

## Synthesis and photochromism in solution of phenoxynaphthacenequinone derivatives

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### Abstract

Two new phenoxynaphthacenequinone derivatives, 6-[4-(2-(4-hydroxyphenyl)isopropyl)phenoxy]-5,12-naphthacenequinone (7) and 6-[4-(potassium sulfophenylazo)phenoxy]-5,12-naphthacenequinone (8), were synthesized, and their photochromism in solution was investigated and compared with that of 6-phenoxy-5,12-naphthacenequinone (1). On the basis of the spectral data and the selective irreversible reaction of ammonia with the colored phenoxy-ana-naphthacenequinone, the concentrations of the ana forms at the photostationary state (PSS), achieved by 365 nm UV irradiation, and the molar extinction coefficients of the pure ana forms at 481–482 nm of compounds 1, 7 and 8 in dimethylsulfoxide (DMSO) were found to be 83 mol.% and  $1.70 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ , 82 mol.% and  $1.62 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  and 16 mol.% and approximately  $1.34 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  respectively; the absorption spectra of the colored ana forms of 7 and 1 in DMSO were estimated; the rate constants of photoconversion induced by 365 nm light were obtained. The results show the strong effect of the structure of the phenoxynaphthacenequinones on their photochromism in solution. In addition to DMSO solution, compound 7 exhibited normal photochromism in toluene, benzene, chloroform and a DMSO–ethanol mixed solvent, but not in dimethylformamide (DMF) in which a photoinduced reaction occurred between 7 and DMF or impurities.

**Keywords:** Photochromism; Phenoxynaphthacenequinone derivative

### 1. Introduction

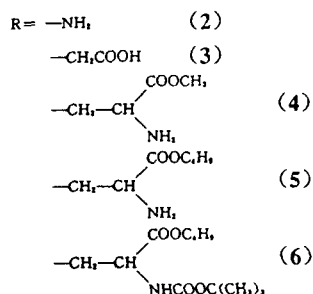
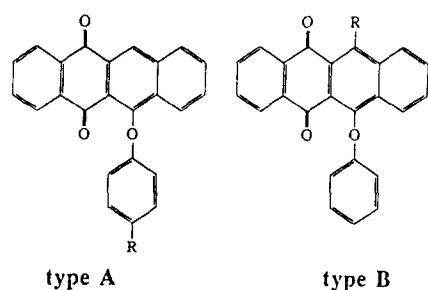
In recent years, work on organic photochromic compounds and polymers as storage media has received considerable attention in view of their high resolution and large storage capacity [1–5]. The possibility of employing photochromic 6-phenoxy-5,12-naphthacenequinone (1) and polymers with phenoxynaphthacenequinone side groups as materials for holographic recording has been explored [6,7]. The photochromism of 1 and its derivatives is based on the photoinduced interconversion of the yellow *trans*-quinone form into the orange-colored ana-quinone [6]. Generally, the photostationary state (PSS) achieved by UV irradiation at up to about 405 nm contains mainly the ana form, whereas irradiation with light above about 460 nm,

where only the ana form absorbs, results in complete photoconversion to the *trans* form [7]. The important features of these materials are their relatively low fatigue and negligible thermal ana to *trans* form reaction. Another important feature is that the hologram obtained by UV irradiation can be fixed by storing in  $\text{NH}_3$  vapor over ammonia solution, which converts the ana form into the stable amino-ana-naphthacenequinone [7].

Several derivatives of 1 have been synthesized (Scheme 1). It was found that the type A derivatives (compounds 2–6) showed normal photochromism, while type B derivatives were only slightly photochromic [7]. Furthermore, the molar extinction coefficients  $\epsilon_{\text{ana}}$  at 470 nm and  $\epsilon_{\text{trans}}$  at 398 nm of 6 in ether solution were found to be  $5.1 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  and  $1.85 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  respectively, only about one-third of the values reported by Gerasimenko et al. [8].

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## Derivatives of 1 in Literature[7]



Scheme 1.

In this study, we synthesized two new type A derivatives, 6-[4-(2-(4-hydroxyphenyl)isopropyl)phenoxy]-5,12-naphthacenequinone (7) and 6-[4-(potassium sulfophenylazo)phenoxy]-5,12-naphthacenequinone (8); their photochromism in solution was investigated in detail and compared with that of 1.

## 2. Experimental details

### 2.1. Chemicals

4,4'-Isopropylidenediphenol (bisphenol-A) was recrystallized from dilute acetic acid. Dimethylformamide (DMF) was dried over  $\text{CaH}_2$  and distilled. Other solvents and chemicals, such as ammonia aqueous solution (25 wt.%), were of analytical grade and used without further purification.

### 2.2. Measurements

IR spectra were recorded on an ALPHA CENTAURI spectrometer (KBr pellet). Measurements of proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were made in  $\text{CDCl}_3$  (using tetramethylsilane as internal standard) or dimethylsulfoxide- $d_6$  ( $\text{DMSO}-d_6$ ) (using the solvent peak at 2.62 ppm as reference) with a JEOL FX-100 NMR spectrometer.

For photoisomerization experiments, a quartz cell (path length, 1 cm) containing the sample solution ( $C = 1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ), which was kept in the dark for about 1 week at room temperature (unless stated

otherwise), was irradiated using a 250 W high-pressure mercury lamp with a light filter which transmitted the 365 nm spectral line of the lamp. The cell was set in a temperature-controlled holder circulated with water (approximately 20 °C). The distance between the centers of the cell and the lamp was 7.5 cm. Absorption spectra were recorded on a Shimadzu UV-3000 spectrophotometer at room temperature.

## 3. Results and discussion

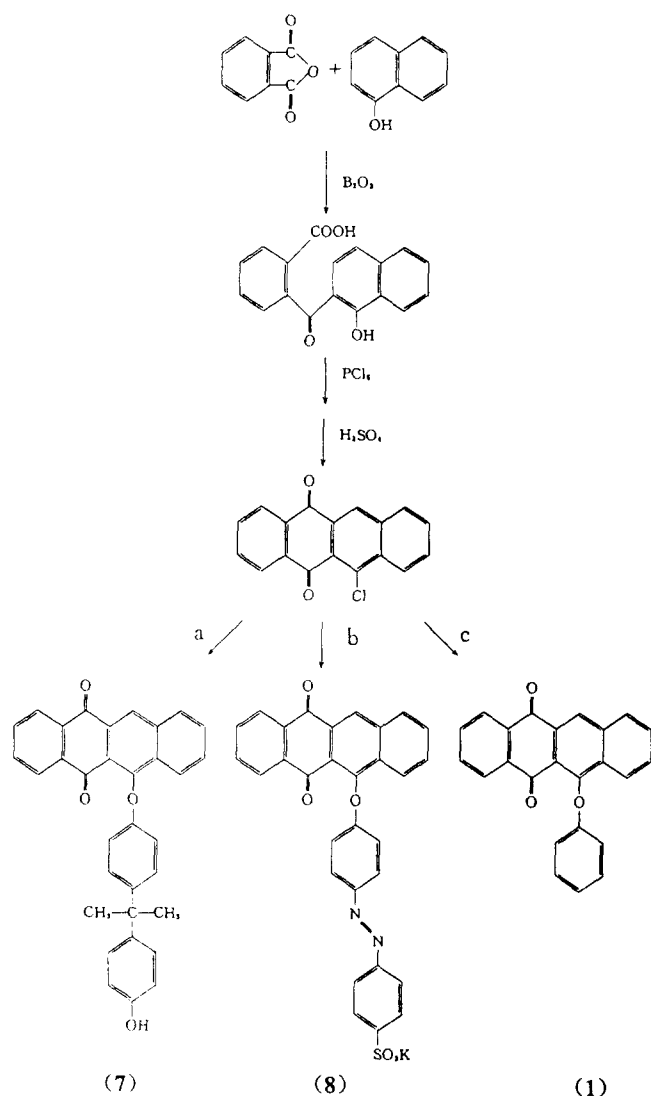
### 3.1. Synthesis

The preparation procedure of 6-phenoxy-5,12-naphthacenequinone (1) and its two new derivatives is given in Scheme 2.

6-Chloro-5,12-naphthacenequinone was synthesized and purified according to the method described by Buchholtz et al. [9], starting from phthalic anhydride and naphthol.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.70–7.86 (m, 4 H), 8.03–8.13 (m, 1 H), 8.27–8.40 (m, 2 H), 8.63–8.73 (m, 1 H), 8.84 (s, 1 H). IR,  $\lambda_{\text{max}}$ : 1679, 1579, 1412, 1384, 1335, 1270, 1210, 983, 857, 748, 712  $\text{cm}^{-1}$ . 4-Hydroxy-4'-(sulfophenyl)azobenzene was obtained by standard diazo reaction with high yield, and the crude product was purified by recrystallization from ethanol–water (2 : 1, v/v) mixed solvent. Melting point (m.p.), 256 °C; IR,  $\lambda_{\text{max}}$ : 1594, 1200, 1122, 1039, 848, 711, 628  $\text{cm}^{-1}$ .

The synthesis of 6-[4-(2-(4-hydroxyphenyl)isopropyl)phenoxy]-5,12-naphthacenequinone (7) was carried out as follows. A mixture of 6-chloro-5,12-naphthacenequinone (6.0 g, 0.021 mol), bisphenol-A (9.6 g, 0.042 mol) and potassium carbonate (7.5 g, 0.054 mol) in dry DMF (120 ml) was heated at 110 °C for 3 h. It was then poured over potassium carbonate aqueous solution. The precipitate was filtered, extracted with potassium hydroxide aqueous solution to remove the excess bisphenol-A, rinsed with water, dried in vacuum and recrystallized from xylene. Yield: 7.1 g (70%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.60 (s, 6 H), 6.65–6.79 (m, 4 H), 7.04–7.14 (m, 4 H), 7.62–7.80 (m, 4 H), 8.08–8.39 (m, 4 H), 8.83 (s, 1 H). IR,  $\lambda_{\text{max}}$ : 2968, 1674, 1582, 1507, 1427, 1398, 1343, 1274, 1216, 1177, 986, 830, 755, 717  $\text{cm}^{-1}$ .

For the synthesis of 6-[4-(potassium sulfophenylazo)phenoxy]-5,12-naphthacenequinone (8), a mixture of 6-chloro-5,12-naphthacenequinone (2.0 g, 0.007 mol), 4-hydroxy-4'-(sulfophenyl)azobenzene (2.3 g, 0.0084 mol) and potassium carbonate (2.4 g, 0.018 mol) in 30 ml dry DMF was heated at 110 °C for 3 h. It was poured over potassium hydroxide aqueous solution (0.5 mol  $\text{dm}^{-3}$ ). The precipitate was successively soaked with KOH aqueous solution (0.5 mol  $\text{dm}^{-3}$ ), water and hot xylene several times. The product was further



- a: bisphenol-A  
 b: 4-hydroxy-4'-(sulfophenyl)azobenzene  
 c: phenol

Scheme 2.

recrystallized from DMSO–H<sub>2</sub>O (2 : 1, v/v) mixed solvent and dried in vacuum at approximately 50 °C. Yield: 2.2 g (65%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 7.14–7.23 (d, 2 H), 7.85–8.02 (m, 10 H), 8.15–8.58 (m, 4 H), 9.00 (s, 1 H). IR, λ<sub>max</sub>: 1675, 1595, 1492, 1429, 1397, 1344, 1276, 1230, 1122, 1035, 848, 711, 628 cm<sup>-1</sup>.

Compound 1 was synthesized using a similar procedure. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.83–7.07 (m, 3 H), 7.20–7.35 (m, 2 H), 7.61–7.79 (m, 4 H), 8.09–8.38 (m, 4 H), 8.86 (s, 1 H). IR, λ<sub>max</sub>: 1675, 1582, 1488, 1429, 1397, 1344, 1275, 1211, 984, 752, 716 cm<sup>-1</sup>.

### 3.2. Photochromic phenomena in DMSO

The new photochromic compound 7 is readily dissolved in DMSO, DMF, tetrahydrofuran (THF) and

CHCl<sub>3</sub>, sparingly soluble in benzene and toluene and insoluble in less polar solvents, such as carbon tetrachloride. DMSO and DMF are two good solvents for the new compound 8. For comparison, the photochromism of 7, 8 and 1 was studied in the same solvent, DMSO.

Fig. 1 shows the photoinduced spectral changes of a DMSO solution of 7 on irradiation with light at 365 nm. The color of the solution turned from yellow to orange. The absorbance at about 290 nm decreased markedly during irradiation and a characteristic double peak at 454 and 482 nm appeared with isosbestic points at 340, 364 and 404 nm. This photochromic behavior is similar to that observed by Zelichenok et al. [7] for a methyl-*tert*-butyl ether solution of 6. The DMSO solution of 1 exhibited similar spectral changes on UV irradiation, in which the isosbestic points were observed at 338, 368 and 405 nm, and the double peak appeared at 453 and 481 nm. As shown in Fig. 2, the PSS for 1 was achieved with only 2 min of UV irradiation, whereas 5 min was required for 7 to reach its PSS under the same experimental conditions. However, an apparent decrease in absorbance at the double peak was observed on prolonged UV irradiation of 1.

The dichromogenic compound 8 structurally contains both azobenzene and phenoxynaphthacenequinone photochromes. Its absorption spectrum before exposure to UV light exhibited two peaks in the UV region as shown in Fig. 3. Compared with the spectrum of 7 in Fig. 1, the peak at 293 nm is attributed to the *trans*-*p*-quinone form of the phenoxynaphthacenequinone photochrome, whereas the intense absorption at 352

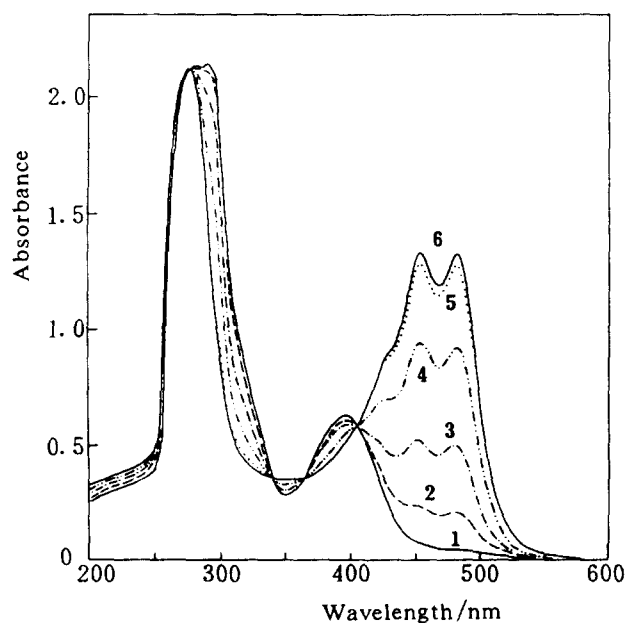


Fig. 1. Spectral change of 7 in DMSO ( $1 \times 10^{-4}$  mol dm<sup>-3</sup>) due to light irradiation ( $\lambda = 365$  nm). Irradiation time (min): curve 1, 0; curve 2, 0.17; curve 3, 0.5; curve 4, 1.5; curve 5, 3.5; curve 6, 5.0.

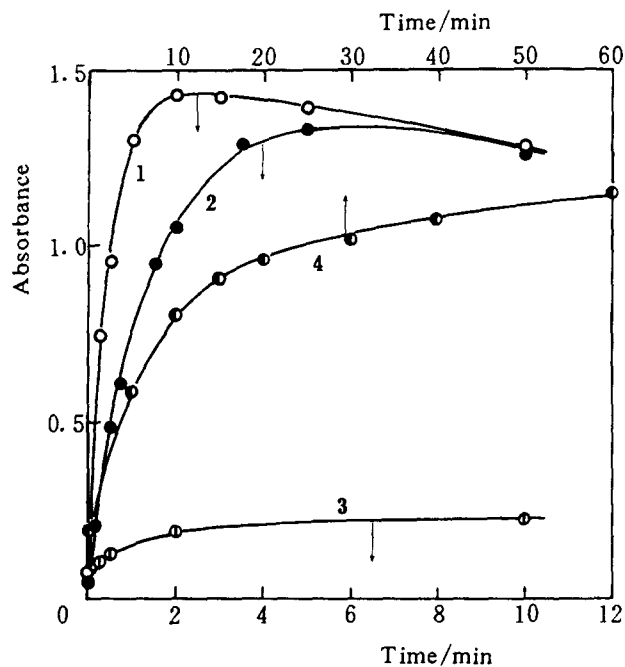


Fig. 2. Variation of the absorbance with irradiation time: curve 1, compound 1 in DMSO at 481 nm; curve 2, compound 7 in DMSO at 482 nm; curve 3, compound 8 in DMSO at 481 nm; curve 4, after addition of ammonia solution to a DMSO solution of compound 8 ( $1 \times 10^{-4}$  mol dm $^{-3}$ ) irradiated for 5 min. NH $_3$ ·H $_2$ O–DMSO, 1:5 (v/v).

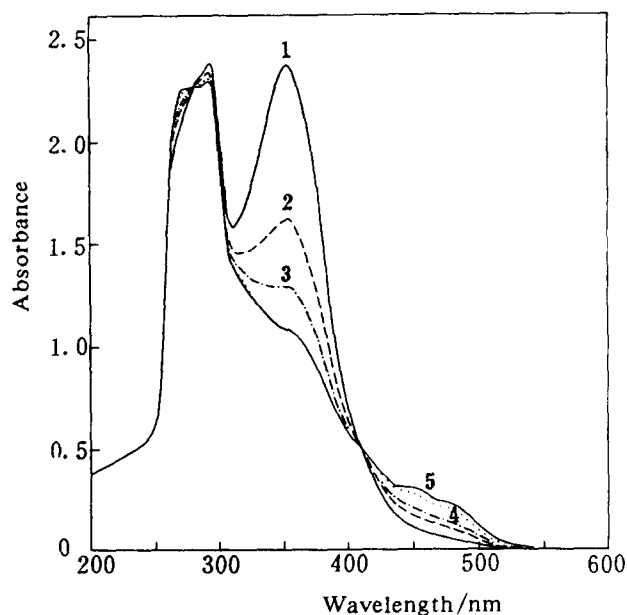


Fig. 3. Spectral change of 8 in DMSO irradiated with 365 nm UV light. Irradiation time (min): curve 1, 0; curve 2, 0.25; curve 3, 0.5; curve 4, 2.0; curve 5, 5.0 or 10.0.

nm is due to the  $\pi$ – $\pi^*$  transition of the *trans*-azobenzene isomer [2]. On irradiation with UV light, the absorbance at 352 nm decreased markedly and reached its equilibrium value within only 2 min, whereas the absorption peak at 293 nm decreased slightly and there was a small increase in the absorbance in the wavelength

region 430–500 nm. Two isosbestic points were found at 271 and 410 nm. The different spectral changes of 8 on UV irradiation indicate the effect of the substituents on photochromism.

### 3.3. Molar extinction coefficients and absorption spectra of the ana forms

The spectrum of a DMSO solution of 7 (kept in the dark for 1 week) before irradiation (Fig. 1, curve 1) showed little absorption at 482 nm and represented the spectrum of the pure *trans* form. From the known molar concentration, the molar extinction coefficients at 291 and 396 nm of the *trans* form of 7 in DMSO can thus be calculated (see Table 1).

In order to obtain the molar extinction coefficient and absorption spectrum of the ana form, we must estimate the molar content of the ana form at the PSS. Gerasimenko et al. [8] and Zelichenok et al. [7] used the selective irreversible reaction of amines with a phenoxy-ana-naphthacenequinone, leading to a stable amino-ana-naphthacenequinone. However, they obtained results with large discrepancies. We also employed this method to estimate the molar extinction coefficients and absorption spectra of the ana forms of 7 and 8. Because of the mutual solubility of DMSO and water, we used an ammonia aqueous solution as the reagent instead of an organic amine.

Fig. 4 shows the absorption spectra of 7 before and after the reaction of the phenoxy-ana-naphthacenequinone with ammonia. After addition of ammonia solution to the DMSO solution at the PSS, the double peak at 454 and 482 nm, characteristic of the ana form, disappeared and a new broad peak at  $\lambda_{\max} = 500$ –540

Table 1  
Spectral properties of photochromic phenoxynaphthacenequinones in DMSO

Compound	Form	Wavelength maxima (nm)	Extinction coefficient (mol $^{-1}$ dm $^3$ cm $^{-1}$ )
1	Trans	292	$2.26 \times 10^4$
		396	$6.10 \times 10^3$
7	Ana	273	$2.25 \times 10^4$
		453	$1.72 \times 10^4$
		481	$1.70 \times 10^4$
		482	$1.62 \times 10^4$
7	Trans	291	$2.14 \times 10^4$
		396	$6.25 \times 10^3$
8	Ana	276	$2.12 \times 10^4$
		453	$1.62 \times 10^4$
		482	$1.62 \times 10^4$
		481	$1.62 \times 10^4$
8	Trans	293	$2.38 \times 10^4$
		352*	$2.37 \times 10^4$ *
8	Ana	481	$1.34 \times 10^4$

\* Attributed to the *trans*-azobenzene units.

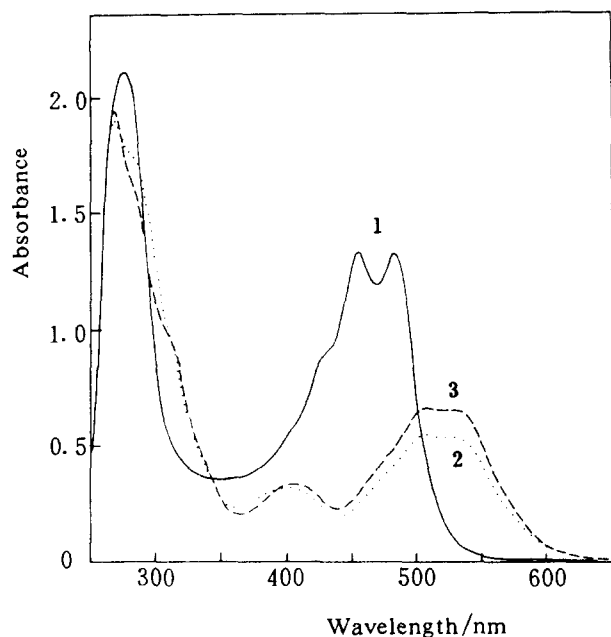


Fig. 4. Reaction of the ana form of compound 7 with  $\text{NH}_3$ ; curve 1, photostationary state (PSS) achieved by 5 min UV irradiation at 365 nm; curve 2, about 10 min after addition of  $\text{NH}_3$  solution to the PSS solution,  $\text{NH}_3\cdot\text{H}_2\text{O}$ -DMSO, 1 : 5 (v/v); curve 3, as curve 2 following a further 5 min of UV irradiation.

nm was formed (curve 2), due to the formation of the amino-ana-naphthacenequinone. A further 5 min UV irradiation of the ammonia-containing solution converted the remaining trans form at the PSS into the ana form, which reacted in turn with the excess ammonia, resulting in an increase in the absorbance of the new peak at 500–540 nm (Fig. 4, curve 3). There was no additional increase in absorbance of the new peak after another 5 min of irradiation, indicating that the reaction of phenoxy-*trans*-naphthacenequinone  $\rightarrow$  phenoxy-ana-naphthacenequinone  $\rightarrow$  amino-ana-naphthacenequinone had reached completion. The ratio of the absorbances of curves 2 and 3 at approximately 540 nm corresponds to the mole fraction of the converted ana form at the PSS. The estimated value was 82 mol.% for 7 in DMSO, which is almost the same as that (83 mol.%) of 6 in an ether solution on 405 nm irradiation [7].

Based on the estimated molar fraction of the ana form at the PSS and the difference between the absorbances of the trans solution (Fig. 1, curve 1) and the PSS solution (Fig. 1, curve 6), the absorption spectrum of the colored ana species of 7 in DMSO was obtained (Fig. 5, curve 1).

Fig. 6 shows the absorption spectra of 1 before and after reaction with ammonia, as well as the spectrum of its trans species. The concentration of the ana form at the PSS was found to be 83 mol.%. The estimated spectrum of the ana form of 1 in DMSO is given in Fig. 5 (curve 2).

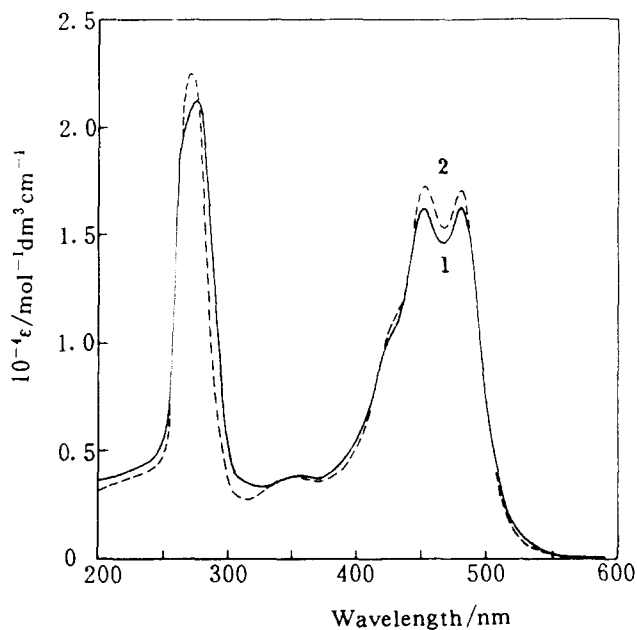


Fig. 5. Estimated absorption spectra of colored ana species: curve 1, compound 7 in DMSO; curve 2, compound 1 in DMSO.

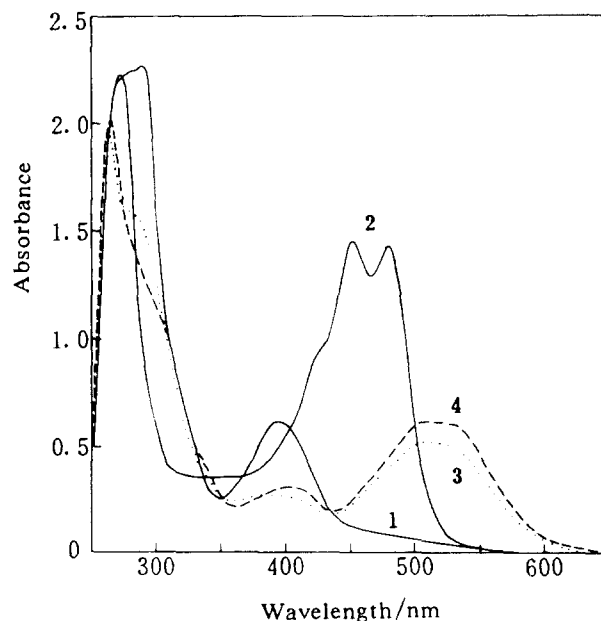


Fig. 6. Reaction of the ana species of compound 1 with  $\text{NH}_3$ ; curve 1, spectrum of the trans form; curve 2, following 3 min 365 nm irradiation to the PSS; curve 3, about 10 min after addition of  $\text{NH}_3$  solution to the PSS solution,  $\text{NH}_3\cdot\text{H}_2\text{O}$ -DMSO, 1 : 5 (v/v); curve 4, as curve 3 following a further 3 min of irradiation.

The two spectra of the colored ana forms of 1 and 7 are almost the same. From Fig. 5, the molar extinction coefficients of the ana forms of 1 and 7 were obtained (see Table 1).

The reaction behavior of compound 8 with ammonia was quite different from that of 1 and 7. As shown in Fig. 7, a much longer UV irradiation time (60 min) was required to complete the reaction. The absorbance

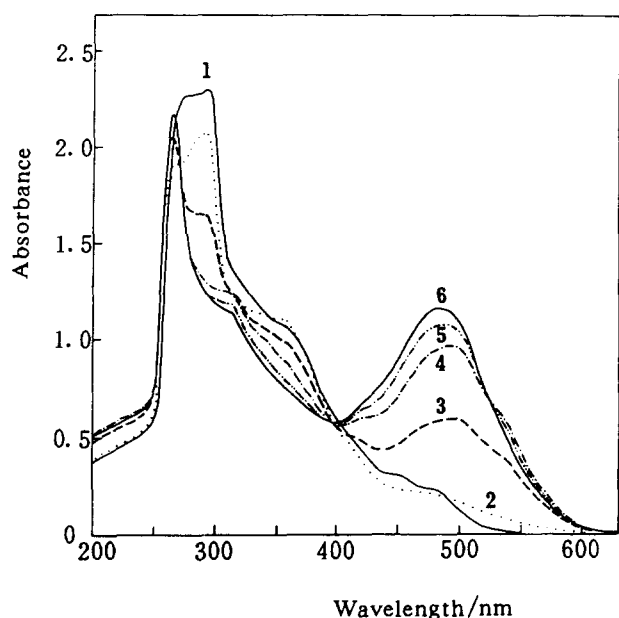


Fig. 7. Photoinduced reaction of compound 8 with  $\text{NH}_3$ : curve 1, DMSO solution ( $C=1 \times 10^{-4} \text{ mol dm}^{-3}$ ) after 5 min 365 nm UV irradiation to achieve the PSS; curve 2, about 10 min after addition of  $\text{NH}_3$  solution to that of curve 1,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ -DMSO, 1:5 (v/v); curves 3–6, as curve 2 following further UV irradiation (time (min): curve 3, 5; curve 4, 20; curve 5, 40; curve 6, 60).

change of the ammonia-containing solution at 485 nm as a function of the irradiation time is shown in Fig. 2 (curve 4). According to the ratio of the absorbances at 485 nm of curves 2 and 6 in Fig. 7, the PSS concentration of the ana form was estimated to be only 16 mol.%. This lower value is consistent with the small decrease in the absorbance at 293 nm of the DMSO solution on UV irradiation as shown in Fig. 3. Thus the molar extinction coefficient at 481 nm was estimated to be approximately  $1.34 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ . Because of the lower PSS concentration of the ana form and the complexity of the dichromogenic structure, we could not estimate accurately the whole absorption spectrum of the colored species of compound 8.

### 3.4. $\text{Trans} \rightleftharpoons \text{ana}$ rate constants on 365 nm UV irradiation

On UV irradiation, both the  $\text{trans} \rightarrow \text{ana}$  isomerization and the reverse  $\text{ana} \rightarrow \text{trans}$  reaction take place, resulting in a PSS



where  $k_t$  and  $k_a$  are the rate constants on UV irradiation for the  $\text{trans} \rightarrow \text{ana}$  and  $\text{ana} \rightarrow \text{trans}$  reactions respectively. At the PSS, we have

$$k_t[\text{T}]_p = k_a[\text{A}]_a \quad (2)$$

where  $[\text{T}]_p$  and  $[\text{A}]_p$  are the concentrations at the PSS of the  $\text{trans}$  form and  $\text{ana}$  form respectively.

Let  $A_a$  be the absorbance of the pure  $\text{ana}$  form and  $A_0$  and  $A$  be the absorbances before irradiation and after irradiation for a certain time respectively. Fig. 8 shows that the  $\text{trans} \rightarrow \text{ana}$  reactions obey first-order kinetics in the initial stage. The rate constants under the experimental conditions mentioned above are listed in Table 2.

Since the colored  $\text{ana}$  species immediately disappeared in the presence of ammonia, the results shown in Fig. 7 can also be used to determine the  $\text{trans} \rightarrow \text{ana}$  rate constant of 8. The data fit first-order kinetics over a much longer time range (Fig. 8, curve 4), and the rate constant obtained is in agreement with that from curve 3.

According to Eq. (2) and the concentration of the  $\text{ana}$  form at the PSS, the  $\text{ana} \rightarrow \text{trans}$  rate constants

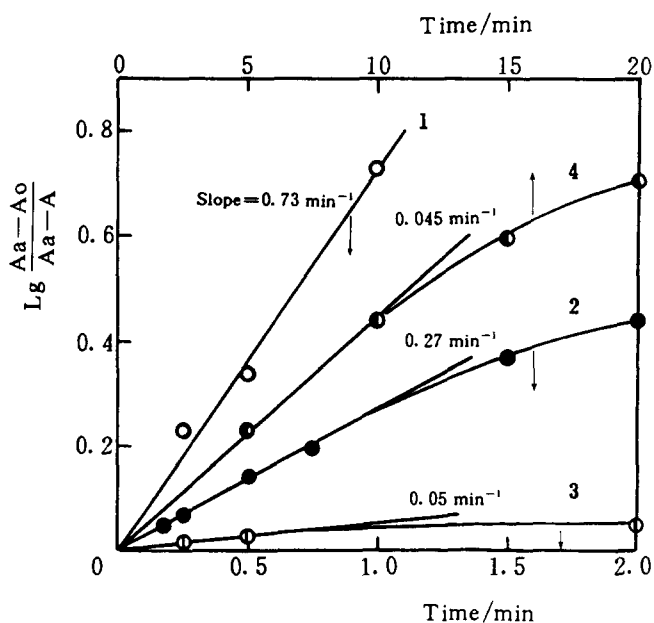


Fig. 8. First-order plots of  $\text{trans} \rightarrow \text{ana}$  reactions induced by 365 nm UV light: 1, compound 1 (absorbance at 481 nm); 2, compound 7 (absorbance at 482 nm); 3, compound 8 (absorbance at 481 nm); 4, compound 8 (irradiation was carried out after addition of  $\text{NH}_3$  solution to the PSS solution, absorbance at 485 nm,  $A_0=0.19$ ,  $A_a=1.15$ ).

Table 2  
Rate constants of photoconversion in DMSO induced by 365 nm light \*

Compound	$k$ ( $\text{min}^{-1}$ )	
	$\text{Trans} \rightarrow \text{ana}$	$\text{Ana} \rightarrow \text{trans}$
1	0.73	0.15
7	0.27	0.06
8	0.05	0.26

\* Under the conditions mentioned in Section 2.

on 365 nm irradiation were also calculated (see Table 2).

The results mentioned above indicate that the nature of the substituent in the type A derivatives (Scheme 1) has a strong effect on the photochromic behavior of the phenoxynaphthacenequinones.

### 3.5. Solvent effect on the photoinduced isomerization of 7

Figs. 9 and 10 show the absorption spectra of 7 in different solvents before and after UV irradiation. Normal photochromism of 7 was observed in toluene, benzene,  $\text{CHCl}_3$  and DMSO–ethanol mixed solvent, although there were some spectral differences in the 200–290 nm UV region. Tajima et al. [10] found that 1-phenoxy-anthraquinone did not exhibit photochromism in ethanol and that the absorption of its colored species in benzene immediately disappeared on addition of one drop of ethanol. This is due to the reaction between the colored species and ethanol. The normal photochromism of 7 in DMSO–ethanol mixed solvent indicates that the colored ana species of 7 is stable in the presence of ethanol.

As shown in Fig. 10, a freshly prepared solution of 7 in DMF exhibits the normal spectrum of the trans form before UV irradiation, and a spectral change after UV irradiation. However, the double peak, characteristic of the ana form, is not observed; instead a red-shifted peak at 524 nm is found. When the DMF solution was

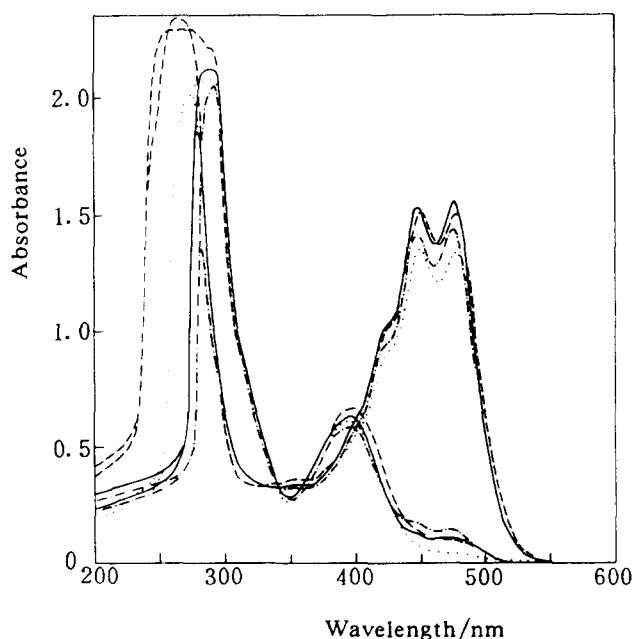


Fig. 9. Absorption spectra of 7 in different solvents before and after 365 nm UV irradiation ( $C=1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ): —, in benzene; ---, in toluene; ···, in DMSO–ethanol (3:1, v/v) mixed solvent; -·-, in  $\text{CHCl}_3$ .

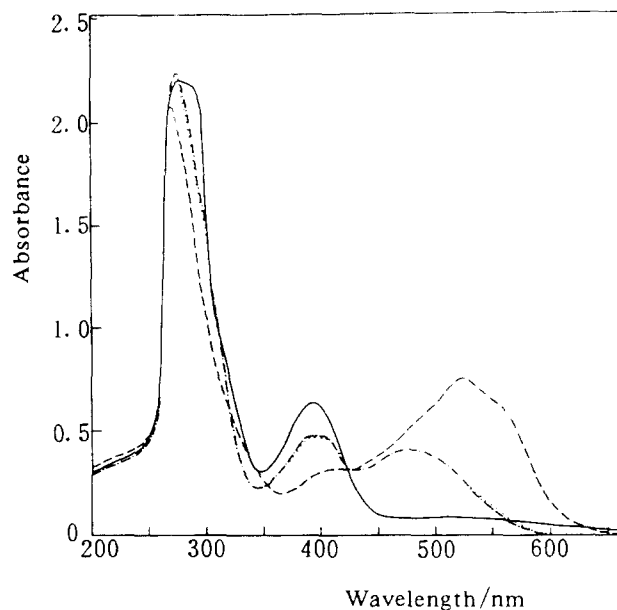


Fig. 10. Absorption spectra of 7 in DMF ( $C=1 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ): —, freshly prepared solution (0.5 h after sample dissolution), before irradiation; ---, the above solution following 5 min irradiation with 365 nm light; -·-, solution kept in the dark for 1 week, before UV irradiation; ···, the above solution following 5 min irradiation.

kept in the dark for 1 week before irradiation, there was an apparent spectral change, and the solution did not exhibit photochromism on UV irradiation. This indicates that reaction occurs between compound 7 and DMF or impurities. It is also of interest to note that the colored species formed by UV irradiation of a freshly prepared DMF solution and that formed by keeping the solution in the dark for a long time have different absorption spectra.

### Acknowledgments

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