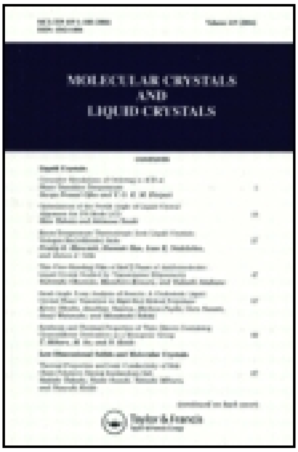

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Structure-Property Relationship of Phenoxynaphthacenequinones and their Relatives

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STRUCTURE-PROPERTY RELATIONSHIP OF PHENOXYNAPHTHACENEQUINONES AND THEIR RELATIVES

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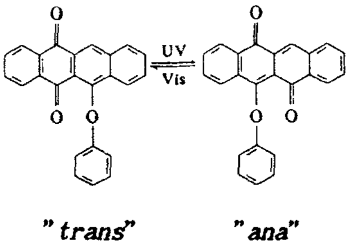
Abstract Like 6-phenoxy-5,12-naphthacenequinone (**1**), 6-[4-(2-(4-hydroxyphenyl)isopropyl)phenoxy]-5,12-naphthacenequinone (**2**) and 6-naphthyloxynaphthacenequinone (**6**) showed normal photochromism. The relative initial rates of *trans* to *ana* photoconversion were in the order: **1**, 100; **2**, 37; **6**, 21. 6-[4-(Phenylazo)phenoxy]-5,12-naphthacenequinone (**3**), 6-[4-(*p*-ethoxyphenylazo)phenoxy]-5,12-naphthacenequinone (**4**), 6-[4-(*p*-nitrophenylazo)phenoxy]-5,12-naphthacenequinone (**5**) had only slight UV-induced photochromism for the phenoxynaphthacenequinone photochrome. 6-(2-Nitrosonaphthyloxy)-5,12-naphthacenequinone (**7**) exhibited no photochromism and underwent irreversible photoreaction.

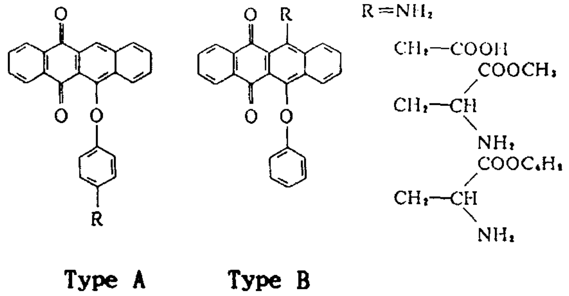
INTRODUCTION

Gerasimenko and Poteleshenko[1] first reported the photochromic phenomenon of 6-phenoxy-5,12-naphthacenequinone(**1**), which is based on photo-induced isomerization of the *trans* *p*-quinone form into the *ana* *p*-quinone form (as shown in Scheme 1). They also found[2] that several derivatives with substituent(s) on the phenyl ring, such as *p*-OH, *p*-OCH_3, *p*-NHC_6H_5, 2,4,6-trimethyl, *p*-$COCH_3$, and *p*-NO_2, had the similar photochromism, and that the longest absorption peak of the *trans* forms in toluene was at ca. 400 nm with molar extinction coefficient of ca. 6

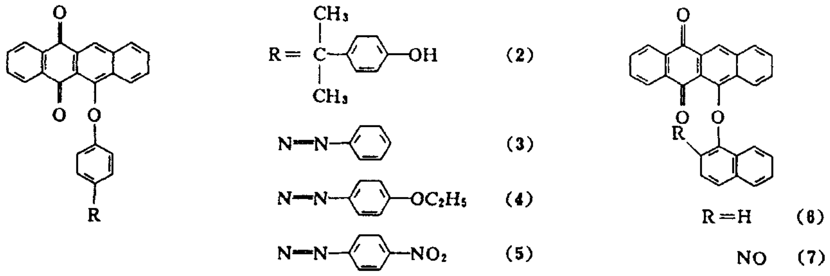
$\cdot 10^3$ mol^{-1}dm^{3}cm^{-1}, and the *ana* forms had characteristic double peaks with maximum molar extinction coefficient of ca. $1.7\cdot 10^4$ mol^{-1}dm^{3}cm^{-1} at ca. 480 nm. Zelichenok et al.[3] studied two types of phenoxynaphthacenequinone derivatives (as shown in Scheme 2) and found that all type A derivatives showed normal photochromism whereas type B compounds were only slightly photochromic. However, they failed to understand the reason why the molar extinction coefficients of a type A derivative with $R=CH_2CH(COOC_4H_9)NHCOOC(CH_3)_3$ were only one third of those reported by Gerasimenko et al. In order to shed more light on the structure-property relationship of derivatives of photochromic compound 1, several new compounds of phenoxynaphthacenequinones or naphthyloxy-naphthacenequinones were synthesized:



SCHEME 1 Photochromic isomerization of 1



SCHEME 2 Two types of phenoxynaphthacenequinone derivatives[3]



and their photochromic behaviours in solution were investigated.

EXPERIMENTAL DETAILS

Chemicals

Dimethylformide(DMF) was dried over CaH_2 and distilled. Other chemicals and solvents were of analytical grade and used as received.

Measurements

IR spectra were recorded on a BIO-RAD Infrared Spectrometer(KBr pellet). Measurements of ^1H NMR spectra were made with a JEOL Unity-400 NMR Spectrometer in $CDCl_3$ using TMS as the internal standard. UV-induce photochromic experiments were carried out as previously reported.[4] Absorption spectra were recorded on a Shimadzu UV-3000 or UV-300 spectrophotometer at room temperature.

Synthesis

6-Chloro-5,12-naphthacenequinone(**8**) and 6-[4-(2-(4-hydroxyphenyl)isopropyl)phenoxy]-5,12-naphthacenequinone(**2**) were synthesized as previously reported[4]. 4-Hydroxyazobenzene, 4-hydroxy-4'-ethoxyazobenzene, and 4-hydroxy-4'-nitroazobenzene were synthesized by standard diazo reaction, and purified by recrystallization from ethanol/water(V/V=1/1), cyclohexane/benzene(V/V=4/1) and ethanol/water(V/V=3/1), respectively.

For the synthesis of 6-[4-(phenylazo)phenoxy]-5,12-naphthacenequinone(**3**), a mixture of **8**(2.05 g, 7 mmol), 4-hydroxyazobenzene(1.67 g, 8.4 mmol), and potassium carbonate(2.40 g, 17.4 mmol) in 30 mL DMF was heated at 115 °C for 3 h. It was poured over potassium hydroxide aqueous solution(0.5 mol/L), and the resulting precipitant was washed successively with 0.5 mol/L KOH solution, 0.5 mol/L HCl solution and water, and dried under vacuum. The crude product(2.91 g) was recrystallized twice from DMSO, yield 1.88 g (59.2%). IR, λ_{max}/cm^{-1}:1669. 1582, 1491, 1428, 1398, 1346, 1278, 1236, 1139, 982, 833, 753, 714. ^1H NMR, δ/ppm: 7.01-7.05(d,2H), 7.42-7.52(m,3H), 7.67-7.73(t,1H), 7.73-7.82(m,3H), 7.82-7.88(d,2H), 7.88-7.94(d,2H), 8.15-8.21(d,1H), 8.21-8.27(d,2H), 8.34-8.39(d,1H), 8.91(s,1H).

6-[4-(*p*-Ethoxyphenylazo)phenoxy]-5,12-naphthacenequinone(**4**) was synthesized using a similar procedure. The crude product was recrystallized twice from DMSO/water(V/V=4/1) and DMSO, yield 1.45 g

(41.6%). IR, λ_{max}/cm^{-1}: 2977. 1675, 1582, 1494, 1427, 1395, 1345, 1276, 1251, 1214, 1146, 1110, 1045, 984, 919, 846,753, 715. ^{1}H NMR, δ/*ppm*: 1.43-1.47(t,3H), 4.08-4.13(m,2H), 6.95-7.02(t,4H), 7.66-7.71(t,1H), 7.74-7.79(m,3H), 7.83-7.87(q,4H), 8.16-8.19(d,1H), 8.22-8.26(m,2H), 8.35-8.38(d,1H), 8.90(s,1H).

6-[4-(*p*-Nitrophenylazo)phenoxy]-5,12-naphthacenequinone(**5**) was similarly synthesized. The crude product was recrystallized twice from DMSO, yield 44.1%. IR, λ_{max}/cm^{-1}: 1674, 1586, 1522, 1491, 1426, 1398, 1342, 1274, 1232, 1137, 1105, 984, 858, 751, 716. ^{1}H NMR, δ/*ppm*: 7.03-7.07(d,2H), 7.69-7.74(t,1H), 7.76-7.82(m,3H), 7.95-7.99(d,4H), 8.18-8.25(q,3H), 8.34-8.39(t,3H), 8.93(s,1H).

The synthesis conditions of 6-naphthyloxy-5,12-naphthacenequinone(**6**) were as follows: **8**(8 mmol), 1-naphthol(10 mmol), potassium carbonate(10 mmol), DMF(40 mL), 115 °C, 4 h; precipitation by pouring the reaction mixure to ice-water and washing with water and ethanol; recrystallization from DMF, yield 58.2%. IR, λ_{max}/cm^{-1}: 1674, 1580, 1426, 1395, 1343, 1270, 1236, 983, 762, 713. ^{1}H NMR, δ/*ppm* : 6.20-6.22(d,1H), 7.08-7.12(t,1H), 7.50-7.52(d,1H), 7.57-7.79(m,6H),

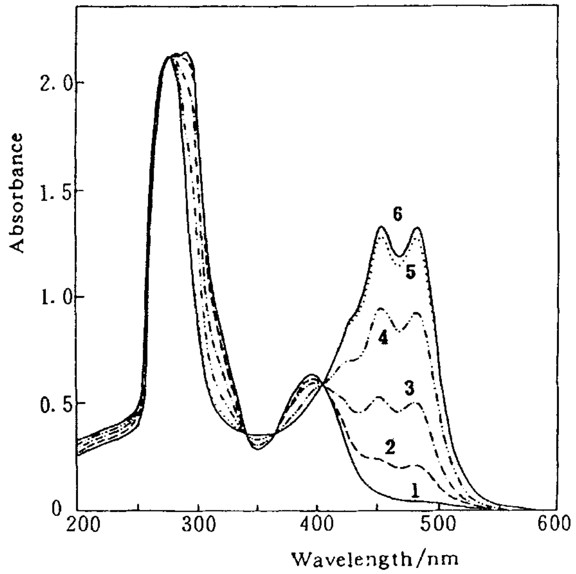


FIGURE 1 Spectral change of **2** in DMSO(1·10^{-4} mol dm^{-3}) induced by 365 nm UV light. Irradiation time/min: 1, 0; 2, 0.17; 3, 0.5; 4, 1.5; 5, 3.5; 6, 5.0

7.92-7.94(d,1H), 8.16-8.20(m,3H), 8.35-8.37(d,1H), 8.75-8.77(d,1H), 8.92(s,1H).

6-[2-nitrosonaphthyloxy]-5,12-naphthacenequinone(**7**) was similarly synthesized: **8**(8 mmol), 2-nitroso-1-naphthol(10 mmol), potassium carbonate(10 mmol), DMF(40 mL), 115 °C, 4 h; recrystallization from DMSO/water mixed solvents twice, yield 27.2%. IR, λ_{max}/cm^{-1}: 1675, 1616, 1592, 1575, 1456, 1387, 1351, 1269, 986, 752, 714. ^{1}H NMR, δ/*ppm*: 7.67-7.85(m,7H), 7.98-8.01(d,1H), 8.09-8.12(d,1H), 8.31-8.42(m,3H), 8.51-8.55(d,1H), 8.69-8.73(d,1H), 8.88(s,1H).

RESULTS AND DISCUSSION

Figure 1 shows the photoinduced spectral change of compound **2** in DMSO on irradiation with 365 nm UV light. Isosbestic points were observed at 404, 364, 340 and 275 nm; the longest absorption peak of the *trans* form

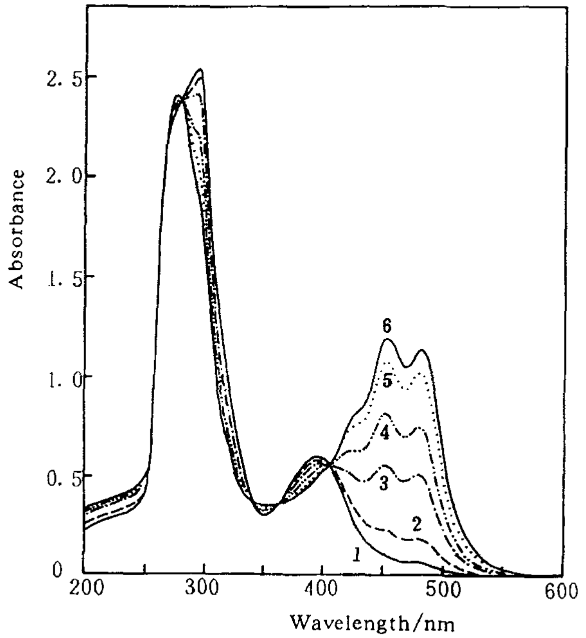


FIGURE 2 Spectral change of **6** in DMSO $(1\cdot10^{-4}$ mol dm$^{-3})$ irradiated with 365 nm light. Irradiation time/min: 1, 0; 2, 0.5; 3, 1.5; 4, 3.0; 5, 5.0; 6, 10.0

was at 396 nm, while the *ana* form has a characteristic double peak at 482 and 454 nm. Similarly, Compound **6** exhibited normal photochromism, as shown in Figure 2. Isosbestic points were found at 405, 362, 342, and 278 nm, and the *ana* form was characterized by a double peak at 483 and 454 nm. Based on the spectral data and the irreversible reaction of ammonia with the coloured *ana* forms[4], the concentrations of the *ana* form at the photostationary state(PSS) and the molar extinction coefficients of the pure *ana* forms at 482-483 nm of **2** and **6** were found to be 82% and $1.70\cdot10^4$ mol^{-1}dm^{3}cm^{-1}, and 83% and $1.36\cdot10^4$ mol^{-1}dm^{3}cm^{-1}, respectively.

As shown in Figure 3, the *trans* to *ana* photoconversion reactions obey first-order kinetics in the first stage, and the initial rate is strongly dependent on the chemical structure of the compounds. The relative initial rates of *ana* formation were in the order: 1, 100; 2, 37; 6, 21, which is in agreement with the photochromic mechanism of migration of aromatic group.

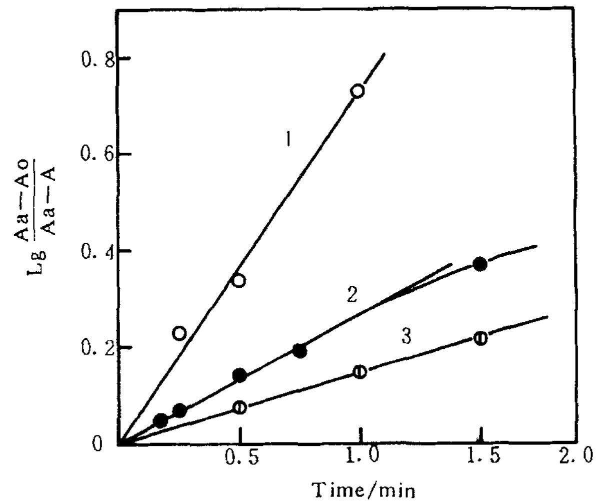


FIGURE 3 First-order plots of *trans* to *ana* reaction induced by 365 nm UV light.
1, compound **1**; 2, compound **2**; 3, compound **6**

However, all of the dichromogenic compounds containing both phenoxynaphthacenequinone and azobenzene photochromes showed only slight UV-induced photochromism for the phenoxynaphthacenequinone photochrome as shown in Figure 4. Based on the irreversible reaction of ammonia with the coloured phenoxy-*ana*-naphthacenequinone, the concentrations of the *ana* forms of compounds **3** and **4** in DMSO at PSS were estimated to be only 22 mol% and 17 mol% respectively[5]. These results are in accordance with 16 mol% obtained for another dichromogenic compound 6-[4-(potassium sulfophenylazo)phenoxy]-5,12-naphthacenequinone in the same solvent[4]. There is either electron-donating group or electron-withdrawing group on the azobenzene moiety, but the different substituents have little to do with the photochromism of phenoxynaphthacenequinone photochrome, indicating that it is the phenylazo-group which effects markedly the photochromic properties of phenoxynaphthacenequinone photochrome. These results also indicate that not all of type A phenoxynaphthacenequinone derivatives in Scheme 2 have normal photochromism.

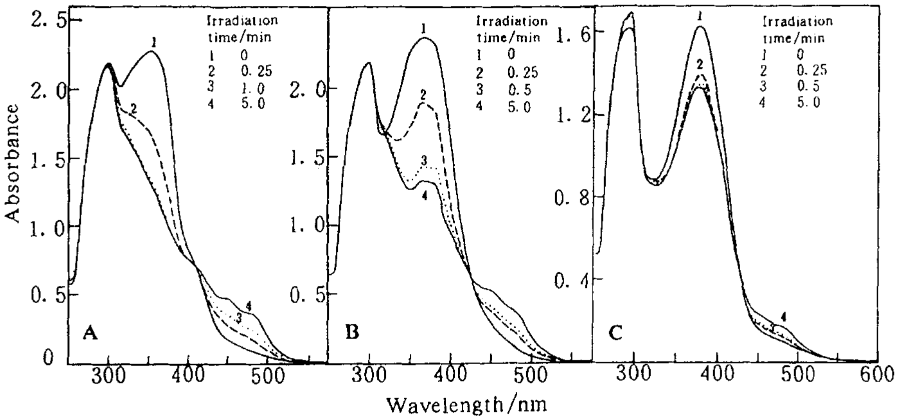


FIGURE 4 Spectral change of **3**(A, $1\cdot10^{-4}$ mol dm^{-3}), **4**(B, $1\cdot10^{-4}$ mol dm^{-3}) and **5**(C, 5·10-5 mol dm^{-3}) in DMSO irradiated with 365 nm UV light.

As can be seen in Figure 4, the intense absorption peak of *trans* azobenzene isomer at 352 - 378 nm (depending on the substituent) decreased markedly on irradiation with UV light and reached its equilibrium value very quickly. Contrary to this, there was no spectral change for 4-hydroxyazobenzene solution in DMSO on the same experimental condition. The results indicate that the *cis* isomers of azobenzene photochromes in the dichromogenic compounds were relatively stable.

Figure 5 shows the absorption spectra of compound **7** in DMSO before and after UV irradiation. It is clear that compound **7** exhibited no photochromism and underwent irreversible reactions.

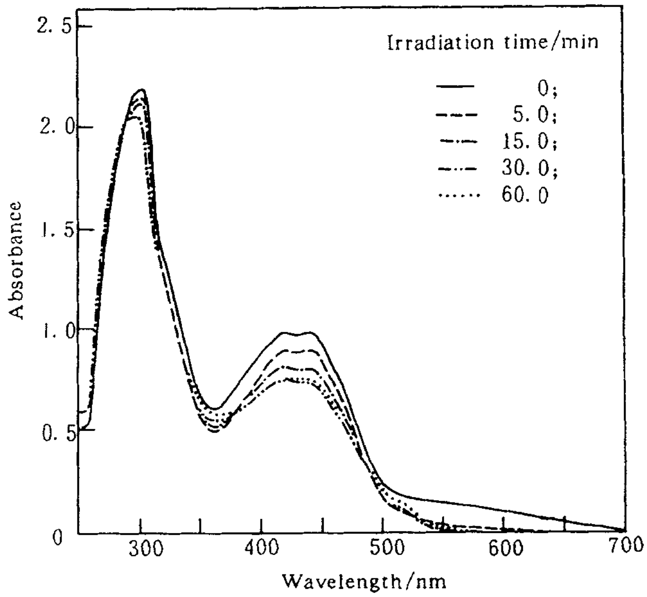


FIGURE 5 Spectral change of **7** in DMSO ($1\cdot10^{-4}$ mol dm^{-3}).

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