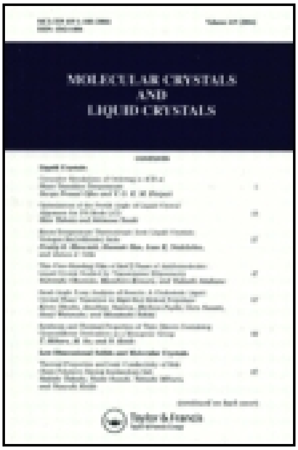

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Photochromic Mechanism of Heterofused Benzopyran Derivatives

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Photochromic Mechanism of Heterofused Benzopyran Derivatives

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ABATRACT The photochromic behavior of 2-phenyl-2-(thien-2-yl)-2H-benzo [b]furano[3,2-f]benzopyran (**1**) and 2,2-diphenyl-2H-benzo[b] furano[3,2-f]benzopyran (**2**) was examined by the nanosecond laser photolysis and normal time scale analysis. The results showed that the thienyl group could stabilize the colored forms as compared with the phenyl group and both singlet and triplet states were involved in the formation of the colored forms.

Keywords: photochromism; benzopyran; laser photolysis

INTRODUCTION

The photochromic behavior of benzopyran derivatives has become more attractive in recent years with the demand for industial application in photochromic ophthalmic lens and other materials undergo variable

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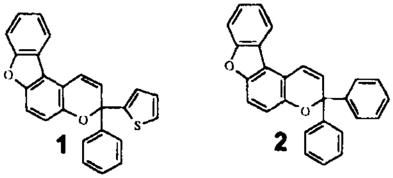
optical absorption [1-4]. In this paper, our interest focused on understanding the photochromic mechanism and the effect of aryl groups of Compound **1** and **2** (SCHEME 1) by means of laser photolysis.



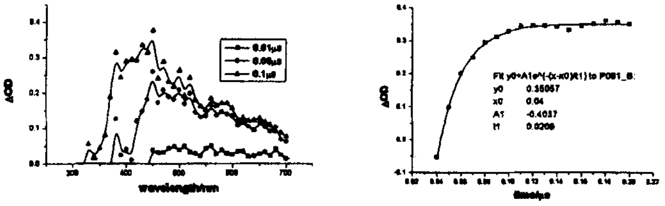
SCHEME 1: Structure of compound **1** and **2**

Compound **1** and **2** were prepared according to the method described in literature [3] and [4]. The structures were identified by NMR and MS. The nanosecond laser flash photolysis was carried out on the apparatus which have been described elsewhere [5].

RESULT AND DISCUSSION

Compound 1 and 2 are colorless.Upon laser photolysis,an absorption band could be observed at visible region.The λ_{max} was ~430nm. FIGURE 1(a) shows the time-resolved absorption spectra based on laser photolysis of **1** after nitrogen bubbling and FIGURE 1(b) is its absorption growth curve observed at 430 nm after photolysis.

The difference of the optical density (ΔOD) after the photolysis reached its maximum during a very short time (~0.1 μ s). This indicates that the colorless forms are responsive to ultraviolet light very rapidly and transfer readily to produce the colored forms. The rate constants of formation of the colored forms (k_f) were calculated by curve fitting and the results are collected in TABLE 1.



(a) (b)

FIGURE 1 (a) The time-resolved absorption spectra of 1
(b)Absorption growth curve of 1 .at 430nm after photolysis

TABLE1. The rate constants k_f of formation of the colored forms

compound	in CH_3CN	in C_6H_{12}
1	$4.78 \times 10^7 s^{-1}$	$2.80 \times 10^7 s^{-1}$
2	$9.37 \times 10^6 s^{-1}$	$1.4 \times 10^7 s^{-1}$

It was found that the oxygen could quench partially the formation of the colored forms of both compound 1 and 2. Figure 2 implies that both excited singlet and triplet states of 1 and 2 may be involved in the formation of the colored forms.

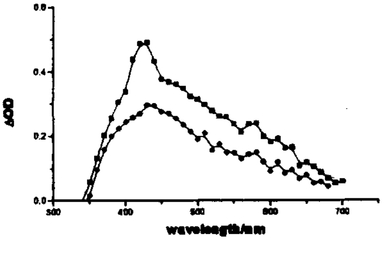
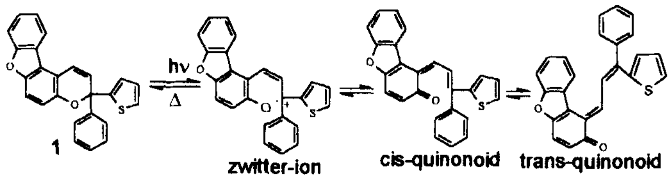


FIGURE 2. Transient Absorption Spectra of Compound 1
Oxygen-saturated (●)and Nitrogen-bubbling(■)

In **1** and **2**, the two aryl rings at 2-position are almost perpendicular to the pyran ring, thus there exists no conjugation among the three moieties. After the heterolytic cleavage of C_{sp3}-O bond (SCHEME 2), the open forms become co-planar to a certain degree, and the conjugation systems are enlarged to result in the longer wavelength absorption. The absorption in the visible region are the sum of the absorption resulted from zwitterion, cis-quinonoid and trans-quinonoid.



SCHEME 2. Photochromic reaction of **1**

After the heterolytic cleavage of the C_{sp3}-O bond. The charge will be delocalized within the whole molecule. The molecules will be weaker polar and show quinonoidal characteristics.

The thermal bleaching process of the colored forms of **2** was observed in microsecond time scale by monitoring the decay of the absorption at 420 nm. As seen in FIGURE 3, the colored forms of **2** decayed following the two-exponential kinetics. The two components were referred to the cis-quinonoid and trans-quinonoid respectively.

The colored forms of compound **1** decayed at a much slower rate and the process could be monitored by UV-Vis spetrophotometer. It can be found in FIGURE 4 that the decay of **1** could be well fitted to single exponential decay. The single components observed were assigned as the trans-quinonoid colored species. The decay rate of cis-quinonoid is fast beyond the detectable time scale of UV-Vis spectrophotometer.

The data of the decay of the colored forms of **1** and **2** were calculated according to the curve fitting and collected in TABLE 2.

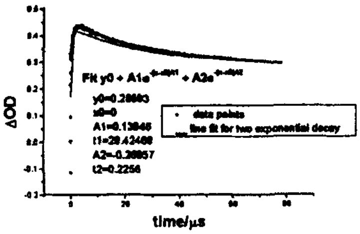


FIGURE 3

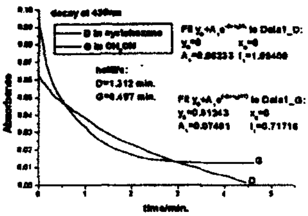


FIGURE 4

FIGURE 3 The absorption of **2** at 420 nm versus time after laser photolysis in cyclohexane

FIGURE 4. The decay curves and the curve fitting results of the colored forms of **1** after irradiation with UV light (9W lamp, λ = 254nm, 30s.)

TABLE 2. The decay constants (k) and lifetime(τ) of the colored forms of **1** and **2** in different solvents

Compd	In acetonitrile		In cyclohexane	
	k(s^{-1})	τ	k(s^{-1})	τ
1	2. 32×10^{-2}	0. 717 min	8. 81×10^{-3}	1. 89 min
2	k_1=6. 4×10^5 k_2=9. 2×10^6	$τ_1$= 1. 55 μ S $τ_2$= 0. 11 μ S	k_1=3. 5×10^4 k_2=4. 3×10^6	$τ_1$=28. 4 μ S $τ_2$=0. 22 μ S

The colored forms of compound **1** decayed much slower than that of **2**. This arises from the difference between the electron density of thiophene ring and benzene ring .The thiophene ring is the five-member ring with six electrons and is electron-rich group compared with benzene ring, consequently it prolong the lifetime of the open form.

The colored forms of **1** and **2** decayed faster in acetonitrile than in cyclohexane. In polar solvent, the open forms are more soluble because of dipole-dipole between solvent and colored forms so that they may be dispersed very well and are easy to undergo single molecular ring-closing reaction. While in the non-polar solvent, the open forms are more likely to form certain aggregates, which in turn prohibit the ring-closing reaction due to interactions within the aggregates.

CONCLUSION

Photochromic mechanism of Compound 1 and 2 were investigated by Laser photolysis. The results show that both siglet and triplet excited states of compound **1** and **2** were involved in the photocoloration processes. The thienyl group could stabilize the corlored forms as compared with the phenyl group. The colored forms decayed faster in polar solvent than in non-polar solvent.

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