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A New Photochromic Vinylnaphthol Derivative

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A vinylnaphthol derivative with a thiophene ring at α-position of the vinyl group underwent photochromic reaction in nonpolor solvents. The structure of the colored form, which was isolated by HPLC, was assigned to a closed-ring naphthopyran.

Photochromic compounds have attracted much attention because of their potential ability for various photoactive devices. The compounds frequently referred, however, are limited to several molecular structures, such as spiropyrans,[1)] fulgides,[2)] bisanthracenes,[3)] and diarylethenes.[4)] During the course of study of chromene derivatives, we found a new type of photochromic vinylnaphthol derivative, 1-(1-(2,5-dimethylthiophen-3-yl)vinyl)-2-naphthol, 1, which undergoes a reversible color change from colorless to yellow upon ultraviolet irradiation in hexane.

Compound 1 was prepared by coupling 2,5-dimethylthiophen-3-yl magnesium iodide with 1-acetyl-2-naphthol. The structure of 1 was fully characterized by NMR, IR, mass spectrum, and elemental analysis.[5)]

Figure 1 shows the absorption spectral change of compound 1 ($\varepsilon_{334\text{nm}}=$ 3.6×10^3 $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$) by irradiation with ultraviolet light (λ=334 nm) at room temperature in hexane. The solution turned yellow upon ultraviolet irradiation and the absorption maximum was observed at 385 nm (ε =

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1.7×10^4 $dm^3mol^{-1}cm^{-1}$). At the photostationary state, the fraction of the colored form was 0.61 and the coloration quantum yield was 0.20. The yellow color disappeared completely by irradiation with visible light (λ >390 nm). At room temperature the colored form was stable and its absorption intensity at 385 nm remained constant in the dark for more than 24 h. At higher temperature the yellow color slowly disappeared. Figure 2 shows decay behavior at 60 °C. Although the decay curve was not expressed by a single exponential, the half life time was independent of the concentration. This suggests that the decoloration is unimolecular but includes more than one step.

In order to know the coloration mechanism, the colored isomer was isolated by HPLC(colum ; Shim-pack CLC-NH_2, eluent ; hexane/ethyl acetate=5/1) and the structure was studied by NMR spectroscopy. Table 1 summarizes the NMR data of 1 and 2. The characteristic difference of the spectrum of 2 in comparison with that of 1 is that a phenolic proton disappears and a new

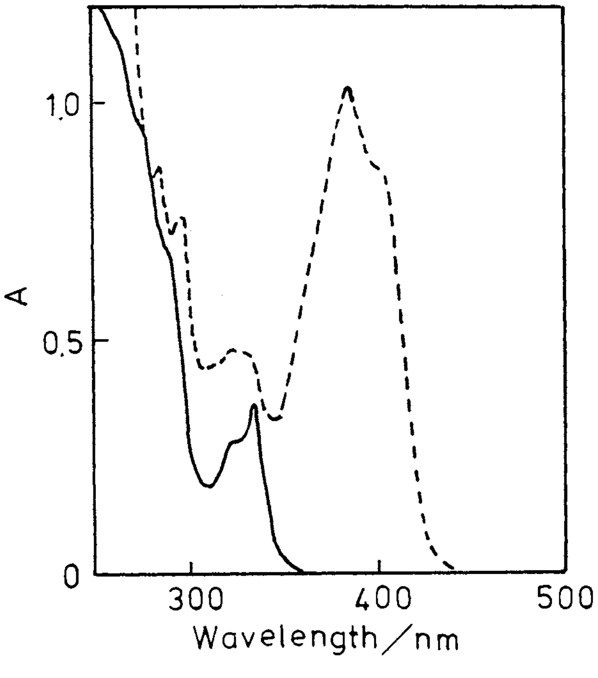


Fig.1. Absorption spectra of 1 (1.0×10^{-4} mol dm^{-3}) (—) and at the photostationary state under irradiation with 334-nm light (---).

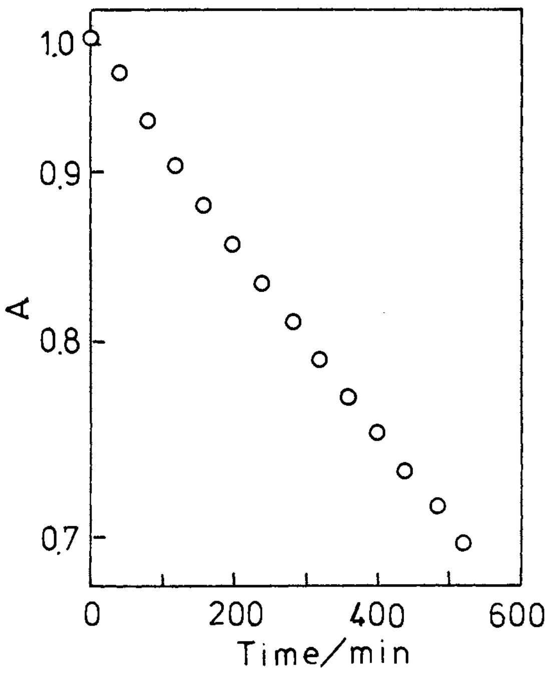


Fig.2. Thermal decay of the absorption at 385 nm of 2 at 60°C.

peak appears at 1.51 ppm. The peak at 1.51 ppm and two peaks at 2 ppm nearby are assigned to an aliphatic methyl group and vinylic methyl groups, respectively. A quartet peak at 5.98 ppm is ascribable to a vinylic proton. The spectrum indicates that structure of the colored form is a closed-ring naphthopyran, as shown below the Table 1.

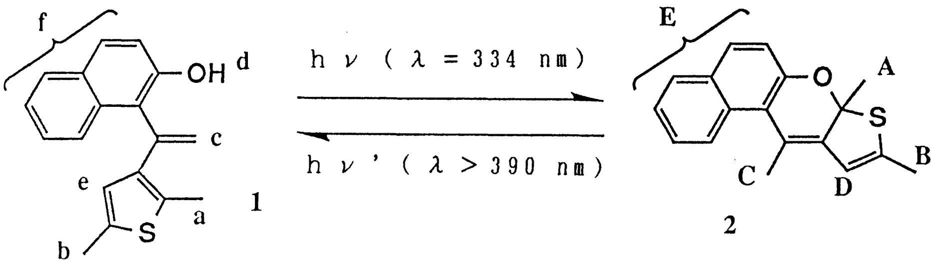
HPLC retention time of the photogenerated isomer(flow rate 1.5 ml/min) was 3 min, while that of compound 1 was 10 min. The short retention time means that the compound becomes less polar by ultraviolet irradiation. IR spectrum showed the decrease of OH group at 3500 cm^{-1} by the photoirradiation. All of these results support the naphthopyran structure.

The naphthopyran structure of the closed-ring form is similar to that of a colorless closed-ring form of benzochromene.[6)] In the case of benzochromene, the closed-ring structure is thermally stable form. This is not the case for the present compound.

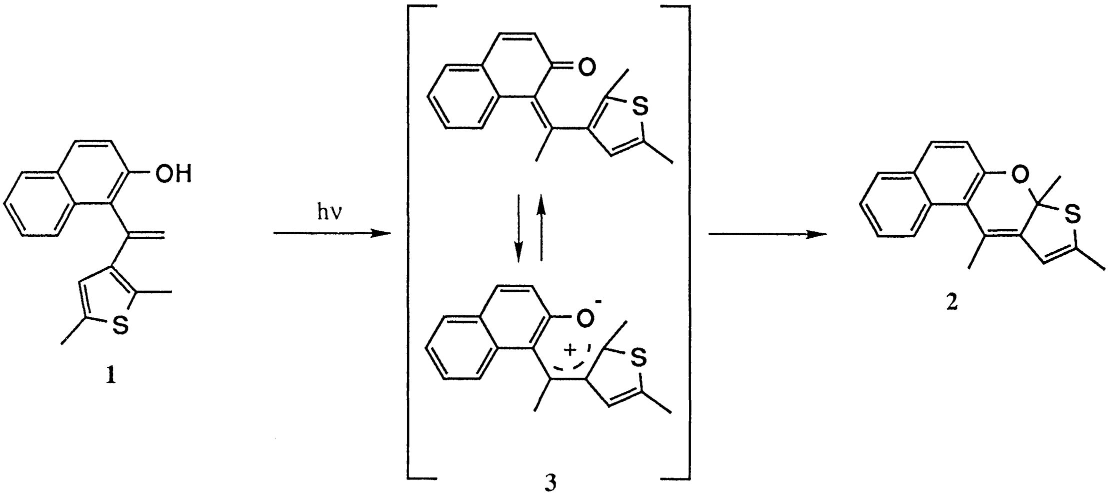
Table 1. NMR spectral data of compound 1 and 2

1 in $CDCl_3$			2 in n-C_6D_{14}		
ppm	Assignment		ppm	Assignment	
2.10 (s)	$-CH_3$	a	1.51 (s)	$-CH_3$	A
2.29 (s)[a)]	$-CH_3$	b	2.12 (d)	$-CH_3$	B
5.48 (d)	=CH	C	2.35 (s)	$-CH_3$	C
5.75 (s)	-OH	d	5.98 (q)	Thi-H	D
5.91 (d)	=CH	c	7.0-8.0 (m)	Ar-H	E
6.51 (q)	Thi-H	e			
7.2-7.8 (m)	Ar-H	f			

a) Peak b was a broad singlet peak and coupled with peak e (J<0.7 Hz).



The conversion from the enol to the keto form was not discerned in the NMR spectrum of the open-ring form. The absence of the keto form in the ground state suggests that hydrogen transfer occurs in the excited state (Scheme 1). The keto form 3 generated in the excited state is considered to undergo the ring closure reaction to the naphthopyran structure. According to the reaction mechanism, methanol is expected to retard the reaction by the formation of a methanol adduct.7) The absence of photochromic reaction in the presence of methanol also supports the mechanism.



Scheme 1.

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5) NMR data is shown in Table 1. IR (liquid film) 3500, 2920, 1600, 1200 cm^{-1}. MS (70 eV) m/z (rel intensity) 280(M^+,19), 265(100). Found: C, 76.96; H, 5.96%. Calcd for $C_{18}H_{16}OS$: C, 77.11; H, 5.75%.

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