.05(q,1H), 8.33 (q,1H), 8.39(s,1H). IR ν_{max} 1668 1602 1277 759 725 cm^{-1}. Anal. Found: C, 90.14; H, 5.24%. Calcd for $C_{26}H_{18}O$: C, 89.85; H, 5.36%. The photogenerated sample **5Z**: ^{1}H NMR δ 2.45(s,3H), 7.20(m,3H), 7.28(d,1H), 7.36(m,2H), 7.47 (m,1H), 7.61(d,1H), 7.63(d,1H), 7.68(d,1H), 7.85(s,1H), 7.87(q,1H), 7.92(m,1H), 7.97(d,1H), 8.00(m,1H). **7**: ^{1}H NMR δ 0.91(s,3H), 2.17(s,1H), 6.37(d,1H), 6.48(d,1H), 7.18(m,2H), 7.26(m,1H), 7.41-7.50(m,2H), 7.56(m,2H), 7.79(q,1H), 7.87(q,1H), 8.24(m,1H), 8.61(q,1H), 8.65 (m,1H). IR ν_{max} 1358 1331 1071 781 778 760 725 cm^{-1}.