

Studies on Synthesis and Photochromism of a Novel Class of Fulgimide: (*Z*)-4-Oxazolyfulgimide

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A novel class of fulgimide, (*Z*)-4-oxazolyfulgimide ((*Z*)-1-benzyl-4-isopropylidene-3-[1-(2-aryl-5-methyl-oxazolyl)ethylidene]tetrahydropyrrole-2,5-dione), was synthesized by the reaction of (*Z*)-4-oxazolyfulgide (4-isopropylidene-3-[1-(2-aryl-5-methyloxazolyl)ethylidene]tetrahydrofuran-2,5-dione) with benzyl amine. Photochromic property of (*Z*)-4-oxazolyfulgimide was studied. Compared with (*Z*)-4-oxazolyfulgide, the absorption maximum of the colored form of (*Z*)-4-oxazolyfulgimide is bathochromic-shifted. Substituents on the aryl ring affect the absorption maximum of the open form and the colored form of (*Z*)-4-oxazolyfulgimide.

Keywords (*Z*)-4-oxazolyfulgimide, synthesis, photochromism

Introduction

Organic photochromic compounds have reversible color changes upon irradiation with suitable wavelength light. This photochromic property makes them applicable in the field of optoelectric materials and devices,^{1,2} for example high-density optical memory devices,^{3,4} holographic recording,⁵ waveguide,⁶ and optical switches.⁷ Fulgide as a kind of photochromic compound has been extensively investigated. Fulgimide, as an important derivative of fulgide, has been also widely studied so far,⁸ because it is convenient to attach another functional group onto the fulgide core. The functional fulgimide will have some integrating properties of photochromic material. For example, the fulgimide moiety was used for attaching to side chains of polymers,^{6,7} attaching a fluorescent group for control of fluorescent device,⁴ and attaching to proteins for regulation of substrate binding.^{9,10}

The synthesis of 4-oxazolyfulgide has been reported,¹¹ but 4-oxazolyfulgimide has not been demonstrated in literature. In this paper, studies on synthesis and photochromism of a novel fulgimide, (*Z*)-1-benzyl-4-isopropylidene-3-[1-(2-aryl-5-methyloxazolyl)ethylidene]tetrahydro-pyrrole-2,5-dione (**II**), are reported for the first time.

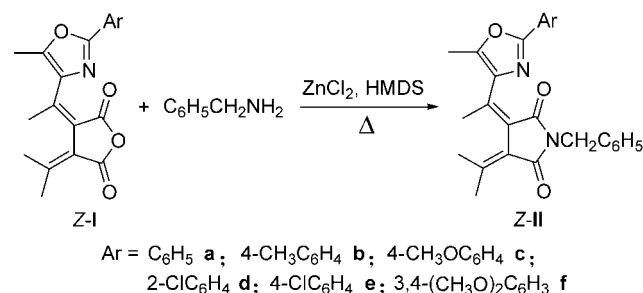
Results and discussion

Synthesis

The fulgimide was normally synthesized by the reaction of fulgide with primary amine. In this study, benzyl amine was used to react with (*Z*)-4-oxazolyful-

gide. Six (*Z*)-4-oxazolyfulgimides were prepared by this method, and the chemical yield was good to excellent. The first step is that (*Z*)-4-oxazolyfulgide (**I**) reacted with benzyl amine to produce monoamide of 3-isopropylidene-2-[1-(2-aryl-5-methyl-oxazolyl)ethylidene]succinic acid with zinc chloride as catalyst. The second step is that the monoamide of succinic acid was dehydrated with hexamethyldisilane (HMDS) to produce fulgimide **II**. The simplified reaction is shown in Scheme 1.

Scheme 1



4-Oxazolyfulgimide **II** was purified by column-chromatography on silica gel. The chemical yield was between 75%—93% for different fulgimide.

Photochromic properties

(*Z*)-4-Oxazolyfulgimide does not have photocyclization properties because the 4*n* π-electron system of *Z*-form is not favorable for the pericyclic reaction. The photoisomerization from (*Z*)-4-oxazolyfulgimide to

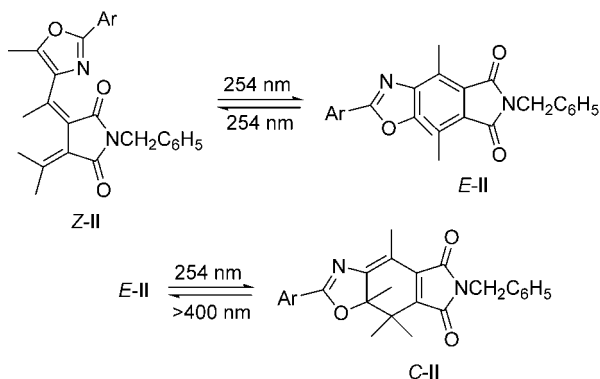
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(*E*)-4-oxazolyl fulgimide occurs when *Z*-**II** is irradiated with UV light. There is an all *cis*-hexatriene like structure system, $4n+2$ π -electron system, of *E*-form. It is favorable for the pericyclic reaction when the (*E*)-4-oxazolyl fulgimide is irradiated by UV light. The photochromic reaction is shown in Scheme 2.

Scheme 2



The product of photocyclization is a hexa-1,3-diene derivative (C-II, normally called colored form) that has more planar configuration structure than its precursor, (*E*)-4-oxazolyl fulgimide. Absorption spectrum is located in visible region. During the photocyclization reaction, the color of reaction system changed to orange because the colored form of *E*-**II** produced. The absorption of reaction system in UV region decreased, at the same time the absorption of reaction system in visible area increased gradually. The absorption spectra changes are shown in Figure 1. This phenomenon can occur reversibly when the photocyclization product is irradiated with visible light.

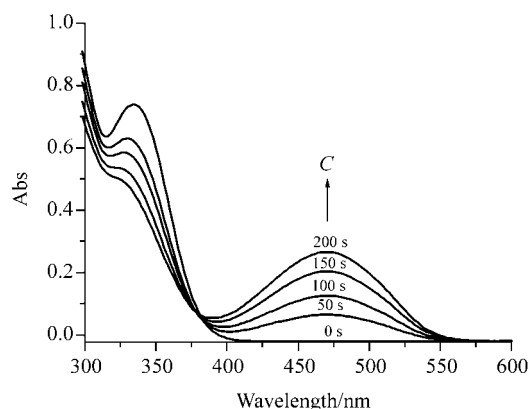


Figure 1 Absorption spectra as function of time of fulgimide (*Z*)-**IIb** in cyclohexane under 254 nm light irradiation. The absorption band of *C* represents colored form of **IIb**.

Structure effect on absorption spectra

The absorption maxima of *Z*-form and *C*-form of fulgimide and fulgide are listed in Table 1.

The 2-aryl substituted group affects the absorption spectra of **I**, **II** and their colored forms. When the *para*

Table 1 Absorption maximum of *Z*-form and *C*-form of fulgide and fulgimide in cyclohexane

Compd	a	b	c	d	e	f
<i>Z</i> - I	345	348	353	—	343	—
<i>C</i> - I	454	456	464	—	451	—
<i>Z</i> - II	331	334	338	328	326	339
<i>C</i> - II	468	470	474	464	466	476

group is electron-donating group, such as methyl and methoxyl, the absorption maximum (λ_{\max}) is bathochromic-shifted. On the other hand, the electron-withdrawing group makes the absorption maximum (λ_{\max}) hypsochromic-shifted. Comparing the absorption maximum of colored form of 4-oxazolyl fulgimide with that of 4-oxazolyl fulgide, it is bathochromic-shifted (Figure 2) because the 1-benzyl group can extend the conjugation system by super conjugated effect of methylene in which the *para* position effect is larger than *meta* position effect.

Figure 2 indicates that the colored form of 4-oxazolyl fulgimide is more compatible with 488 nm laser.

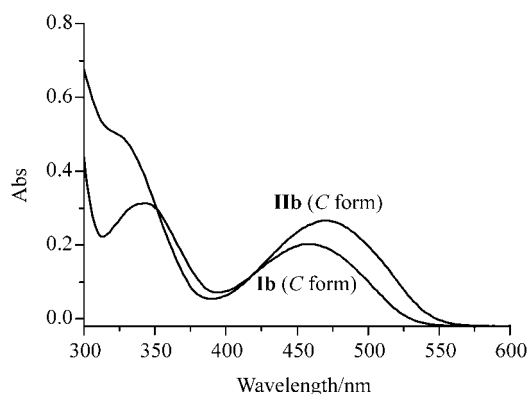


Figure 2 Absorption spectra of the colored form (*C*) of fulgide **Ib** and fulgimide **IIb** in cyclohexane.

Experimental

Reagent and apparatus

Toluene was distilled over sodium prior to use. (*Z*)-4-Oxazolyl fulgide was prepared by the Stobbe condensation of diethyl isopropylidene succinate and 4-acetyl oxazole that was synthesized according to the reported method.¹¹ Melting points were measured on an X₄-data microscopic melting point apparatus and the thermometer is uncorrected. ¹H NMR spectra were obtained using a Varian Germina-300 spectrometer. IR spectra (KBr) were recorded on a Perkin Elmer 83 instrument. MS spectra were recorded on a TRIO-2000 GC-MS instrument. All spectra were measured in 1-cm quartz cells at room temperature and the UV-vis absorption spectra were recorded on a Hitachi U-3010 spectrophotometer. Elemental analysis was taken on a CHN

2400 elementary analysis instrument.

General procedure

(*Z*)-4-Oxazolyl fulgide and benzyl amine were dissolved in the dried toluene, and zinc chloride powder was added to the solution. The solution was heated to 80 °C, and HMDS was slowly added to it during 10–15 min. After the addition was complete, the solution was kept at 80 °C until the (*Z*)-4-oxazolyl fulgide disappeared completely followed by TLC. The solvent was removed, (*Z*)-4-oxazolyl fulgimide was isolated and purified by column-chromatography on silica-gel, and recrystallized from cyclohexane.

IIa m.p. 184–186 °C; yield 80%; ¹H NMR (CDCl₃) δ: 1.95 (s, 3H, CH₃), 2.25 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 2.46 (s, 3H, CH₃), 4.68 (s, 2H, CH₂), 7.27 (d, *J*=6.9 Hz, 2H, Ar), 7.37–7.39 (m, 3H, Ar), 7.42–7.44 (m, 3H, Ar), 8.02 (d, *J*=6.3 Hz, 2H, Ar); IR (KBr) ν: 1745 (C=O), 1701 (C=O), 1385 (C–N) cm⁻¹; MS *m/z*: 412 (M⁺), 397, 264, 236, 175, 105, 91, 77, 65, 43. Anal. calcd for C₂₆H₂₄O₃N₂: C 75.73, H 5.82, N 6.79; found C 75.41, H 6.01, N 6.63.

IIb m.p. 178–180 °C; yield 91%; ¹H NMR (CDCl₃) δ: 1.94 (s, 3H, CH₃), 2.24 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 2.39 (s, 3H, CH₃), 2.45 (s, 3H, CH₃), 4.67 (s, 2H, CH₂), 7.23 (d, *J*=7.8 Hz, 2H, Ar), 7.26 (d, *J*=6.6 Hz, 2H, Ar), 7.36–7.39 (m, 3H, Ar), 7.90 (d, *J*=7.8 Hz, 2H, Ar); IR (KBr) ν: 1747 (C=O), 1698 (C=O), 1387 (C–N) cm⁻¹; MS *m/z*: 426 (M⁺), 411, 278, 133, 119, 105, 91, 77, 65, 43. Anal. calcd for C₂₇H₂₆O₃N₂: C 76.06, H 6.10, N 6.57; found C 75.73, H 6.15, N 6.54.

IIc m.p. 138–140 °C; yield 93%; ¹H NMR (CDCl₃) δ: 1.95 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 2.34 (s, 3H, CH₃), 2.45 (s, 3H, CH₃), 3.87 (s, 3H, CH₃), 4.68 (s, 2H, CH₂), 6.96 (d, *J*=8.5 Hz, 2H, Ar), 7.25 (d, *J*=6.2 Hz, 2H, Ar), 7.36–7.39 (m, 3H, Ar), 8.02 (d, *J*=8.5 Hz, 2H, Ar); IR (KBr) ν: 1759 (C=O), 1703 (C=O), 1392 (C–N) cm⁻¹; MS *m/z*: 442 (M⁺), 427, 294, 266, 188, 160, 135, 102, 91. Anal. calcd for C₂₇H₂₆O₄N₂: C 73.30, H 5.88, N 6.33; found C 73.12, H 5.96, N 6.23.

IIId m.p. 186–188 °C; yield 75%; ¹H NMR (CDCl₃) δ: 1.96 (s, 3H, CH₃), 2.27 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 2.46 (s, 3H, CH₃), 4.69 (s, 2H, CH₂), 7.24–7.26 (m, 2H, Ar), 7.28 (d, *J*=7.8 Hz, 2H, Ar), 7.36–7.39 (m, 3H, Ar), 7.49 (d, *J*=6.9 Hz, 1H, Ar), 7.99 (d, *J*=7.5 Hz, 1H, Ar); IR (KBr) ν: 1739 (C=O), 1679 (C=O), 1376 (C–N) cm⁻¹; MS *m/z*: 449, 446 (M⁺), 431, 298, 174, 139, 104, 91, 77, 65, 43. Anal. calcd for C₂₆H₂₃O₃N₂Cl: C 69.88, H 5.15, N 6.27; found C 69.59, H 5.27, N 6.17.

IIe m.p. 180 °C; yield 83%; ¹H NMR(CDCl₃) δ: 1.95 (s, 3H, CH₃), 2.24 (s, 3H, CH₃), 2.36 (s, 3H, CH₃),

2.46 (s, 3H, CH₃), 4.68 (s, 2H, CH₂), 7.28 (d, *J*=6.6 Hz, 2H, Ar), 7.36–7.38 (m, 3H, Ar), 7.42 (d, *J*=8.4 Hz, 2H, Ar), 7.96 (d, *J*=8.4 Hz, 2H, Ar); IR (KBr) ν: 1741 (C=O), 1681(C=O), 1382(C–N) cm⁻¹; MS *m/z*: 449, 446 (M⁺), 431, 298, 139, 105, 91, 77, 65, 43. Anal. calcd for C₂₆H₂₃O₃N₂Cl: C 69.88, H 5.15, N 6.27; found C 69.62, H 5.20, N 6.09.

IIf m.p. 158–159 °C; yield 79%; ¹H NMR (CDCl₃) δ: 1.96 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 2.46 (s, 3H, CH₃), 3.95 (s, 3H, OCH₃), 3.98 (s, 3H, OCH₃), 4.69 (s, 2H, CH₂), 6.93 (d, *J*=8.3 Hz, 1H, Ar), 7.27–7.29 (m, 3H, Ar), 7.38 (d, *J*=6.9 Hz, 2H, Ar), 7.54 (s, 1H, Ar), 7.61 (d, *J*=8.3 Hz, 1H, Ar); IR (KBr) ν: 1764 (C=O), 1706 (C=O), 1401(C–N) cm⁻¹; MS *m/z*: 472 (M⁺), 457, 324, 296, 164, 133, 91, 43. Anal. calcd for C₂₈H₂₈O₅N₂: C 71.19, H 5.93, N 5.93; found C 70.85, H 5.97, N 5.76.

In conclusion, six (*Z*)-4-oxazolyl fulgimides, as novel derivatives of fulgide, are synthesized in good to excellent yields. The fulgimide has very good photochromic properties. The absorption maxima of 4-oxazolyl fulgide, 4-oxazolyl fulgimide and their colored form were measured. Substituent effects on the absorption spectra were discussed. The absorption maximum of colored form of 4-oxazolyl fulgimide is bathochromic-shifted compared with that of 4-oxazolyl fulgide.

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