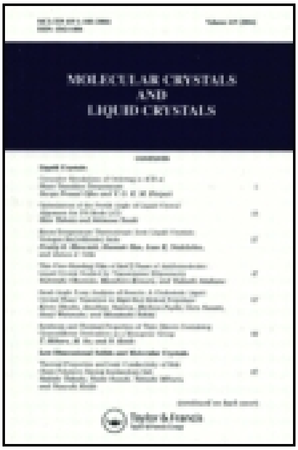

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Synthesis and Photochromic Mechanism of 3-Phenyl-3-[1,2-Dimethylindol-3-yl]-3H-Naphtho[2,1-b]Pyran

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Synthesis and Photochromic Mechanism of 3-Phenyl-3-[1,2–Dimethylindol-3-yl]-3H-Naphtho[2,1-b]Pyran

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A novel photochromic compound, 3-phenyl-3-(1,2-dimethylindol-3-yl)-3H-naphtho[2,1-b] pyran (I) was synthesized and the mechanism for photochromic process of **I** was investigated by nanosecond laser flash photolysis.

Keywords: photochromism; 3H-naphtho[2; 1-b]pyran; laser photolysis; heterocycle

INTRODUCTION

The photochromism of chromene derivatives has been received increasing attention from the standpoint of their application in ophthalmic lenses [1-2]. Nanosecond laser flash spectroscopy [3], UV and NMR spectroscopy [4] have been employed to identify the photophysical path involved in photochromic process. In this paper, a novel photochromic compound, 3-phenyl-3-(1,2-dimethylindol-3-yl)-3H-naphtho[2,1-b]pyran (**I**) was synthesized and the mechanism for photochromic process of **I** was investigated by nanosecond laser flash photolysis.

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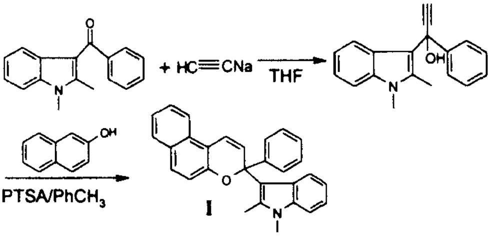
EXPERIMENTAL

The synthetic route for **I** is shown in SCHEME **1**:



SCHEME 1 Synthesis of Compound I

The starting materials, 1,2-dimethyl-3-benzoylindole was synthesized according to the reference[5]. The procedure of the addition reaction of the alkyne to the ketone and the condensation of the propargylic alcohol with 2-naphthol were carried out according to the similar method described previously[6-7].

I: yield: 10(%). m.p. 208-210℃. MS (m/z): 401(M+, 100), 386(M-15, 40), 324(M-76, 50), 232, 201, 145, 115, 77. ^{1}HNMR(δ ,CDCl$_3$): 3.61(3H,s,-CH$_3$), 5.73(3H,s,-CH$_3$), 7.10-7.82(17H,m,Ar-H).

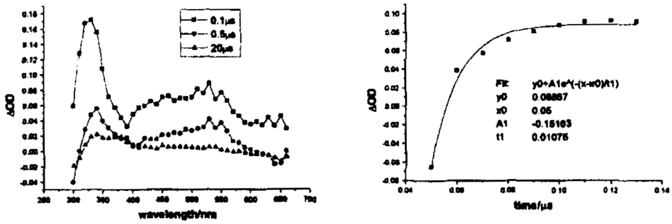
The nanosecond laser flash photolysis was carried out on the apparatus which have been describe elsewhere [8]. The excimer laser (KrF, 248nm) was used as the excitation light source. Pulse width is 20 ns and the maximum energy per pulse is about 50 mJ.

RESULTS AND DISCUSSION

Transient Absorption Spectra

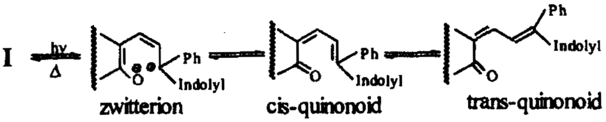
Excimer laser excitation (248nm) of solution of **I** in acetonitrile or cyclohexane lead to transient absorption in visible region. The λ max was 330, 530nm in acetonitrile and 330, 480nm in cyclohexane respectively. FIGURE 1 (A) shows the time resolved absorption spectra of **I** in acetonitrile and (B) presents the absorption growth curve monitored at 530nm.

The colored forms, which were produced in less than 0.1μs, are assigned to be the mixture of the opened forms, including zwitterion, cis-quinonoid and trans-quinonoid (as seen in SCHEME 2).



(A) **(B)**

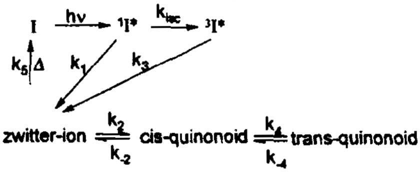
FIGURE 1. **(A)Transient absorption spectra of I in** ***nitrogen-degassed*** **acetonitrile recorded after a 248nm laser pulse. (B) The absorption growth curve monitored at 530nm.**



SCHEME 2. **Photochromism of Compound I**

It should be noted that either cis-quinonoid or trans-quinonoid should include two isomers. While our experiments did not distinguish between different isomers. On the other hand, the lifetimes of the cis- and trans- isomer were quite different and could be distinguished according to the decay kinetics analysis (*vide infra*).

Oxygen bubbling prior to the photolysis caused significant quenching of the entire spectrum either in acetonitrile or in cyclohexane. The intensity of the ΔOD spectra were decreased about 70%. On the basis of the very large quenching by oxygen, we believed that the colored forms must dominantly arise from the triplet excited state although a small part is originated from singlet excited state due to the lack of total quenching in the presence of oxygen. A very fast decaying species with the lifetime of 0.23μs in acetonitrile and 0.39μs in cyclohexane was found when the nitrogen-degassed samples were used. The short-lived species was ascribed to the triplet excited state of I because of its absence in oxygen-saturated samples. Thus, the photochromic mechanism of I was proposed as SCHEME 3:

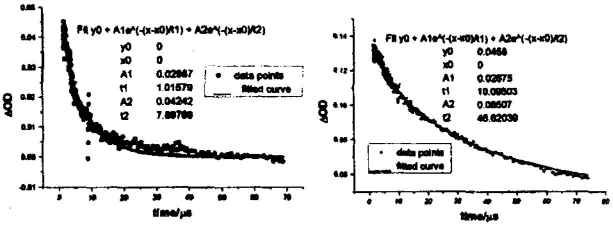


SCHEME 3. **Photochromic Mechanism of Compound I**

After irradiation with UV light, the ground state (I) was transferred to the singlet excited state (^{1}I*), which in turn underwent intersystem crossing (isc) to produce the excited triplet state (^{3}I*). The ring opening reaction could take place from both ^{1}I* and ^{3}I*, resulting in the zwitterion as the first product. Thereafter, the charge redistribution and bond tautomerization occurred to yield the cis- and trans-quinonoid isomers.

Decay Kinetics of The Colored Forms

The colored forms were observed to decay with the time evolution. We monitored the decay kinetics of the colored forms at their λ_{max} (530nm in acetonitrile and 480nm in cyclohexane respectively). It was found that in the nitrogen-degassed samples, the colored forms decayed according to the two-exponential kinetics (as shown in FIGURE 2) and the decay curves could be well fitted. The two detectable decaying species were assigned as cis- and trans-quinonoid isomers. It was believed that the cis-isomers should decay faster than trans-isomers. The process of the ring-closing of the zwitterion of **I** might be a very fast step and beyond the instrument's detectable limitation.



(A) (B)

FIGURE 2. The decay curves of the colored forms of I and the curve fitting results. (nitrogen-degassed samples; A: in acetonitrile; B: in cyclohexane)

With the oxygen-saturated samples, the colored forms decayed following the single exponential kinetics. The plot of ln (ΔOD) versus time yielded a linear dependence (as can be seen in FIGURE 3). The decay speed of this species was found faster than that of the trans-quinonoid isomer and slower than that of the cis-quinonoid isomer which were observed in the nitrogen-degassed samples. The colored forms in the oxygen-saturated samples were proposed to be a kind of complex formed between oxygen and cis-quinonoid isomer. The formation of the complex hindered the cis-quinonoid from transforming to the trans-quinonoid.

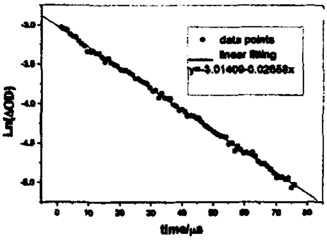


FIGURE 3. The plot of ln (ΔOD) of the colored form versus time (oxygen-saturated sample in cyclohexane, monitored at 490nm)

The data of the decay kinetics were calculated according to the curve fitting. The results are collected in TABLE1.It can be found that the colored forms decayed faster in acetonitrile than in cyclohexane. This could be ascribed to the different interaction between solvents and the decay species. In polar solvent, the open forms are more soluble due to their stronger dipole-dipole interaction with solvent molecules, so that they may be dispersed very well in polar solvent, just as hiding themselves in the solvent cage, thus they 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.

TABLE 1.Decay rate constants(k) and lifetimes(τ) of the colored forms

in acetonitrile			
Nitrogen-degassed		Oxygen-saturated	
k (s^{-1})	τ (μs)	k (s^{-1})	τ (μs)
9.90×10^5(cis) 1.26×10^5(trans)	1.01 7.89	2.79×10^5 (complex)	3.58
in cyclohexane			
Nitrogen-degassed		Oxygen-saturated	
k(s^{-1})	τ (μs)	k (s^{-1})	τ (μs)
1.0×10^5(cis) 2.14×10^4(trans)	10.0 46.6	3.25×10^4 (complex)	30.69

CONCLUSION

Both singlet and triplet excited states could take part in the photocoloration. When the nitrogen-degassed samples were used, two colored species were observed and they were ascribed to the cis- and trans-quinonoid forms respectively. While only one colored species was observed in the oxygen-saturated samples and it was assumed to be a kind of complex between oxygen and cis-quinonoid isomer. All colored forms decay faster in polar solvent than in non-polar solvent.

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