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Photochromic Properties of Naphthopyrans – PMMA Thin Film

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A class of naphthopyran derivatives (3a–10a) with electron-donating and electron-acceptor substituent is prepared by condensation of 1,2-diaryl-2-propyn-1-ol with β*-naphthol in the presence of pyridinium* para*-toluenesulfonate (PPTS) as catalyst. All compounds go ring-opening isomerization in polymethylmethacrylate (PMMA) matrix with UV light irradiation (30 watt) and the maximum absorption of ring-opening isomers is at the range of 426–556 nm. Ring-opening isomers are completely back to ring-closing isomers when samples are kept in darkness, the bleach rate of ring-opening isomers in PMMA film increased significantly when temperature is more than 45°C. Fatigue testing showed that no significant change of optical density was detected after 10 cycles.*

Keywords: naphthopyrans; photochromism; PMMA thin film; synthesis

INTRODUCTION

Interest in the photochromism of benzopyrans and naphthopyrans has been sparked by commercialization of photochromic plastic ophthalmic lenses and glasses in the early 1990s [1]. Benzopyrans and naphthopyrans display highly desirable photochromic properties and have thus been the subject of intense investigations aimed at developing novel materials with useful applications [2]. Although there are many publications [3–7] and patents [8–13] on benzopyrans and naphthopyrans including the synthetic methodology, photochromism, and applications, the design and synthesis of novel photochromic benzopyrans and naphthopyrans with improved properties have

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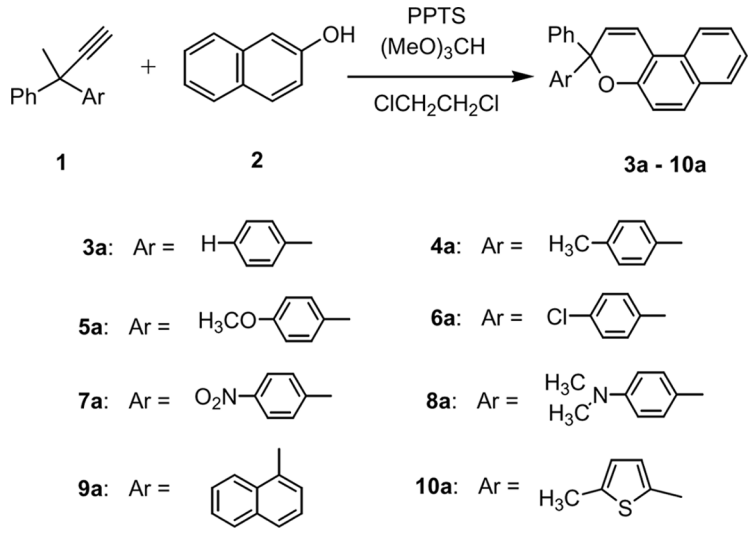
always been attracting attention because of their widespread use in photon device applications [14–16]. In general, there are three approaches to the preparation of benzopyrans and naphthopyrans: 1) the Kabbe synthesis, commences with chromanones and necessitates a multistep sequence of reactions [17,18]; 2) the reaction of aryl Grignard with benzocoumarins, followed by dehydrations [19]; and 3) the Claisen rearrangement of propargyl-aryl ethers prepared in situ from naphthol and a diaryl propargyl alcohol under acidic conditions [20–23]. Among the three methodologies, the third one is most expeditious and popular. The disadvantages of these approaches are in generality and in poor yields. Recently, E. M. Carreira, et al. reported a facile one-pot synthesis of photochromic pyrans in excellent yields with modification of reaction conditions by employing PPTS as catalyst [24,25]. In contrast to synthesis, the properties of photochromic naphthopyrans are less reported, especially in solid state. In this article, we prepared a class of naphthopyran derivatives with electron-donating and electron-acceptor substituted groups by condensation of 1,2-diaryl-2-propyn-1-ol (**1**) with β-naphthol (**2**) (Scheme 1), and we also present photochromic properties of naphthopyran derivatives in solid state (PMMA film) including the absorption bands, the rate of coloration and bleaching, and fatigue resistance. This may provide useful information for further applications of photochromic naphthopyran derivatives.



SCHEME 1 Synthesis of photochromic naphthopyran derivatives **3a–10a**.

EXPERIMENTAL

Instrumentation

^{1}H NMR spectra were recorded at 400 MHz with Tetramethylsilane (TMS) as an internal reference and $CDCl_3$ as solvent. Mass spectra (MS) were recorded with as Trio-2000 GC-MS spectrometer. UV absorption spectra were measured on an absorption spectrophotometer (Hitachi U-3010). Coloration was carried out with a UV light (Power: 30 watt, $\lambda = 254$ nm).

Chemicals

All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Compounds **3a–10a** were prepared according to the literature [**9a**], and the general procedure for the preparation of compounds **3a–10a** is as follows: treatment of 1,2-diaryl-2-propyn-1-ol (1.1 equiv) and β-naphthol (1 equiv) in 1,2-dichloroethane with 2 equivalant of $(MeO)_3CH$ and 5 mol% PPTS furnished the desired product in high yields (72–95%) except for **7a** (10%) and **8a** (18%).

3a: Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (d, 1H, $J = 8.5$ Hz), 7.72 (d, 1H, $J = 8.2$ Hz), 7.67 (d, 1H, $J = 8.8$ Hz), 7.50–7.44 (m, 5H), 7.33–7.30 (m, 6H), 7.25–7.22 (m, 2H), 7.21 (d, 1H, $J = 8.8$ Hz), 6.29 (d, 1H, $J = 9.9$ Hz). MS: m/z [M^+]: 334. Anal. Calcd for $C_{25}H_{18}O$: C, 89.80; H, 5.42. Found: C, 89.88; H, 5.40.

4a: Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (d, 1H, $J = 8.5$ Hz), 7.72 (d, 1H, $J = 8.3$ Hz), 7.66 (d, 1H, $J = 8.8$ Hz), 7.50–7.43 (m, 3H), 7.37–7.29 (m, 6H), 7.24–7.18 (m, 2H), 7.12 (d, 1H, $J = 8.1$ Hz), 6.27 (d, 2H, $J = 9.9$ Hz), 2.30 (s, 3H). MS: m/z [M^+]: 348. Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.78. Found: C, 89.58; H, 5.74.

5a: Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$ (d, 1H, $J = 8.5$ Hz), 7.72 (d, 1H, $J = 8.1$ Hz), 7.66 (d, 1H, $J = 8.8$ Hz), 7.49–7.46 (m, 3H), 7.44–7.38 (m, 2H), 7.33–7.29 (m, 4H), 7.25–7.24 (m, 1H), 7.20 (d, 1H, $J = 8.8$ Hz), 6.84 (d, 2H, $J = 8.8$ Hz), 6.25 (d, 1H, $J = 9.9$ Hz), 3.77 (s, 3H). MS: m/z [M^+]: 364. Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.72; H, 5.49.

6a: Yield: 70%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (d, 1H, $J = 8.4$ Hz), 7.73 (d, 1H, $J = 8.1$ Hz), 7.68 (d, 1H, $J = 8.8$ Hz), 7.49–7.41 (m, 5H), 7.34–7.26 (m, 7H), 7.19 (d, 1H, $J = 8.8$ Hz), 6.22 (d, 1H, $J = 9.9$ Hz). MS: m/z [M^+]: 368. Anal. Calcd for $C_{25}H_{17}ClO$: C, 81.40; H, 4.64. Found: C, 81.48; H, 4.60.

7a: Yield: 10%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (d, 2H, $J = 8.9$ Hz), 7.97 (d, 1H, $J = 8.4$ Hz), 7.74 (d, 1H, $J = 8.2$ Hz), 7.70 (d, 3H, $J = 8.9$ Hz), 7.49–7.44 (m, 3H), 7.41–7.28 (m, 5H), 7.21 (d, 1H, $J = 8.9$ Hz), 6.25 (d, 1H, $J = 9.9$ Hz). MS: m/z [M^+]: 363. Anal. Calcd for $C_{25}H_{17}NO_2$: C, 82.63; H, 4.71. Found: C, 82.58; H, 4.74.

8a: Yield: 18%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (d, 1H, $J = 8.5$ Hz), 7.71 (d, 1H, $J = 8.1$ Hz), 7.65 (d, 1H, $J = 8.8$ Hz), 7.51–7.44 (m, 3H), 7.32–7.23 (m, 8H), 7.19 (d, 1H, $J = 8.8$ Hz), 6.66 (d, 1H, $J = 8.9$ Hz), 6.25 (d, 1H, $J = 9.9$ Hz), 2.91 (s, 6H). MS: m/z [M^+]: 377. Anal. Calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14. Found: C, 86.11; H, 6.21.

9a: Yield: 78% ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.30$ (d, 1H, $J = 8.6$ Hz), 8.01 (d, 1H, $J = 8.5$ Hz), 7.81 (d, 1H, $J = 8.0$ Hz), 7.78 (d, 1H, $J = 8.2$ Hz), 7.72–7.68 (m, 2H), 7.59 (d, 1H, $J = 8.8$ Hz), 7.50–7.48 (m, 3H), 7.46–7.10 (m, 8H), 7.11 (d, 1H, $J = 8.8$ Hz), 6.26 (d, 1H, $J = 9.9$ Hz). MS: m/z [M^+]: 384. Anal. Calcd for $C_{29}H_{20}O$: C, 90.59; H, 5.24. Found: C, 90.68; H, 5.22.

10a: Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.97$ (d, 1H, $J = 8.4$ Hz), 7.73 (d, 1H, $J = 8.1$ Hz), 7.68 (d, 1H, $J = 8.8$ Hz), 7.59–7.57 (m, 2H), 7.47–7.45 (m, 1H), 7.36–7.27 (m, 5H), 7.21 (d, 1H, $J = 8.8$ Hz), 6.73 (d, 1H, $J = 3.5$ Hz), 6.54 (d, 1H, $J = 3.6$ Hz), 6.27 (d, 1H, $J = 9.9$ Hz), 2.40 (s, 3H). MS: m/z [M^+]: 354. Anal. Calcd for $C_{24}H_{18}OS$: C, 81.32; H, 5.12. Found: C, 81.40; H, 5.15.

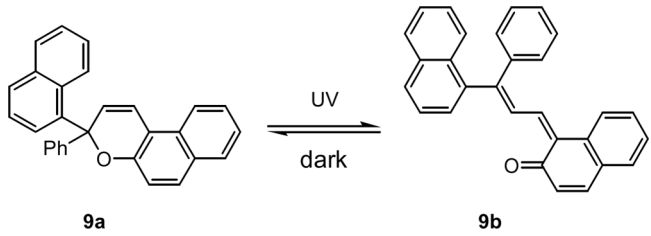
Naphthopyrans-PMMA Thin Film

Compounds **3a–10a** (2.0 mg) were dissolved in PMMA-cyclohexanone solution (10% w/w, 1.0 ml). The mixture solution was then spin-coated on a glass substrate, which was then dried in air and kept in darkness at room temperature. The thickness of the film was about 10 μm.

RESULTS AND DISCUSSION

Photochromic Properties of Naphthopyran Derivatives 3a–10a in PMMA Thin Film

Preliminary investigation showed that all compounds **3a–10a** underwent ring-opening and ring-closing photoisomerization in PMMA film. The photoisomerization of **9a** is described in Scheme 2, and absorption spectra changes are presented in Fig. 1. Before irradiation, there are three absorption bands at 360, 294, and 252 nm, respectively, which are attributed to the ring-closing isomer **9a**. Upon irradiation with UV light, a new band appeared at 428 nm, which corresponds to the



SCHEME 2 Ring-opening and ring-closing isomerization of **9a** in PMMA thin film.

ring-opening isomer **9b**, and absorption intensity increased with increasing the irradiation time until the photostationary state is reached. The process was companied by the color change of PMMA film from colorless to bright yellow. The new band at 428 nm decreased and disappeared when the sample was kept in darkness, accompanying the color change of PMMA film from bright yellow to colorless. Similar results were obtained when other compounds performed ring-closing and ring-opening isomerization. The absorption data of ring-closing and ring-opening isomers in PMMA media are presented in Table 1. As shown in Table 1, it is found that the absorption band of ring-opening isomers occurred red shift when the substituent in the benzene ring is changed from an electron-acceptor to an electron-donator, and the stronger the electron-donator, the greater the red shift. It is probable because of decreasing the density of electron cloud of

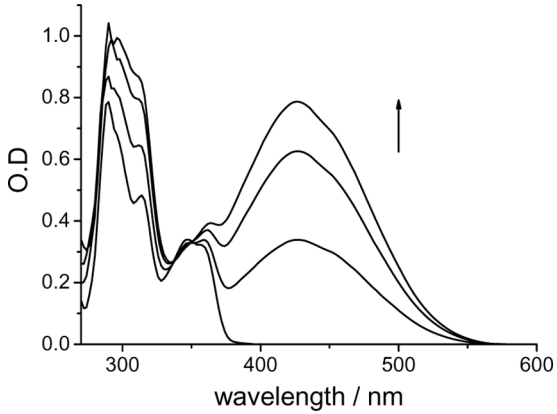


FIGURE 1 Absorption changes of **9a**–PMMA thin film with UV light irradiation (0, 20, 40, 60s).

TABLE 1 Absorption Data of Ring-Opening and Ring-Closing Isomers in PMMA Thin Film

Compounds	λ_{max} (nm) Closing isomer (**a**)	λ_{max} (nm) Opening isomer (**b**)
3	346	454
4	346	456
5	346	466
6	346	452
7	344	426
8	346	556
9	360	428
10	346	490

ring-opening isomers resulted from strong electronic properties, which resulted in a decreasing energy gap between the ground states and the excited states.

Coloration and Bleach of Naphthopyran Derivatives 3a–10a in PMMA Thin Film

The investigation of coloration of naphthopyran derivatives **3a–10a** found that all compounds undergo coloration with UV light or sunlight. It took about 1–2 min for naphthopyran derivatives to get photostationary state with 30 watt UV light (it took much longer time under sunlight), and the color of film changed from colorless to colored. The bleaching of film was carried out in darkness at room temperature (15°C). It is found that the color of film was faded fast during the first one to two minutes and one half optical density of colored isomer was detected during that time. It took, however, much longer (10–30 min) to completely bleach back to colorless, and one-tenth optical density of colored isomer was detected in these cases. Generally, naphthopyrans with electron-donating groups bleach faster than those with electron-acceptor groups. It is worth noting that the bleach of **9b** took much longer time (2 hrs) to back to colorless at room temperature by comparison with others although the mechanism is not clear. Both coloration and bleach of the naphthopyran derivatives **9a** are presented in Figs. 2a,b.

Temperature Influence on the Bleach of Naphthopyran Derivatives 3a–10a in PMMA Thin Film

It is well known that temperature has great influence on the bleach of photochromic pyrans and naphthopyrans. In this article, a

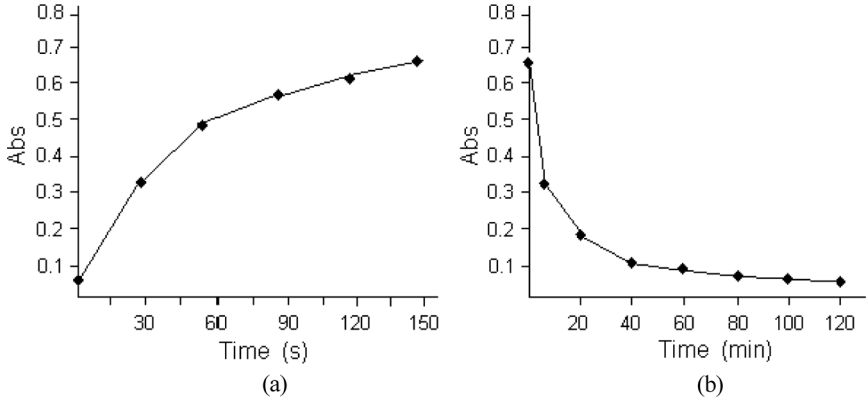


FIGURE 2 Coloration and bleach of **9a–**PMMA thin film (a: coloration; b: bleach).

preliminary investigation of temperature effects the color fade was carried out by the following way: a photostationary state naphthopyran–PMMA thin film was covered with foil paper and placed in temperature-controlled oven until the color of film faded completely. Figure 3 shows the results of fade time of **9b** at different temperature. It is found that it took more than one and half hours for **9b** to bleach completely back to colorless at 25°C (room temperature), but it only took less than 5 min to do it when temperature is over 45°C. It is also found that the higher the temperature is, the less time the fade takes. Similar results are obtained when other naphthopyrans–PMMA thin films were measured in the same way and the fade is much faster when the temperature is over 45°C although the fade time to colorless is somewhat different at room temperature with different compounds.

Fatigue Resistance of Naphthopyran Derivatives 3a–10a in PMMA Thin Film

Fatigue resistance is one of important factors to evaluate material applications. It is known that photochromic naphthopyrans exhibit good fatigue resistance. A preliminary investigation of fatigue resistance for naphthopyran derivatives **3a–10a** was performed by the following way: a naphthopyrans–PMMA thin film was irradiated to the photostationary state with UV light and the optical density of ring-opening isomers was measured, then bleach the colored film to

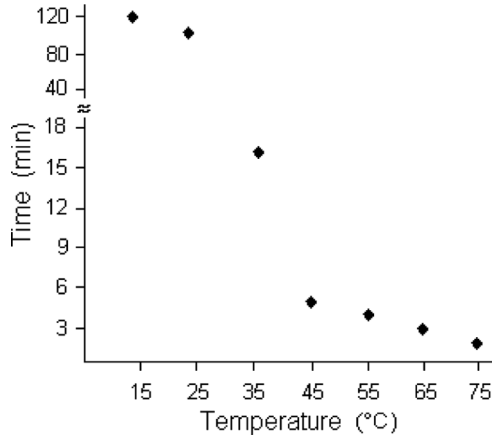


FIGURE 3 The fade time of **9b**–PMMA thin film at different temperature.

colorless (optical density of ring-opening isomer decreased to one tenth of ring-opening isomer at photostationary state) at darkness, this is defined one cycle. Figure 4 represented the fatigue testing results of **9a**–PMMA thin film. It is found that no significant change of optical density (ring-opening isomer) was detected after 10 cycles, suggesting **9a** exhibited good fatigue resistance. Other naphthopyran derivatives also showed good fatigue resistance and no significant change of optical density was detected after 10 cycles.

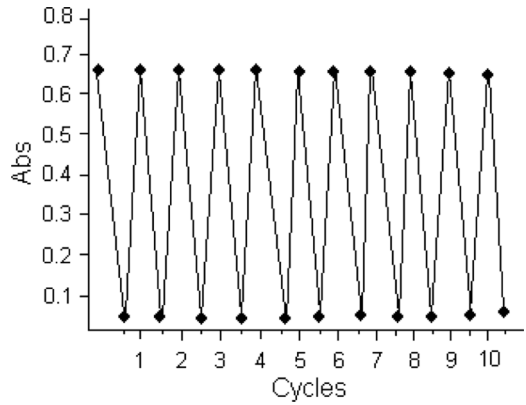


FIGURE 4 Fatigue resistance of **9a**–PMMA thin film.

CONCLUSIONS

In summary, a class of naphthopyran derivatives with different electronic property substituent has been prepared by the condensation of 1,2-diaryl-2-propyn-1-ol with β-naphthol, and their photochromic behavior in PMMA thin film has been investigated. With UV light or sunlight irradiation, the colorless ring-closed isomers transform to the yellow or orange ring-opening isomers, and the yellow or orange ring-opening isomers reverse back to the colorless ring-closed isomer when they are kept in darkness. All ring-opening isomers are sensitive to temperature and back to ring-closed isomers quickly when temperature is over 45°C.

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