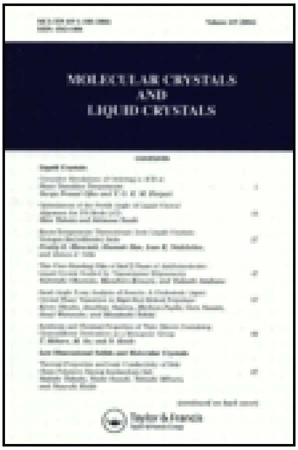

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Photochromism of (R)-Binaphthol-Condensed Benzofurylfulgide and Control of Properties

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Photochromism of (*R*)-Binaphthol-Condensed Benzofurylfulgide and Control of Properties

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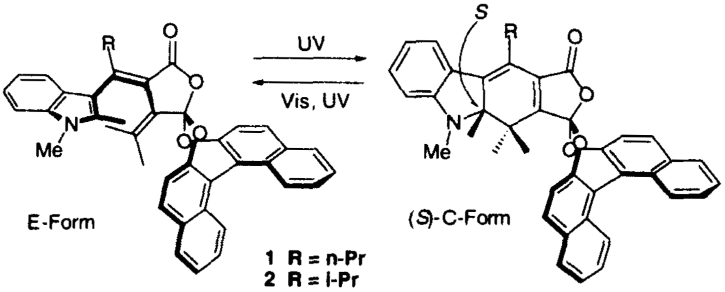
(*R*)-Binaphthol-condensed benzofurylfulgide **3** was synthesized and its photochromic properties as well as the change in other properties associated with photochromism were investigated. Like its indole analogue **1**, **3** showed diastereoselective photochromism. Change in CD spectra, on/off switching of fluorescence, and reversible change in pitch length of induced cholesteric liquid crystalline phase, were observed.

Keywords: photochromism; fulgide; binaphthol; diastereoselectivity; cholesteric liquid crystalline pitch; fluorescence

INTRODUCTION

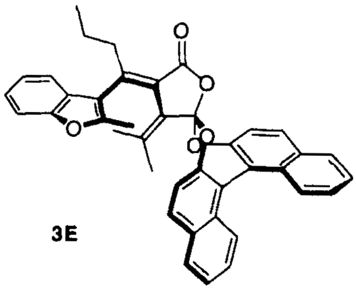
Diastereoselective Photochromism of Fulgide Derivatives

We have recently demonstrated that (*R*)-binaphthol-condensed indolylfulgides **1** and **2** showed diastereoselective photochromic reactions.[1,2] Chiroptical properties such as CD spectra and optical rotation values were changed reversibly upon irradiation of UV and visible light in solution or in polymer film media. In addition, fluorescent ability of **1** was changed in the ON/OFF mode.[3] The E-form did not emit light upon UV excitation in any wavelength region, while C-form emitted 640-nm fluorescence light by the excitation of either on visible region or on UV region. Also, **1** and **2** induced cholesteric phases when mixed with a nematic liquid crystal, and the cholesteric pitch values were changed dramatically by photochromic reactions.[4,5]



1 R = n-Pr
2 R = i-Pr

We here report the photochromic reaction of a propyl-substituted, (*R*)-binaphthol-condensed benzofurylfulgide **3**, and control of properties associated with the photochromism of **3**.



3E

RESULTS AND DISCUSSION

Synthesis of Binaphthol-condensed Benzofurylfulgide 3E

Benzofurylfulgide was synthesized with the traditional Stobbe condensation of 3-butanoyl-2-methylbenzofuran and dimethyl isopropyridenesuccinate employing lithum diisopropylamide as base followed by base hydrolysis and dehydrative acid anhydride formation, in 7 % yield from the benzofurylketone. Condensation of *(R)*-binaphthol was carried out as previously reported method,[1] to give **3E** in 33 % yield from the fulgide. Isolation of **3C** was done for 313-nm light irradiationd 1,2-dichloroethane solution of **3E** (36 %).

Diastereoselective Photochromism of 3

Investigation of ^{1}H NMR spectra of **3C** (λ_{max} 398 nm, ε_{max} 10850 mol^{-1} dm^{3}cm^{-1} in toluene) in chloroform-*d* indicated that **3C** was formed diastereoselectively. The integration of signals proved that the diastereomeric excess (de) was 88 %. Irradiation of >420 nm light to this solution generated **3E** (λ_{max} 313 nm, ε_{max} 19340 mol^{-1}dm^{3}cm^{-1} in toluene), and the successive irradiation of 313-nm light to this solution afforded 41/59 **3E/3C** mixture with the same de for **3C**. The absolute stereochemistry was assigned to be *S* because of the CD Cotton effect (*vide infra*).

Irradiation of 405-nm light to the UV-photostationary state solution of **3** caused complete restoration of **3E** again. The quantum yields of photoreactions are summarized in Table 1, and the absorption spectra of **3E** and **3C** are shown in Fig. 1.

TABLE 1. Quantum yields of photoreactions in toluene.

313 nm		405 nm
Φ_{EC}	Φ_{CE}	Φ_{CE}
0.18	0.15	0.17

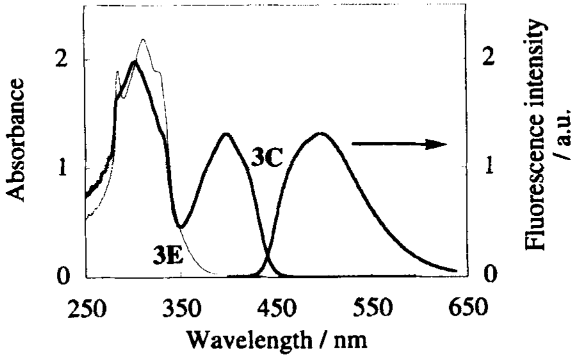


FIGURE 1. Absorption and fluorescence spectra of **3** in toluene. Concentration: 1.16 x 10^{-4} mol dm^{-3}. Excitation: 325 nm.

Change in Chiroptical Properties

The change in CD spectra by photoreactions was measured (Fig. 2). The Cotton effect of **3C** in the visible region was plus. Because those of indolylfulgide derivatives **1C** and **2C** were also plus, and the absolute stereochemistry of **2C** was unequivocally established by X-ray crystallographic analysis, the absolute stereochemistry of the stereogenic carbon atom of **3C** was determined to be *S*.

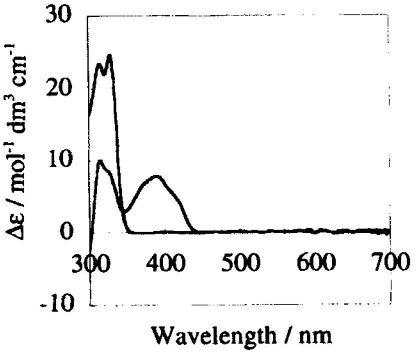


FIGURE 2. CD spectra of **3** in toluene.

The optical rotation values were also measured in toluene, and the data are shown in Table 2.

TABLE 2. Specific optical rotation values of **3** in toluene.

$[\alpha]_{820}$ / deg		$[\alpha]_D$ / deg		
3E$^{a)}$	**3C**$^{a)}$	**3E**$^{b)}$	PSS$^{b)}$	**3C**$^{b)}$
-211	-142	-457	-363	-160

a) c: 0.068 g / 100 cm^3 (27.1 °C). b) c: 0.068 g / 100 cm^3 (28.5 °C).

On-off Switching of Fluorescent Property

While **3E** does not emit fluorescent light, **3C** does in toluene. This property is the same as **1**. The fluorescent spectrum of **3C** excited by 325-nm light is shown in Fig. 1.

Change in Pitch of Cholesteric Liquid Crystals by Photochromism

We have reported that when **1** was doped in a nematic liquid crystal, a cholesteric phase was induced and the cholesteric pitch length[6,7] was changed reversibly by alternative irradiation of UV- and Vis-light. In the similar manner, when **3C** was mixed with a nematic liquid crystal (4-cyano-4'-pentylbiphenyl (5-CB)), a cholesteric phase was generated. While irradiation of 405-nm light increased the pitch length, irradiation of 313-nm light decreased the cholesteric pitch again (Table 3). The β_M-values (twisting power[8]) of **3E**, photostationary state, and **3C** are 10.8, 20.0, and 31.8 μm^{-1}, respectively.

TABLE 3. Change in cholesteric pitch of **3** – 5CB at 30.0 °C.

	Cholesteric pitch values / μm		
Concentration / (w/w %)	**3E**	PSS	**3C**
0.5098	10.9	6.33	3.48
0.5573	9.36	5.08	3.39
0.6653	8.29	4.29	2.80

Acknowledgments
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