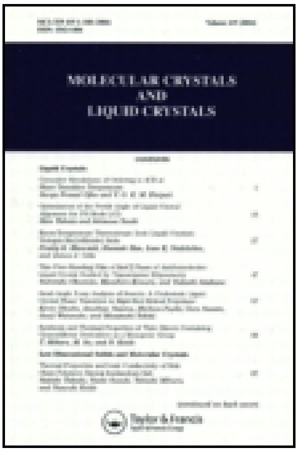

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Synthesis and Photochromism of 5-Dicyano-Methylene-4 isopropylidene-3-[1-(1-p-methoxy-phenyl-2-methyl-5-phenyl-3-Pyrryl)ethylidene]-tetrahydrofuran-2-one

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SYNTHESIS AND PHOTOCHROMISM OF 5-DICYANO-METHYLENE-4-ISOPROPYLIDENE-3-[1-(1-P-METHOXY-PHENYL-2-METHYL-5-PHENYL-3-PYRRYL)-ETHYLIDENE- TETRAHYDROFURAN-2-ONE

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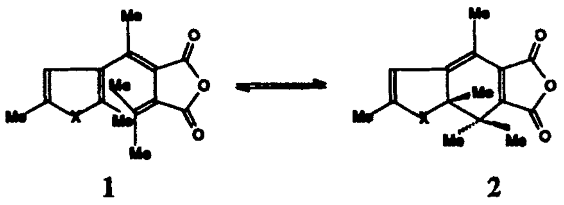
Abstract Synthesis and Photochromic behavior of an IR sensitive photochromic fulgide derivative: 5-Dicyanomethylene-4-isopropylidene-3-[1-(1-*p*-methoxyphenyl-2-methyl-5-phenyl)-3-pyrryl-ethylidene] tetrahydrofuran-2-one (3) are reported. The results show that after the replacement of one carbonyl oxygen of the anhydride ring in pyrryl fulgide by the strong electron-withdrawing dicyanomethylene group, the absorption maximum wavelength of their corresponding colored forms (4 and 7) shifts from λ_{max} = 640nm to λ_{max} = 820nm in acetonitrile.

INTRODUCTION

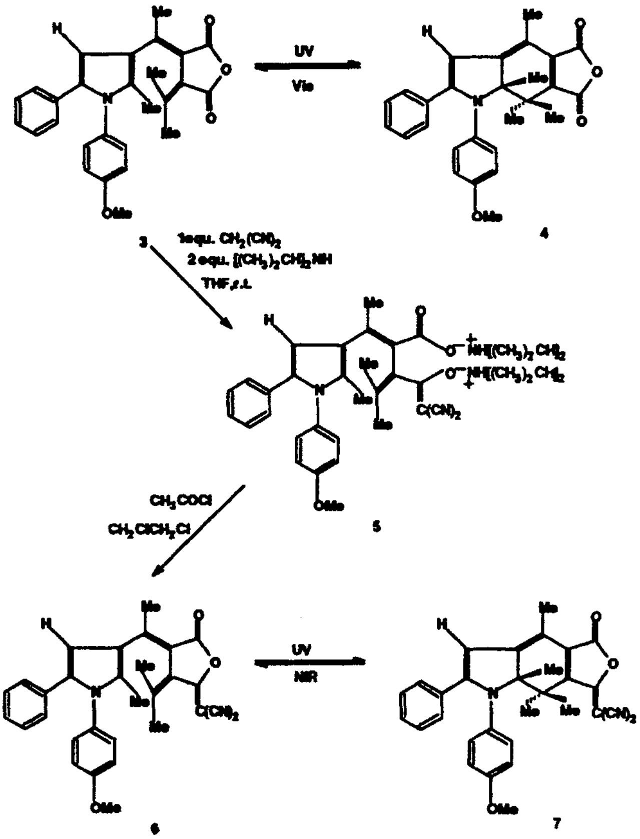
Thermally irreversible organic photochromic compounds, such as fulgides[1] are potential candidates for application in erasable optical information media, much attention have been made to improve their photochromic properties.[2,3] Previous paper[4] reported that the color of the ring-colsed form of fulgides can be altered to deep blue by replacing the 3-furyl or 3-thienyl group by a 3-pyrryl group (scheme1). The absorption maximum wavelength (λ_{max}) of 2 in toluene is 494 nm (X=O); 520 nm (X=S) and 610 nm (X=NPh).

In order to match commercial diode laser which emits radiation at wavelength 780-830 nm region, it is necessary and of great interest to modify the structure of



Scheme 1

photochromic fulgides so that their colored forms can absorb in the near infrared wavelength region. Our recent interests in photochromic fulgides with diode laser compatibility have led us to synthesis a series of pyrryl substituted fulgides.[5-9] Up to now, few compounds can match the emmision of diode laser, but none has a λ_{max} over



Scheme 2

800 nm. We report here a convenient method for the synthesis of a real near infrared sensitive photochromic dicyanomethylene compound (**6**, Scheme 2), derived from 3-pyrryl fulgide (**3**).

The replacement of one carbonyl oxygen of the anhydride ring in photochromic pyrryl fulgide by the strong electron-withdrawing dicyanomethylene group can cause a significantly bathochromic shift (180nm) of the long wavelength absorption band of the coresopnding colored forms.

EXPERIMENTAL

Absorption spectra were measured on Hitachi-557 spectrometer, NMR spectra were recorded with a Varian XL-400 (400MHz) instrument. Mass spectra were obtained using a Finnigan 4021C mass spectrometer with an electron-impact at 70ev. Reagents and solvents were purified before use. In the photocoloration experiment, 366nm light (selected from an 8W UV-lamp) was used as the irradiation source. The measurement were performed in a 1cmx1cmx4cm quartz cell. In the photobleaching experiment, the visible light ($\lambda_{max} \geq$ 600nm, from 500W iodine-tungsten lamp) was used as the bleaching source.

Synthesis of the Title Compound (6)

Our key starting material, 3-pyrryl fulgide (3) was prepared from 1-*p*-methoxylphenyl-2-methyl-5-phenyl-3-acetyl pyrrole[10] and diethyl 2-isopropylidene-succinate[11] *via* Stobbe condensation, which has been described in reference[12].

Equal molar of pyrryl fulgide (3): and malononitrile were dissolved in dry tetrahydrofuran (THF), 2 equivalent molar of diisopropylamine dissolved in dry THF was added dropwise to the above solution, after addition, the mixture were maintained at ambient for 2.5 hrs, and the white precipate appeared (disalt, **5**, 30%). The disalt (**5**) was filtered off and thoroughly dried under vacumm pressure, then dissolved in 1,2-dichloroethane and treated with acetyl chloride (2 hrs) without exposure to UV light. Remove of the solvent and purified by silica-gel column chromotagraphy using dichloromethane/light petroleum ether (1:2) as eluent, after working up, give photochromic compound **6** as yellow crystal (40%), after recrystalized from diethyl ether/light petroleum ether. M.P. 160-162°C; ^{1}H NMR ($CDCl_3$) δ ppm, 1.53 (s,3H, Me); 1.78(s,3H,Me); 2.24 (s,3H, Me); 2.76 (s,3H, Me); 3.83 (s,3H, Me); 6.48 (s,1H, Pyrryl-H); 6.92-7.40(m,9H,Ar-H). IR, (ν,cm^{-1}), 2229(CN), 1801(C=O), 1547, 1509, 1483 (Ph). MS(EI), m/z=475(100%). Elemental analysis, Calculated for $C_{30}H_{25}O_3N_3$, C:75.77; H:5.30; N:8.84; found C:75.12; H: 5.55; N: 8.45.

DISCUSSION

One of the carbonyl group of the anhydride ring which located at juxtaposition to the ethylidene group is well-resonace conjugated with the pyrryl nitrogen atom, and thus is relatively deactived as compared with the other carbonyl group[13]. The result in preferential nucleophic attack of the malononitril negative anion at the latter carbonyl group.

Upon irradiation at λ_{max} 366nm, a 10^{-4} mol/dm^3 solution of **6** in acetonitrile revealed a marked bathochromic shift to the near infrared region with a λ_{max} = 820nm. By contrast, irradiation of a similar solution of **3** at 366nm gave an absorption peak at λ_{max} = 640nm. It can be inferred, therefore, that the introduction of a dicyanomethylene group into the succinic anhydride ring of fulgide **3** results in a further significant bathochromic shift of about 180nm with respects to their respective colored forms (**4** and **7**). However, such molecular modification has little effect on the absorption spectra of the ring-opened form (see figure 1, absorption bands of compound **3** and **6**). Figure 1 illustrated that a new kind of infrared active photochromic compound was synthesized by replacing the oxygen of appropriate carbonyl in fulgides by a dicyanomethylene group through the molecular design and tailoring. This system is matched very well with commercial diode laser.

Figure 2 shows time-resolved absorption spectral changes during the coloration and bleaching processes of compound **6**. By irradiation with 366 nm light, the pale

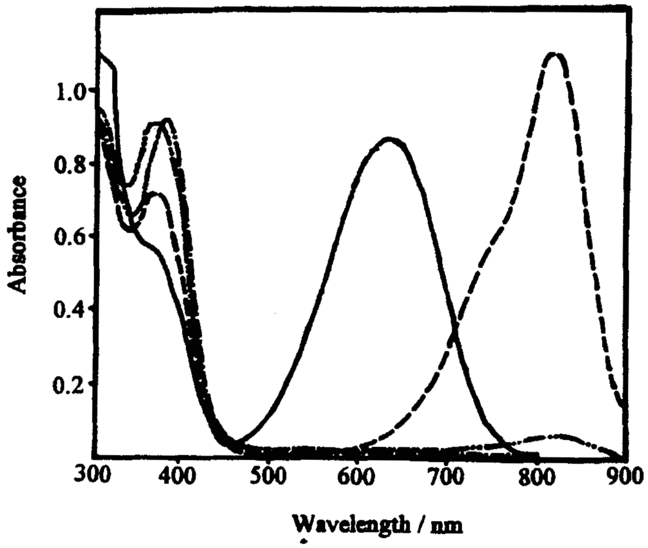


FIGURE 1 Absorption spectra of compound 3, 4, 6 and 7 in acetonitrile.

—·—·—(3); ————(4); —.. —.. —(6); — — — —(7).

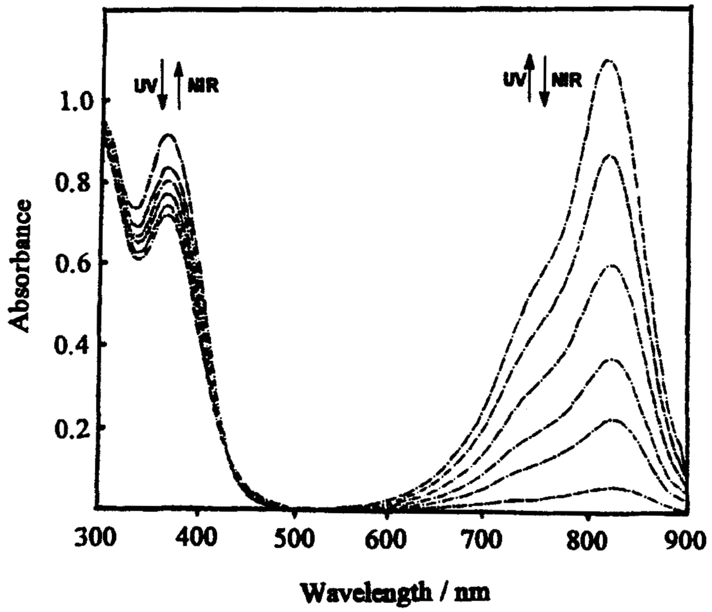
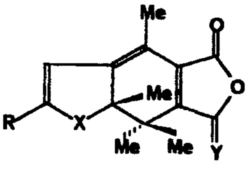
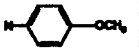
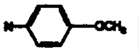


FIGURE 2 Absorption spectral changes of comound 6 during the photochromic processes in acetonitrile solution. Coloring with 366nm light, bleaching with ≥ 600nm light.

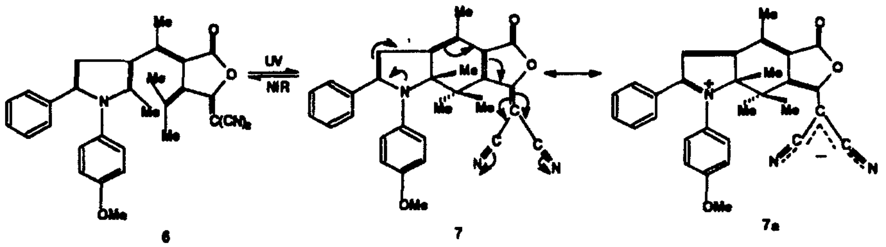
yellow solution of **6** was converted to a green solution, which does not fade in the dark, can be ascribed to the thermally stable 7,7a-dihydroindole derivatives (**7**), and the absorption band in ultra violet region decreased, while the absorption band in the near infrared region increased simultaneously, this is so-called photocoloration process. The reaction can be reversed and the color bleached by exposure to visible light or near infrared light, the absorption band of the colored form (**7**) in the near infrared region decreased while the absorption band in ultra violet region increased until fading out of the colored solution, this is referred to photobleaching process. These reversible spectral changes indicate that such new kind of the title compound possesses excellent photochromic properties.

As for furyl and thienyl fulgides, the same molecular modification of the anhydride moiety can also led to a large bathochromic shift of the λ_{max} of the corresponding colored form,[13-15]. The bathochromic shifted values are around 150nm, which is smaller than for the corresponding pyrryl substituted molecule, and the λ_{max} of the colored form of dicyanomethylene derivatives of furyl and thienyl fulgides are shorter than 700nm. Table 1 shows the λ_{max} values of colored forms, illustrating the major bathochromic shifts caused by replacing the oxygen of appropriate carbonyl by the dicyanomethylene group.

TABLE 1 Comparison of fulgide and its dicyanomethylene derivative in acetonitrile.

	Substituents			λ_{max}/nm	$\Delta\lambda_{max}$/nm
	R	X	Y		
	CH_3	O	O	507	158
	CH_3	O	$C(CN)_2$	665	
	Ph	S	O	544	140
	Ph	S	$C(CN)_2$	684	
	Ph		O	640	180
	Ph		$C(CN)_2$	820	

Such a large bathochromic shift of λ_{max} between the colored form 4 and 7 can be hardly rationalized only by the long conjugated π-electron system existing in the colored forms 4 and 7. Nevertheless, the strong electron withdrawing group, dicyanomethylene group, linked with the much stronger electron donating group, dihydropyrryl moiety (compared with the corresponding furyl and thienyl derivatives), through the long conjugated π-electron system, it may contribute to such a large bathochromic shift of λ_{max} between 4 and 7.



Scheme 3

The introduction of a dicyanomethylene group at the 5-position of the tetrahydrofuran ring of 6 would provide an extended conjugation in the cyclized products 7 (see Scheme 3). This conjugation would extend from the heteroatom of the (1-*p*-methoxylphenyl-2-methyl-5-phenyl) pyrrole ring to the one of nitrogen atoms of the nitrile groups at the end, resulting in a resonance-delocalized species, such as 7a. Intramolecular electron transfer proceeded through the π-conjugation system and a zwitterionic like species formed. Thus the large bathochromic shift was observed.

The resonance stabilization of the colored form is believed to be partially responsible for the good thermal stabilities of fulgides and their derivatives. In fact, when the compound (6) was heated up to the melting point (160°C) the photochromism is not destroyed, showing that the title compound has excellent thermal stability.

Investigation on the application of photochromic compound (6) in the optical information recording compatible with semiconductor diode laser are undergoing in our group.

CONCLUSION

In summary, the replacement of one carbonyl oxygen of the anhydride ring in pyrryl fulgides by the strong electron-withdrawing dicyanomethylene group, led to the preparation of an IR sensitive, thermally stable photochromic compound **6**. The optical sensitivity of the colored form (**7**) at λ_{max} = 820nm (*i.e.*, sensitivity to the emission wavelength of commercial diode laser) is of much interest for practical application.

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