Trifluoromethyl-substituted Photochromic Indolylfulgide. A Remarkably Durable Fulgide towards Photochemical and Thermal Treatments

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An indolylfulgide having a 1-(1,2-dimethyl-3-indolyl)-2,2,2-trifluoroethylidene group on the succinic anhydride showed an excellent resistivity towards the repetition of photochromic transformation between the photostationary states of UV- and visible-light irradiation both in toluene and in a PMMA film under the atmospheric environment. The colored form also showed the remarkable thermal stability.

Fulgides such as **1** and **2** have been regarded as the representative of thermally irreversible photochromic compounds.[1] However, the gigantic problem to be solved before applying them to the photofunctional materials is that their fatigue resistivity is not very excellent.[2,3] Once this defect should be overcome, a number of application possibilities will become close to the realization.[4] We here disclose the first finding how to give the fatigue resistivity to fulgides.

Although the photochemical decomposition pathways of the fulgide molecules are complicated and no major decomposition compound was obtained particularly in the presence of oxygen,[5] one major degradation path could be initiated with the hydrogen abstraction by the carbonyl oxygen in the excited state from the neighboring allylic carbon atom in a manner of antarafacial 1,5-sigmatropic rearrangement that is allowed for photochemical reactions. Abstraction of a hydrogen atom from the closely located carbon atom by the excited carbonyl group of a fulgide derivative was preceded.[6] Therefore a fulgide with no hydrogen on the alkyl group near the carbonyl group might be durable towards photochemical decomposition. On the basis of this hypothesis we planned to synthesize an indolylfulgide **3**, since the indolylfulgides had been known to be more durable to repetition of photochromic reactions and thermal decomposition than other heterocyclic fulgides.[2,7]

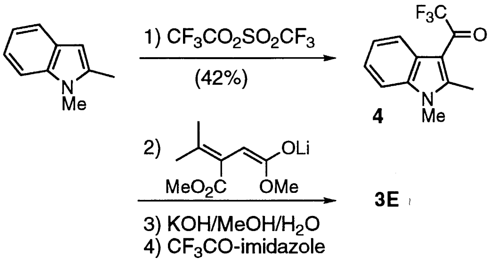
Synthesis of **3** was carried out as illustrated in Scheme 1. Treatment of 1,2-dimethylindole with trifluoroacetyl trifluoromethanesulfonate[8] in the presence of 2,6-di-*t*-butyl-4-methylpyridine in benzene below room temperature afforded 1,2-dimethyl-3-trifluoroacetylindole **4** in 42% yield. Stobbe condensation of **4** with dimethyl isopropylidenesuccinate followed by hydrolysis, dehydrative anhydride formation from the dicarboxylic acid, and purification with silica-gel thin layer chromatography afforded **3E**[9] in 3% yield for **4**. Photoreaction was done after recrystallization from ether-hexane mixture.

Properties of **3** concerning the photochromic reactions in toluene, determined by the methods as previously described,[10] are shown in Table 1, together with those of the indolylfulgide **1**. It is notable that the proportion of **3Z** at the photostationary state of UV-light irradiation (UV-pss) is much larger than that of **1Z**. This is ascribable to the small ε of **3Z** as well as small Φ_{ZE} value of UV-light irradiation. Since **3E** is rather unstable than **3Z** because the dipole moments of electron-withdrawing trifluoromethyl group and the adjacent carbonyl group that is also electron-withdrawing in **3E** are lying close and pointing to the same direction, Φ_{ZE} became relatively small.

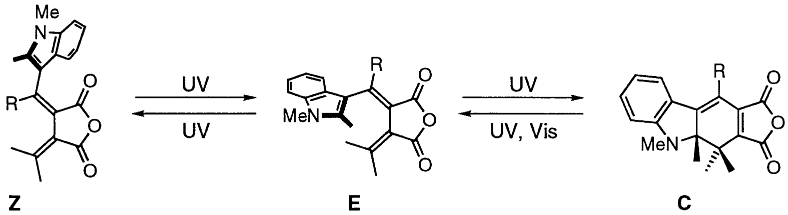
We carried out the repetition of photochromic transformation between the UV-pss and vis-pss in toluene and in a PMMA film.[11] After 300 times of repetition in toluene, no decrease of the absorption of the C-form of **3** was observed. Similar result was obtained in a PMMA film under the atmospheric circumstances. The absorbance of **3C** at UV-pss *vs.* number of repetition is plotted in Figure 1. After about 10^3 times of repetition, no decrease of absorbance of **3C** was observed. Results obtained by Tomoda *et al.* for the fulgides **1** and **2**, which decompose rather quickly,[2] are also shown in Figure 1.

The thermal stability of the UV-pss was also examined in a PMMA film.[11] As shown in Figure 2, after 10 days kept at 80 °C under the atmospheric condition, no decrease of the absorption of **3C** was observed. The increase in the absorption after the initial 2 days might be caused by the shrinkage of the polymer film.

In summary, the new indolylfulgide **3**, which has a trifluoromethyl group on the indolylmethylidene group instead of a methyl group of **1**, showed (i) the remarkably high fatigue resistivity towards the repetition of photochromic reactions, and (ii) the remarkably high resistivity towards the thermal decomposition of the colored form. These results confirmed that fulgides are now ready to be applied to the long-lasting photoswitchable functional materials, as the diarylethenes are.[12]

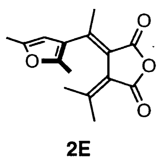


Scheme 1.



Z E C

1 R = CH_3
3 R = CF_3



2E

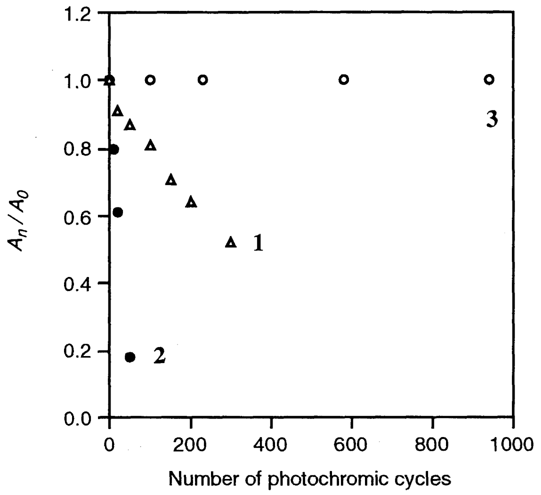


Figure 1. Photochemical fatigues of fulgides in PMMA.
1 and 2: Taken from reference 2.
3: See reference 11 for experimental conditions.
A_n: Absorbance of *C*-form after *n*th repetition of visible- and UV-light irradiation cycles. A_0: Absorbance of *C*-form obtained by irradiation of UV-light for the first time.

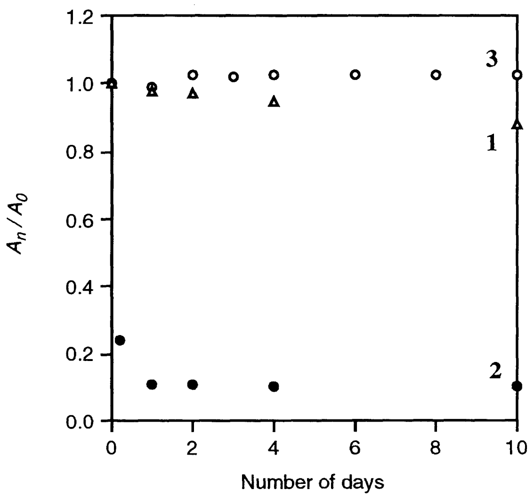


Figure 2. Thermal resistivity of fulgides in PMMA.
1 and 2: Taken from reference 2.
3: See reference 11 for experimental conditions.
A_n: Absorbance of *C*-form after *n*th days kept at 80 °C under the atmospheric condition in the dark. A_0: Initial absorbance of *C*-form.

Table 1. Absorption spectroscopic properties and quantum yields of photoreactions of indolylfulgides **1** and **3** in toluene

	λ_{max}/nm (ε_{max}/(mol^{-1} dm^3 cm^{-1}))			*E*:*Z*:*C*	UV irradiation				Vis irradiation
	E-form	*Z*-form	*C*-form	at UV-pss^a	Φ_{EC}	Φ_{CE}	Φ_{EZ}	Φ_{ZE}	Φ_{CE}
1	385 (6810)	397 (14300)	585 (7080)	35: 9:56	0.045	0.16	0.040	0.072	0.051^b
3	426 (4140)	432 (4200)	571 (7920)	23:44:33	0.14	0.26	0.034	0.040	0.042^c

^{a}Photostationary state of 405-nm light irradiation. ^{b} 608-nm light (Xenon lamp) irradiation. ^{c} 559-nm light (Xenon lamp) irradiation.

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References and Notes

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9 **3E**. Mp 141—2 °C; ^{1}H NMR (CDCl$_3$) δ = 0.98, 2.17, 2.28, 3.72 (each s, 3H), 7.12—7.31 (4H, m); IR (Nujol) 1775, 1740, 1551, 1187 cm^{-1}; MS (EI, 70 eV) *m/z* (rel intensity) 363 (M$^+$, 100), 297 (70), 222 (89), 172 (91). Found: *m/z* 363.1078. Calcd for $C_{19}H_{16}O_3NF_3$: 363.1082. The synthetic yield was not optimized.

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11 a) The conditions of repetition of photochromic reaction of **3** are as follows: In toluene; 1 x 10^{-5} mol dm^{-3}, cell length 1 cm. In PMMA; 9.5 x 10^{-4} mol dm^{-3}, film thickness 30 µm. UV light; 405 nm. Visible light; 559 nm. b) The experimental conditions of thermal resistivity of **3** in a PMMA film are as follows: 11.9 x 10^{-3} mol dm^{-3} in PMMA, film thickness 67 µm. Temperature; 80 °C.

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