Role of the Methoxy Substituents on the Photochromic Indolylfulgides. Absorption Maximum *vs.* Molar Absorption Coefficient of the Colored Form

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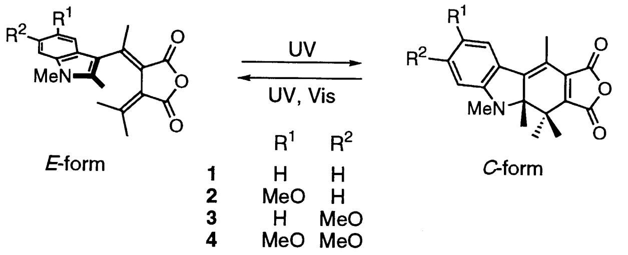
While the introduction of a methoxy group to C-5 of the indole ring of the indolylfulgide caused a large bathochromic shift of the absorption maximum of its colored form, introduction of a methoxy group to C-6 resulted in enlargement of the molar absorption coefficient of the colored form. The 5,6-dimethoxy-substituted indolylfulgide has both properties.

Fulgides such as **1** have been known as the representative of thermally irreversible photochromic compounds.[1] We have been studying the effects of electron-donating[2] and -withdrawing[3] groups on the indole ring of **1**, and have reported that the introduction of an electron-donating group, on the basis of the prediction of PPP-CI molecular orbital calculations, to C-5 of the indole ring resulted in the bathochromic shift of the absorption of the colored form.[2] This kind of modification, however, decreased the quantum yields of photoreactions,[2—4] and did not increase in the molar absorption coefficients of the absorption maxima of the colored forms. Since the rate of photoreaction depends on the product of molar absorption coefficient (ε), quantum yield (Φ), and irradiation-light intensity (I_0), enlargement of ε is just as important as the enlargement of Φ.[5—7] We here report that the introduction of a methoxy group to C-6 of the indole ring resulted in, independent of the effect of the methoxy group on C-5, enlargement of the molar absorption coefficient of the colored form.

Photochromic properties and absorption spectral properties of **2** were reported previously.[2] Synthesis of **3E** and **4E** were carried out as Scheme 1. Reaction of 2-methoxy-1,4-benzoquinone with 2-methylamino-2-penten-4-one gave 3-acetyl-5-hydroxy-6-methoxy-1,2-dimethylindole (**5**). Trifluoromethanesulfonylation (triflation) of 6-hydroxy group of **5** followed by the reduction by treating the triflate **6** with palladium(II) acetate and formic acid in the presence of triphenylphosphine and triethylamine in DMF[8] gave the corresponding 6-methoxyindolylketone **7**. Stobbe condensation of **7** with the cerium enolate[2,5,9] of dimethyl isopropylidenesuccinate followed by hydrolysis, dehydration, column chromatographic separation, and recrystallization afforded only the *E*-form of the 6-methoxyindolylfulgide **3** in 19 % yield for **7**. Methylation of **5**, in turn, gave the 3-acetyl-5,6-dimethoxy-1,2-dimethylindole **8**. The *E*-form of 5,6-dimethoxyindolylfulgide **4** was obtained in a similar manner in 12 % yield for **8**.



	R1	R2
1	H	H
2	MeO	H
3	H	MeO
4	MeO	MeO

The absorption spectroscopic data and decoloring quantum yields of **1**, **2**, **3**, and **4** are summarized in Table 1.

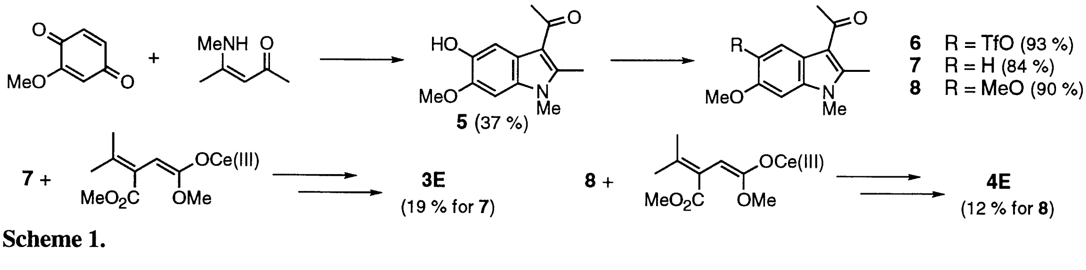
While the 5-methoxy group caused the bathochromic shift of the absorption of the colored forms, the 6-methoxy group increased their molar absorption coefficient values. Furthermore, the absorption bands of **2C** and **4C** in the visible region are wider than those of **1C** and **3C**.

According to PPP-CI calculations,[10] the LCAO coefficient of C-5 of HOMO is much larger than that of LUMO, whereas that of C-6 of HOMO is slightly smaller than that of LUMO (Figure 1). As the introduction of an electron-donating group to the atom with a large LCAO coefficient should push up the energy level, introduction of the electron-donating group on electron-rich C-5 might induce the bathochromic shift (corresponding to **2C**), and little change is expected for C-6 substitution (corresponding to **3C**). The tendency of the observed results was thus reproduced by the PPP-CI calculation. With regard to the molar absorption coefficient, however, the calculated oscillator strengths (*f*) are not consistent with the observation.

To the contrary, ZINDO calculation[11] for PM3-optimized conformation of the *C*-forms[12] predicted the large ε of C-6-methoxy-substituted colored forms **3C** and **4C**, while the calculated absorption maximum wavelengths were not in accord with the observed values.

Different from the spectroscopic properties of *C*-forms, those of *E*-forms were affected little. Slight tendency is that (i) either of the methoxy groups are effective to cause the bathochromic shift of the absorption maximum, (ii) C-5 methoxy group is effective to enlarge the molar absorption coefficient.

While the furylfulgides do not isomerize between *E*- and *Z*-forms thermally, indolylfulgides do at room temperature. This property is enhanced when electron-donating ability of the



Scheme 1.

Table 1. Absorption spectroscopic properties, calculation results, and quantum yields of decoloring reaction of fulgides **1**—**4** in toluene

	Observed λ_{max}/nm (ε_{max}/(mol^{-1} dm^3 cm^{-1}))		$(E+Z)$:C	PPP-CI of C-form	ZINDO of C-form	Quantum yield of visible
	E-form	C-form	at UV-pss[a]	λ_{max}/nm (f)[b]	λ_{max}/nm (ε_{max})	light irradiation (Φ_{CE})
1	385 (8150)	584 (6810)	44:56	603 (0.627)	419 (27200)	0.051[c]
2	393 (9530)	625 (7060)	30:70	630 (0.679)	419 (26900)	0.012[c]
3	397 (7790)	594 (10300)	47:53	601 (0.674)	426 (30100)	0.038[d]
4	396 (8820)	639 (11700)	25:75	623 (0.744)	429 (30200)	0.010[c]

[a] Photostationary state of 405-nm light irradiation. [b] Oscillator strength. [c] 608-nm light (Xenon lamp) irradiation. [d] 612-nm light (Xenon lamp) irradiation.

substituents attached on the indole ring becomes stronger.[3] Therefore, the quantum yields of UV-light irradiation were not determined. As for the decoloring quantum yield of the colored form by visible-light irradiation, C-5 methoxy group reduces it.

At the photostationary state of 405-nm light irradiation, the ratio of population is large for 5-methoxy-substituted fulgides **2C** and **4C**. It might be due to the small Φ_{CE} of UV-light irradiation that is parallel to the value of Φ_{CE} of visible-light irradiation.

In summary, introduction of a methoxy group to C-5 of the indole ring of the indolylfulgide is effective for the bathochromic shift of the absorption maximum of the colored form, whereas introduction of a methoxy group to C-6 resulted in enlargement of the molar absorption coefficient. Both effects are independent, therefore introduction of methoxy groups to C-5 and C-6 gave an indolylfulgide that exhibits both properties.

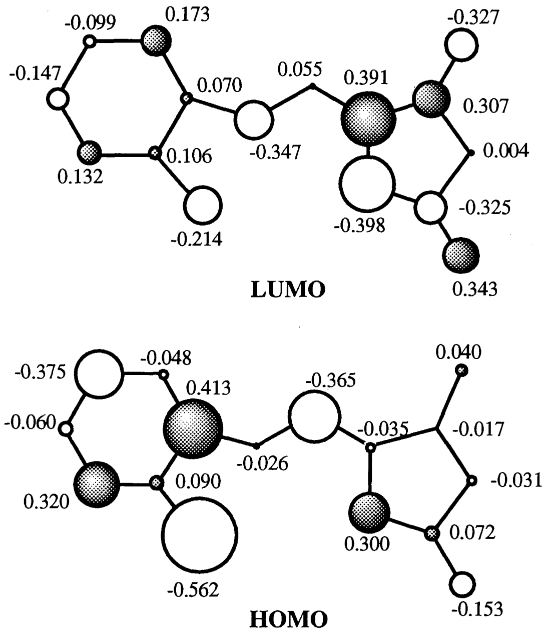


Figure 1. LCAO coefficients of LUMO and HOMO of **1C** (PPP-CI).

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References and Notes

1 J. Whittall, "Fulgides" in "Photochromism: Molecules and Systems," ed by H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam (1990).
2 Y. Yokoyama, T. Tanaka, T. Yamane, and Y. Kurita, *Chem. Lett.*, **1991**, 1125.
3 S. Uchida, Y. Yokoyama, J. Kiji, T. Okano, and H. Kitamura, *Bull. Chem. Soc. Jpn.*, **68**, 2961 (1995).
4 Y. Yokoyama, T. Yamane, and Y. Kurita, *J. Chem. Soc., Chem. Commun.*, **1991**, 1722.
5 Y. Yokoyama, T. Inoue, M. Yokoyama, T. Goto, T. Iwai, N. Kera, I. Hitomi, and Y. Kurita, *Bull. Chem. Soc. Jpn.*, **67**, 3297 (1994).
6 J. Kiji, T. Okano, H. Kitamura, Y. Yokoyama, and Y. Kurita, *Bull. Chem. Soc. Jpn.*, **68**, 616 (1995).
7 S. Uchida, S. Yamada, Y. Yokoyama, and Y. Kurita, *Bull. Chem. Soc. Jpn.*, **68**, 1677 (1995).
8 S. Cacchi, P. G. Ciattini, E. Morera, and G. Orter, *Tetrahedron Lett.*, **27**, 5541 (1986).
9 T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, and Y. Kamiya, *J. Am. Chem. Soc.*, **111**, 4392 (1989).
10 H. Kihara and S. Tokita, "PPP-PC," Maruzen, Tokyo (1989), was used as the software for PPP-CI calculations.
11 ZINDO calculations were done on a CAChe system.
12 J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209, 221 (1989). PM3 calculations were done on a CAChe system to give the most stable conformation, for which vibrational analysis ascertained its appropriateness.