Photochromic Properties of Thermally Irreversible 6-Aryloxy-5,12-naphthacenequinones

Yasushi Yokoyama,* Shin-ya Fukui, and Yayoi Yokoyama†
Department of Materials Chemistry, Faculty of Engineering, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240
†Faculty of Home Economics, Tokyo Kasei Gakuin University, Aihara-cho, Machida 194-02

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Spectroscopic and photochromic properties of five 6-(4-substituted)phenoxy-5,12-naphthacenequinones were studied. The quantum yields of fading with the visible light were first reported. The electron-donating substituents on the phenyl ring decreased the fading quantum yields of both UV- and visible-light irradiation. Absorption spectra were merely influenced by the substituents.

Anthraquinones[1] and naphthacenequinones[2] possessing an aryloxy group on the *peri* position to the carbonyl have been known to be photochromic since 1971. The latter is thermally irreversible at room temperature.[3] Their photochromism involves the mutual transformation between the yellow 6-aryloxy-5,12-naphthacenequinones (*para*-form) and the orange-colored 6-aryloxy-5,11-naphthacenequinones (*ana*-form).[2] The *para*-form turns to the photostationary state by UV light (UV-pss) in which the *ana*-form is predominant, and the *ana*-form turns to the *para*-form by visible light. Although this photochromic family has the history over twenty years, and even picosecond transient absorption spectral studies have been carried out,[4] their comprehensive photochromic properties have not been reported.[5] Particularly, the molar absorption coefficients of the *ana*-forms have not been determined directly from the absorption spectra and the component concentration,[5—7] and the quantum yields of fading reactions of *ana*-forms upon visible-light irradiation have not been reported so far.[4,5] We here report the basic photochromic properties of five 6-(4-substituted)phenoxy-5,12-naphthacenequinones in toluene.

Syntheses of 6-aryloxy-5,12-naphthacenequinones (**1**—**5**) were carried out as described in the literature.[8] Reaction of 4-substituted phenols with 6-chloro-5,12-naphthacenequinone in DMF in the presence of K_2CO_3 gave **1**—**5**-*para* in 36—54% yields after chromatographic purification and recrystallization.

Photoreactions were carried out in toluene (1 x 10^{-4} mol dm^{-3}) at ambient temperature by 366-nm light of a high pressure mercury lamp and 505-nm light from a xenon lamp. Change in component concentration as the function of irradiation time was monitored by a high pressure liquid chromatography (HPLC) and a UV-vis spectrometer, and was analyzed to give molar absorption coefficients and quantum yields of photoreactions.[9] As the typical spectral changes, those between 6-(4-acetoxyphenoxy)-5,12-naphthacenequinone (**2**) and its UV-pss are shown in Fig. 1. Spectroscopic data and quantum yields of photoreactions of **1**—**5** are listed in Table 1.

The *para*-forms of **1**—**5** have an absorption maximum in the range of 394—397 nm. The molar absorption coefficient values are between 5.1 x 10^3 and 5.9 x 10^3 mol^{-1} dm^3 cm^{-1}.

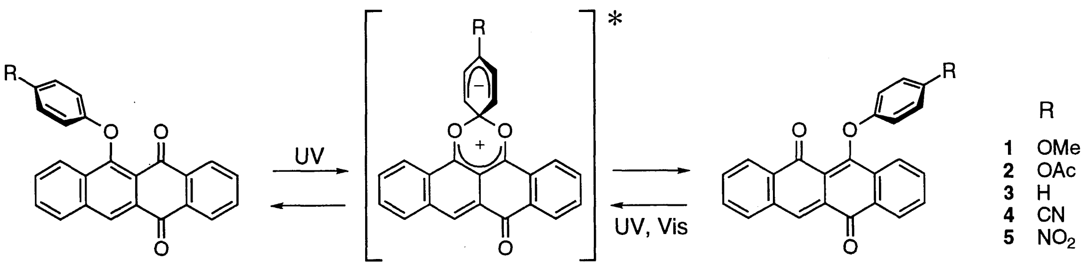
Irradiation of 366-nm light to the *para*-form solutions resulted in the formation of the *ana*-forms with the ratio of *para*/*ana* in the range of 12/88—28/72. The *ana*-forms have two large absorption maxima at 449—450 nm area (ε: 14.6—16.9 x 10^3) and 478—479 nm area (ε: 14.8—17.1 x 10^3) as well as two shoulder peaks in the shorter-wavelength regions. Irradiation of 505-nm light to the UV-pss solution afforded the *para*-form solution. That the photoreaction involves only the *para*- and *ana*-forms is proved by the isosbestic points appeared on the spectra.

The absorption maximum wavelengths and the molar absorption coefficients of both *para*- and *ana*-forms are affected little by the electronic properties of substituents on the phenoxy group. This is because the electronic effects of the substituent are buffered by the oxygen atom between the naphthacenequinone and the phenyl group. Results of ZINDO calculation[10] of **1**—**5** for the AM1-optimized structures[11] are also shown in Table 1.

As a whole, the quantum yields of photoreactions are larger for the compounds with the stronger electron-withdrawing groups, except for the nitro-substituted **5**. This can be explained that the electron-donating groups destabilize the well accepted[5] (but not experimentally confirmed) $\pi\pi^*$-excited zwitter-ionic common intermediate **6** between the *para*- and *ana*-forms. The reason of the smallness of the quantum yields of **5** is not clear.

The coloring quantum yields of UV-light irradiation are not affected largely except for the methoxy-substituted compound. The strongly electron-donating methoxy group destabilizes the zwitter-ionic intermediate **6** more than other compounds.

In summary, five thermally irreversible photochromic 6-(4-substituted)aryloxy-5,12-naphthacenequinones were synthesized and their spectroscopic and photochromic properties were measured. The quantum yields of fading photoreactions by visible-light irradiation were reported for the first time. The quantum yields of photoreactions are generally larger for those



Para-form **6** *Ana*-form

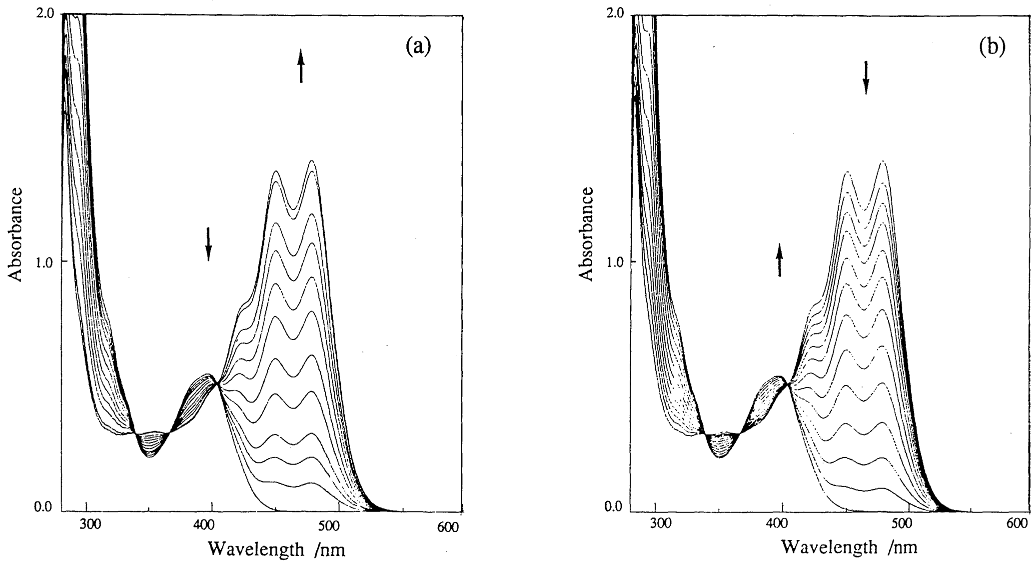


Figure 1. Change of absorption spectra of **2** in toluene.
(a) Irradiation of 366-nm light to *para*-form (0.950 x 10^{-4} mol dm^{-3}. light intensity: 0.57 mW cm^{-2}. irradiation time/min: 0, 0.5, 1, 1.5, 2.5, 3.5, 5, 6.5, 8.5, 11, 20, 45 (pss)). (b) Irradiation of 505-nm light to the UV-pss solution (light intensity: 1.12 mW cm^{-2}. irradiation time/min: 0, 1, 1.5, 3, 4.5, 6, 8, 10.5, 13.5, 17.5, 22.5, 30, 90).

Table 1. Absorption spectroscopic properties and quantum yields of photoreactions of naphthacenequinones **1**—**5** in toluene

	R	λ_{max}/nm (ε_{max}/(10^3 mol^{-1} dm^3 cm^{-1})) *Para*-form	*Ana*-form		ZINDO λ_{max} of *Ana*-form/nm	*Para*/*Ana* at UV-pss	UV irradiation $\Phi_{PA(366)}$	$\Phi_{AP(366)}$	Vis irradiation $\Phi_{AP(505)}$
1	OMe	394 (5.6)	449 (15.9)	479 (15.6)	404	28/72	0.07	0.035	0.035
2	OAc	396 (5.8)	450 (16.2)	478 (16.6)	403	12/88	0.28	0.035	0.039
3	H	397 (5.9)	450 (16.5)	479 (16.5)	405	12/88	0.34	0.048	0.049
4	CN	394 (5.1)	450 (14.6)	479 (14.8)	404	19/81	0.26	0.055	0.075
5	NO_2	394 (5.9)	450 (16.9)	479 (17.1)	409	16/84	0.20	0.035	0.040

with stronger electron-withdrawing groups on the phenyl group. Absorption spectra were merely influenced by the substituents.

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