Effect of Two Electron-Donating Substituents on Photochromism of Aryl Fulgide, 2-(2,6-Dimethyl-3,5-substituted benzylidene)-3-isopropylidenesuccinic Anhydride

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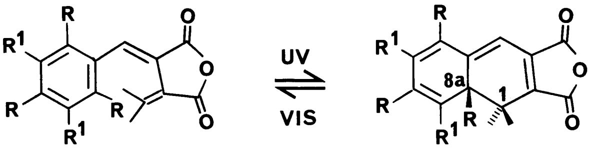
Two electron-donating substituents (e.g. *p*-diethylaminostyryl) were introduced to an aryl structure of fulgide and photochromic performance was investigated. It was found that the strong electron-donating ability of the substituents caused a significant red shift of the colored form to the near-infrared region (λ_{max}; 633 nm), resulting in a high molecular extinction coefficient (ε_{max}; 24300 mol^{-1} cm^{-1}). Furthermore, rapid reactions of both coloration and discoloration were observed; the quantum yields (ϕ_{EC} and ϕ_{CE}) were 0.65 and 0.052, respectively.

Recently, work on organic photochromic compounds has been animated because of their high potential as a data-storage media. Photochromic compounds including spirobenzopiran derivative have been studied in depth. However, the colored form has usually exhibited thermal bleaching and the performance has often been associated with data-storage instability.

Photochromic "fulgide" is a derivative of 2,3-bis(methylene)succinic anhydride with at least one aryl group. Heller[1] has promoted the study of photochromic fulgide since the 1970's and exemplified that a structure of fulgide which was designed by the Woodward–Hoffman selection rules was effective in improving the thermal stability of the colored state. First, they revealed that a mesityl structure in place of a phenyl derivative of fulgide, (*E*)-2-isopropylidene-3-(mesitylmethylene)succinic anhydride, caused a steric interaction between the **1** and **8a** methyl groups of the colored form, 1,8a-dihydro-1,1,5,7,8a-pentamethylnaphthalene, which inhibited thermal electro-cyclic ring opening and significantly improved thermal stability (Scheme 1, a). This meant that it was possible to preserve data over a long period of time, and raised the possibility of using organic photochromic compounds as data storage media. After that, a hetero-aromatic structure, e.g. furyl, was introduced to a derivative of fulgide, (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride and a higher coloration quantum yield (ϕ_{EC}=0.20) on irradiation with 366 nm light was obtained.

In previous studies,[2] various heterocyclic derivatives of fulgides were prepared and the relationship between chemical structure and photochromic properties, e.g. thermal stability or photochemical fatigue resistance in poly(methyl methacrylate) film, was clarified. Further, an electron-donating substituent, e.g. *p*-dimethylaminophenyl was introduced to the oxazole structure of fulgide, (*E*)-2-[1-(5-methyl-2-*p*-dimethylaminophenyl-4-oxazolyl)ethylidene]-3-isopropylidenesuccinic anhydride and the effect of the substituent on photochromism was investigated. The results implied that the effect involved a significant increase in absorption intensity and a red shift of the colored fulgide.[3] In this paper, we report the effect of the introduction of two electron-donating substituents on the photochromism of the mesityl derivative of fulgide.



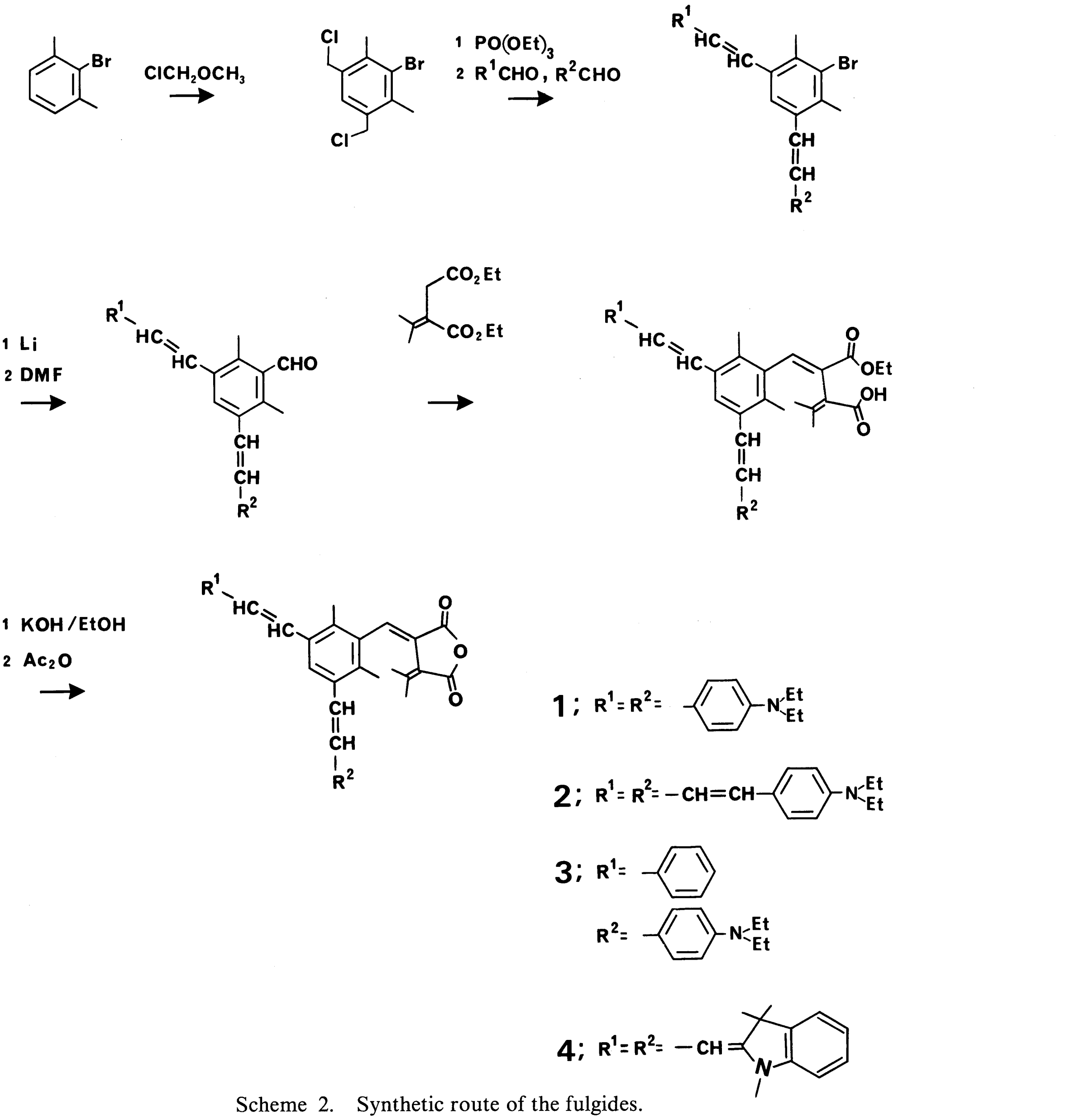
Scheme 1. Photochromism of the aryl derivatives of fulgide (a; R=CH$_3$, R^1=H, b; R=H, R^1=OCH$_3$).

Results and Discussion

Synthesis of Fulgides. Scheme 2 illustrates the synthetic route and structures of the novel fulgides **1**—**4**. First, in the presence of sulfuric acid as a catalyst, 2-bromo-*m*-xylene was chloromethylated by reaction with chloromethyl methyl ether to give 2-bromo-4,6-bis(chloromethyl)-*m*-xylene. The chloride was then converted into a diethyl phosphate derivative by the usual manner[4] and reacted with *p*-diethylaminobenzaldehyde to give 2-bromo-4,6-bis(*p*-diethylaminostyryl)-*m*-xylene. The bromide was lithiated with butyl lithium and treated with dimethylformamide (DMF) in situ at −70 °C and 3,5-bis(*p*-diethylaminostyryl)-2,6-dimethylbenzaldehyde was obtained.

According to the method described in the literature,[5] a Stobbe condensation reaction of the aldehyde and diethyl 3-isopropylidene succinate in the presence of lithium diisopropylamide (LDA) gave a half ester. The ester was then hydrolyzed with 10% ethanolic potassium hydroxide and dehydrated in acetic anhydride to give fulgide **1**. Fulgides **2**—**4** were also produced by a similar synthetic route (Scheme 2).

Absorption Spectra and Photochromic Properties. Figure 1 illustrates the absorption spectra of fulgide **1** in a dilute toluene solution (5×10^{-5} mol dm^{-3}) and their change on irradiation with UV (a) and vis light (b). A



Scheme 2. Synthetic route of the fulgides.

photostationary state (pss) of coloration was attained by 366 nm light irradiation in 60 s and the pale yellow color changed to blue. The absorption maxima of colored fulgide was located at 633 nm and the cut off wavelength was 850 nm. Subsequent irradiation of the solution of colored fulgide **1** with vis light (>500 nm) caused bleaching reaction in 30 s. NMR measurements of the photochromic reaction of fulgide **1** in C_6D_6 solution (1.7×10^{-2} mol dm^{-3}) indicated that 91% of the fulgide was converted into a colored form, e.g. a ring-closure structure, with UV light irradiation. Uncolored fulgide was recovered quantitatively (100%) with vis light irradiation.

In Fig. 2, a similar absorption spectra change of fulgide **3** which featured two different substituents on the aryl structure, e.g. *p*-diethylaminostyryl and styryl, is shown. It would be expected that the unsymmetrical structure of the aryl group of the fulgide would produce two different colored forms with UV light irradiation. In the coloration reaction, however an isosbestic point was observed at 400 nm and it was suggested that one coloration reaction occurred selectively.

Figure 3 illustrates the absorption spectra of colored fulgides **1**, **2**, and **4** in dilute toluene solution and the absorption spectra properties are summarized in Table 1. All colored fulgides had a sensitivity in the near-infrared region. Particularly, a significant red shift of colored fulgide **4** was observed and the spectra showed that a susceptibility at semi-conductor laser oscillation wavelengths (780 and 830 nm) was acquired. In previous papers,[2,3] we clarified that the absorption maxima of a colored heterocyclic derivative of fulgide tended to red shift with an increase of the electron-donating ability of the heterocyclic group, and thus the absorption, e.g. the electronic transition of the colored form involved intra-

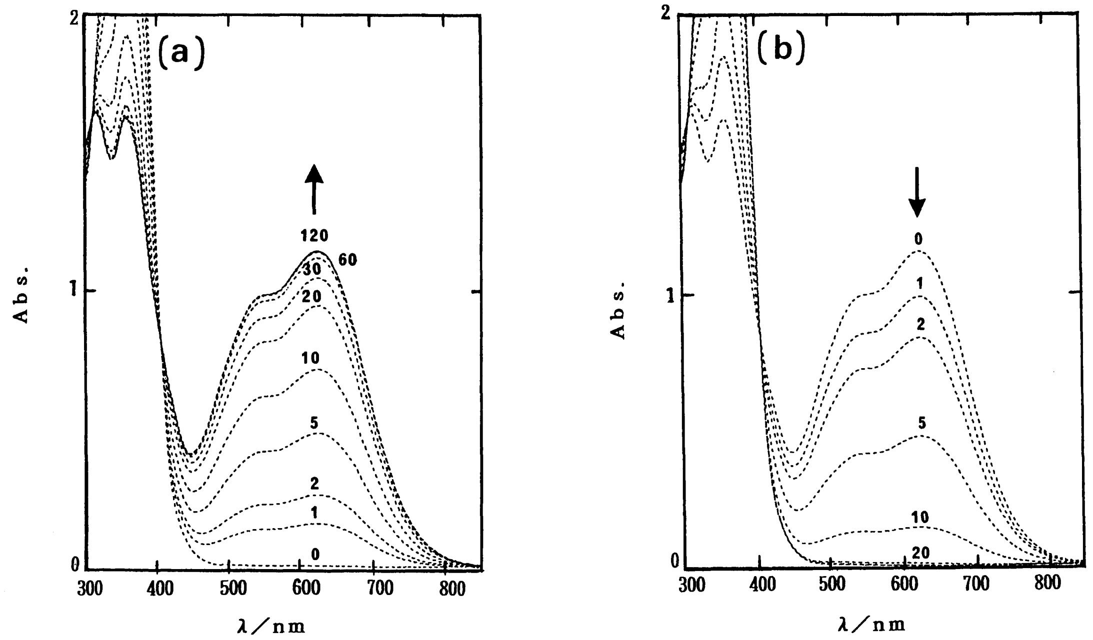


Fig. 1. Absorption spectra change of fulgide **1** by irradiation with 366 nm light (a) and visible light (>500 nm) (b). Absorption curves in the visible region refer to colored forms after 0 to 120 s irradiation with UV light (a) and 0 to 20 s irradiation with visible light (b).

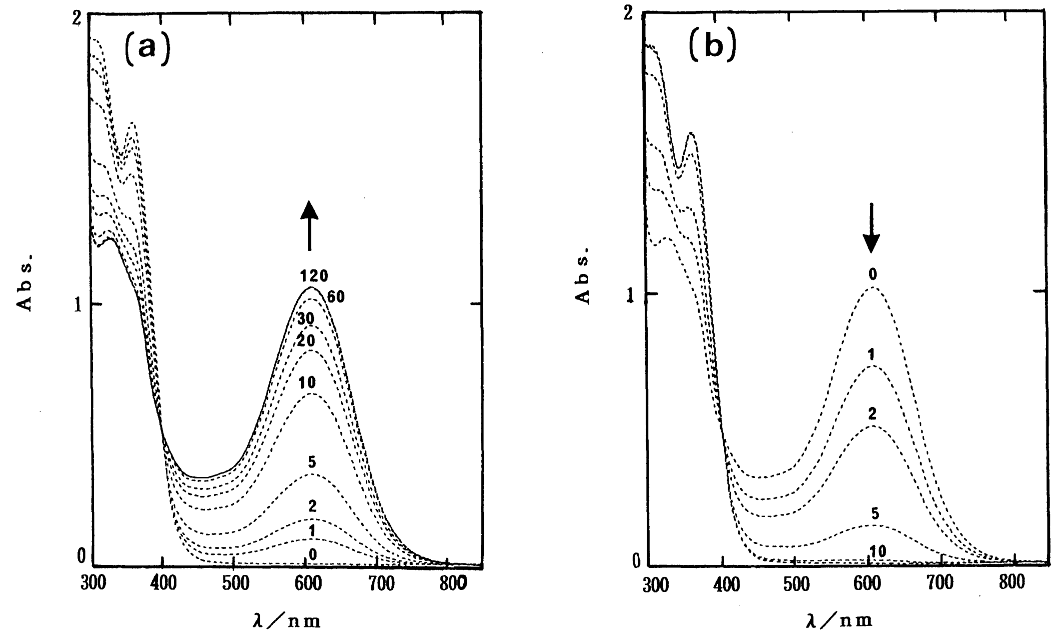


Fig. 2. Absorption spectra change of fulgide **3** by irradiation with 366 nm light (a) and visible light (>500 nm) (b). Absorption curves in the visible region refer to colored forms after 0 to 120 s irradiation with UV light (a) and 0 to 10 s irradiation with visible light (b).

molecular electron migration from the heteroatoms to the carbonyls. In this work, the observed bathochromic shifts were also attributable to the strong electron-donating ability of the aryl strcture in which two powerful electron-donating substituents are positioned in conjugation with the main chromophore of the colored fulgide molecule.

The molecular extinction coefficient of the colored form of fulgide **1** in toluene solution was determined by NMR measurement and was 24300 $M^{-1}\,cm^{-1}$ (1 M= 1 mol dm^{-3}) which was about four times as much as of that of a 3,5-dimethoxyaryl derivative of fulgide, e.g. 2-

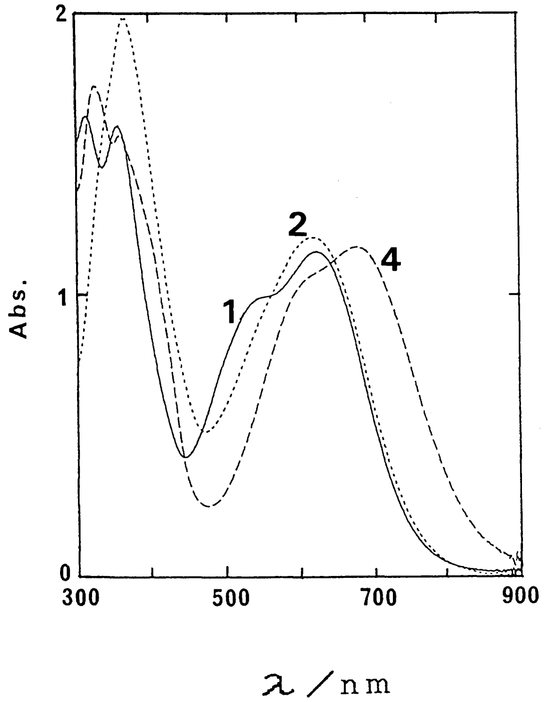


Fig. 3. Absorption spectra of colored fulgides **1**, **2** and **4** in toluene (5×10^{-5} mol dm^{-3}) after UV light irradiation to pss.

Table 1. Absorption Properties of Fulgides in Toluene Solution

Fulgide	E[a)]	C
	λ_{max}/nm	λ_{max}/nm
1	366	633
2	382	618
3	361	610
4	368	678

a) The fulgides in toluene solution (5×10^{-5} mol dm^{-3}) were previously converted to colored forms by irradiation with UV light to pss and were reversed to uncolored E-forms by subsequent irradiation with visible light.

(3,5-dimethoxybenzylidene)-3-isopropylidenesuccinic anhydride (Scheme 1, b). The significant increase of the absorption intensity implies the improvement of optical disk read-out sensitivety and is also an important characteristic in obtaining an efficient read-out signal.[6)]

Figure 4 illustrates the absorption spectra of colored fulgide **1** in various solvents after an exposure of UV light to pss. In hexane and toluene, the fulgide was markedly photochromic and a large absorption spectra change was acquired. However, the photochromic property was very weak in polar solvents, e.g. ethyl acetate and acetonitrile; the coloration reaction was significantly dependent upon the polarity of the solvent. On the other hand, Kurita et al.[7)] reported that the quantum yield for coloration of the 3-furyl derivative of fulgide was not as affected by the kind of solvent, e.g. ϕ_{EC} was 0.18, 0.20, and 0.17 in toluene, ethyl acetate and acetonitrile, respectively. The observed significant dependence of fulgide **1** on the solvent was presumably due to the strong electron-donating ability of the two *p*-diethylaminostyryl groups which increased the polarity of the aryl moiety of the fulgide; the structure of the fulgide was readily stabilized by the polar solvent.

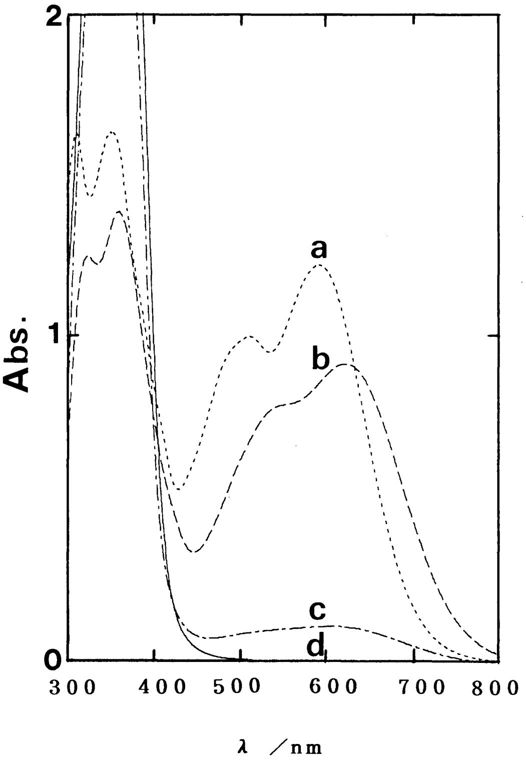


Fig. 4. Absorption spectra of fulgide **1** after UV light irradiation to pss in various solvents (5×10^{-5} mol dm^{-3}, a; hexane, b; toluene, c; ethyl acetate, d; acetonitrile).

Photo-Responsiveness of Fulgides. Figure 5 illustrates the photo-responsiveness for coloration of fulgides **1**—**4** in dilute toluene solution (1×10^{-4} mol dm^{-3}) which absorbs 99.9% of UV light (366 nm); the absorption change was monitored at the λ_{max} of the various colored fulgides. The coloration rate increased in the following order: **1**=**2**>**3**>**4** and the quantum yield (ϕ_{EC}) of fulgide **1** was 0.65. Again, Kurita et al.[8)] prepared a bulky substituent, e.g. an isopropyl-introduced 3-furyl derivative of fulgide, (*E*)-2-[1-(2,5-dimethyl-3-furyl)-3-methylpropylidene]-3-isopropylidenesuccinic anhydride, in the position β to the carbonyl in place of the methyl, and successfully obtained a higher ϕ_{EC} (0.18 to 0.58). They explained that the high efficiency of the cyclization reaction was due to steric repulsion between the bulky isopropyl and isopropylidene group, which inhibited the undesired *E*–*Z* isomerization. On the other hand, Heller et al.[9)] and Illge et al.[10)] independently studied the relationship between the quantum yield for coloration and the structure of methoxyphenyl derivative of fulgide

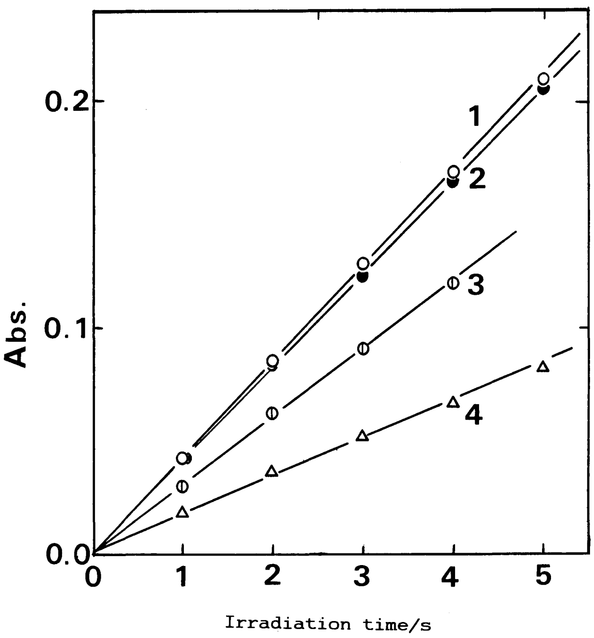


Fig. 5. Photo-coloration of fulgides **1**—**4** in toluene solution (1×10^{-4} mol dm^{-3}). A UV light beam was irradiated on the solution which absorbed 99.9% of 366 nm light and the absorption change was monitored at the $\lambda_{\max}$ of colored fulgides.

Table 2. Quantum Yields for Discoloration of Fulgide **1** in Toluene Solution

λ/nm[a)]	ϕ_{CE}
556	0.052
591	0.052
603	0.052
634	0.052
705	0.042
732	0.028

a) Wavelength of irradiation light beam for the discoloration reaction.

Table 3. Photochemical Fatigue of Fulgides in Toluene Solution

Fulgide	Photochemical fatigue[a)]		
	Cycle	$(A_0-A_n)/A_0$	PF/%
1	500	0.45	0.09
2	500	0.51	0.10
3	300	0.66	0.22
4	100	0.67	0.67

a) PF=$(A_0-A_n)/nA_0$, as a measure for photochemical fatigue, where n is the number of repeated cycles, e.g. coloration and discoloration of dilute toluene solutions of the fulgides (5×10^{-5} mol dm^{-3}).

(Scheme 1, b) and reported that the sensitivity to coloring was increased by methoxy groups at both the 3- and 5-position of ary structure; ϕ_{EC} was changed from $<10^{-3}$ to 0.085. It can be speculated that the high ϕ_{EC} of fulgide **1** in this work is caused by the strong electron-donating ability of the two *p*-diethylaminostyryl groups. Furthermore, a lower bleaching rate of fulgide **3** in comparison with **1** is also attributable to the difference in the electron-donating ability between the substituents, e.g. *p*-diethylaminostyryl and styryl. In the excited state of the colored fulgide, it has been suggested that a higher delocalization of electrons over the molecule occurred because of the electron-migration from the aryl to the carbonyls;[2,11)] the polar state was more stabilized, particularly by the strong electron-donating substituents, e.g. *p*-diethylaminostyryl, than the excited state of the uncolored fulgide and the resulting energy gap between the two states lead to an increase of ϕ_{EC}.

The quantum yields for the discoloration reaction of fulgide **1** in dilute toluene solution (5×10^{-5} mol dm^{-3}) by vis light (634 nm) irradiation was 0.052. The quantum yields at various irradiation wavelengths are summarized in Table 2. In a previous paper,[3)] we investigated the effect of similar substituents of 4-oxazolyl derivatives of fulgide, e.g. 2-[1-(5-methyl-2-*p*-dimethylaminostyryl-4-oxazolyl)ethylidene]-3-isopropylidenesuccinic anhydride, on the discoloration reaction and reported that the replacement of the substituent on the heteroaromatic ring, from phenyl to *p*-dimethylaminostyryl, exhibited a significant decrease of ϕ_{CE} (0.054 to 0.00019). To the contrary, the aryl derivative of fulgide **1** still exhibits a high bleaching rate in spite of the presence of two *p*-diethylaminostyryl groups and this implies that it may be possible to record on an optical fulgide disk with low power, a high-frequency laser and high speed spinning of the disk.

Photochemical Fatigue and Thermal Stability. Reversibilities of fulgides **1**—**4** for the coloration–discoloration cycles were measured in dilute toluene solution (5×10^{-5} mol dm^{-3}) in the presence of air. As listed in Table 3, relative photochemical fatigue (PF=$(A_0-A_n)/nA_0$) was evaluated, where A_0 and A_n are the absorbance values at pss attained on the 1st and nth cycles of coloration. Fulgides **1** and **2** showed excellent fatigue resistance, while **3** and **4** showed fairly good and poor resistance, respectively. The fatigue resistance of fulgides **1**—**4** are related to the responsiveness to coloration as shown in Fig. 5, i.e. the fatigue is dependent on the time of exposure to UV light.

On the other hand, the colored fulgides **1**—**4** showed excellent thermal stability in toluene solution (5×10^{-5} mol dm^{-3}). The solution of fulgide was previously irradiated with UV light to pss and the absorption spectra change at room temperature in the dark was monitored. Two months later, no spectra change was observed and the solution exhibited the same photochromic performance.

In conclusion, two electron-donating substituents were successfully introduced to the aryl derivative of fulgide and the absorption of the colored form showed a significant red shift to the near-infrared region with a high molecular extinction coefficient. Furthermore, the substituents also caused a remarkable increase in the coloration rate, while at the same time, the bleaching rate was still fairly good.

Experimental

UV and ^{1}H NMR spectra were measured with a Hitachi U-3200 spectrophotometer and 60- and 90-MHz spectrometers (JEOL JNM-PMX60 and EX-90 NMR). A mercury lamp (Ushio, 250 W) and a xenon lamp (Ushio, 300 W) were used as light sources for the coloration and discoloration reactions, respectively. A mercury line at 366 nm (ca. 50 mJ) and a visible light beam were isolated by passing the light through glass filters (UV light; Toshiba UV-D36C and UV-35, visible light; 0—50). Qunatum yields for coloration were determined by measuring the rate of the photoreaction,[5,12] which was carried out in a toluene solution (coloration; 1×10^{-4} mol dm^{-3}, discoloration; 5×10^{-5} mol dm^{-3}) by irradiation with UV and visible light isolated through glass filters (visible light; 556 nm/Toshiba 0—54 and KL-55, 591 nm/0—58 and KL-58, 603 nm/R-60 and KL-60, 634 nm/R-60 and KL-63, 705 nm/R-68 and KL-70, 732 nm/R-72 and KL-73). The light intensity of visible and UV light was measured with a power meter AQ2710 (ANDO) and chemical actinometer (3-furyl derivative of fulgide), respectively. The photochemical fatigue of the fulgides was investigated by measurements of the absorption spectra change of the colored fulgide. In the presence of air, toluene solutions of fulgide (5×10^{-5} mol dm^{-3}) were irradiated with UV and visible light, alternately, using a photo-irradiater cycle test systems (OMROM). For the measurement of thermal stability, a dilute toluene solution of fulgide (5×10^{-5} mol dm^{-3}) was prepared. After the coloration to pass with UV light, the solution was stored in the dark at room temperature and the absorption spectra change at $\lambda_{\max}$ was monitored.

Materials. Fulgides **1**—**4** were prepared by Stobbe condensation of 2,6-dimethyl-3,5-bis(substituted)benzaldehyde with diethyl 2-isopropylidene succinate using lithium diisopropylamide as a base; this was followed by hydrolysis and dehydration reactions. Yields, physical constants, and analytical data are summarized in Table 4.

2-Bromo-4,6-bis(chloromethyl)-*m*-xylene. Sulfuric acid (25 g) was added to an ice cooled mixture of 2-bromo-*m*-xylene (78 g, 0.42 mol) and chloromethyl methyl ether (75 g, 0.93 mol) with stirring. After the solution was further stirred for 1 night at room temperature, the mixture was poured onto crushed ice. The resulting oil was extracted with chloroform and the organic layer was washed with water and dried over anhydrous magnesium sulfate. After removing the solvent, the resulting white solid was recrystallized from hexane and 43 g (0.15 mol, 36%) of 2-bromo-4,6-bis(chloromethyl)-*m*-xylene was obtained. Mp 113—117 °C; ^{1}H NMR (CDCl$_3$) δ=2.36 (s, 6H), 4.53 (s, 4H), 6.75 (s, 1H).

2-Bromo-4,6-bis(*p*-diethylaminostyryl)-*m*-xylene. The dichloride above was readily converted to a diethyl phosphate derivative by the usual method.[4] A mixture of the diethyl phosphate derivative (29 g, 0.070 mol) and *p*-diethylaminobenzaldehyde (25 g, 0.14 mol) was added dropwise to a solution of sodium hydride (60% suspension in oil, 5.4 g, 0.14 mol) and 160 ml of 1,2-dimethoxyethane at room temperature. The reaction mixture was warmed to 60 °C with stirring. When gas evolution ceased, the solution was refluxed for half an hour, and then poured onto crushed ice. The resulting solid was collected by filtration and washed with water. Recrystallization from benzene–ethanol gave 22.7 g (0.043 mol, 61%) of 2-bromo-4,6-bis(*p*-diethylaminostyryl)-*m*-xylene. Mp 154—156 °C; ^{1}H NMR (CDCl$_3$) δ=1.18 (t, 12H), 2.52 (s, 6H), 3.38 (q, 8H), 6.67 (d, 2H), 7.05 (d, 2H), 7.24—7.64 (m, 9H).

2,6-Dimethyl-3,5-bis(*p*-diethylaminostyryl)benzaldehyde. 16 ml of a hexane solution of butyl lithium (1.6 mol dm^{-3}) was added dropwise at −70 °C under nitrogen to a solution of 2-bromo-4,6-bis(*p*-diethylaminostyryl)-*m*-xylene (10 g, 0.019 mol) in 150 ml THF and stirred for 20 min. 5 ml of DMF was then added, the reaction mixture was further stirred for 2 h at room temperature and poured onto ice-cooled water. The resulting oil was extracted with benzene, washed with water, and dried over anhydrous magnesium sulfate. The benzene solution was evaporated and the pale yellow solid was recrystallized from benzene–methanol to give 8.4 g (0.018 mol, 95%) of 2,6-dimethyl-3,5-bis(*p*-diethylaminostyryl)benzaldehyde. Mp 168—169 °C; ^{1}H NMR (CDCl$_3$) δ=1.18 (t, 12H), 2.53 (s, 6H), 3.40 (q, 8H), 6.67 (d, 2H), 6.86 (d, 2H), 7.04—7.85 (m, 9H), 10.7 (s, 1H).

2-[2,6-Dimethyl-3,5-bis(*p*-diethylaminostyryl)benzylidene]-3-isopropylidenesuccinic Anhydride; Fulgide 1. Diethyl 2-isopropyllidene succinate (1.5 g, 69 mmol) was added at −70 °C to a THF solution of lithium diisopropylamide, which was freshly prepared from diisopropylamine (2.1 ml), 2,2′-bipyridyl (15 mg) and butyl lithium hexane solution (16 ml) in THF (150 ml). The mixture was then stirred for 30 min, and 2,6-dimethyl-3,5-bis(*p*-diethylaminostyryl)benzaldehyde (3.0 g, 63 mmol) was added. The solution was warmed to room temperature and further stirred for 1 h. The reaction mixture was then poured onto ice-cooled water and acidified with 6 M (1 M=1 mol dm^{-3}) HCl. The solution was extracted with ether, dried over abhydrous magnesium sulfate, and the solvent

Table 4. Yields, Physical Constants, and Analytical Data of Fulgides

Fulgide	Yield	Mp	^{1}H NMR, δ in CDCl$_3$		Found (Calcd)/%			m/z
	%	θ_m/°C	–CH$_3$ (3H, s)	–CH= and others	C	H	N	M$^+$
1Z	20	211—213	2.28 (6H) 2.40 2.62 1.20 (12H, t)	3.40 (8H, q) 6.60—7.80 (14H, m)	79.47 (79.70)	7.70 (7.69)	4.70 (4.65)	603
2Z	13	137—139	2.22 (6H) 2.36 2.58 1.17 (12H, t)	3.38 (8H, q) 6.59—7.71 (17H, m)	80.64 (80.70)	8.17 (7.71)	4.35 (4.28)	
3Z	14	193—194	2.28 (6H) 2.40 2.61 1.18 (6H, t)	3.43 (4H) 6.63—7.60 (14H, m)	80.50 (81.32)	7.02 (7.76)	2.64 (2.63)	531
4Z	14	164—169	1.66 (6H) 2.23 (6H) 2.39 2.61 3.13 (6H)	5.50 (2H, d) 6.42—7.67 (14H, m)	80.82 (81.20)	7.12 (7.12)	4.13 (4.30)	651

was removed. The oily product was mixed with 10% ethanolic potassium hydroxide (30 ml) and boiled for 3 h. After cooling, the mixture was poured onto water, acidified with 6 M HCl and extracted with ether. After drying, the solvent was removed and the resulting dicarboxylic acid was boiled with acetic anhydride. After removing the solvent, 0.70 g of fulgide **1** was purified by recrystallization from chloroform-hexane.

2-Bromo-4,6-bis[4-(*p*-diethylaminophenyl)-1,3-butadienyl]-*m*-xylene. A Wittig reaction of *p*-diethylaminocinnamaldehyde (5.0 g, 0.025 mol) and the diethyl phosphate derivative (5.2 g, 0.0125 mol) by the method described above for the synthesis of 2-bromo-4,6-bis(*p*-diethylaminostyryl)-*m*-xylene, gave 1.5 g (0.0026 mol, 21%) of 2-bromo-4,6-bis[4-(*p*-diethylaminophenyl)-1,3-butadienyl]-*m*-xylene. Mp 214—216 °C; ^{1}H NMR ($CDCl_3$) δ=1.17 (t, 12H), 2.49 (s, 6H), 3.38 (q, 8H), 6.59—7.60 (m, 17H).

2-[3,5-Bis(1-*p*-diethylaminophenyl)-1,3-butadienyl]-2,6-dimethyl benzylidene-3-isopropylidenesuccinic Anhydride; Fulgide 2. 2-Bromo-4,6-bis[4-(*p*-diethylaminophenyl)-1,3-butadienyl]-*m*-xylene was converted into 3,5-bis[4-(*p*-diethylaminophenyl)-3,5-butadienyl]-2,6-dimethylbenzaldehyde. 0.13 g of fulgide **2** were obtained by Stobbe condensation reaction of the benzaldehyde (0.80 g, 1.5 mmol) and diethyl 2-isopropylidene succinate (0.40 g, 1.8 mmol) by the method described for fulgide **1**.

2-Bromo-4-(*p*-diethylaminostyryl)-6-styryl-*m*-xylene. A Wittig reaction of the diethyl phosphate derivative (1.35 g, 12.5 mmol), benzaldehyde (1.35 g, 12.5 mmol) and *p*-diethylaminobenzaldehyde (2.2 g, 12.5 mmol) gave 1.50 g (3.3 mmol, 26%) of 2-bromo-4-(*p*-diethylaminostyryl)-6-styryl-*m*-xylene. Mp 138—139 °C; ^{1}H NMR ($CDCl_3$) δ=1.18 (t, 6H), 2.53 (s, 6H), 3.38 (q, 4H), 6.62—7.65 (m, 14H).

3-(*p*-Diethylaminostyryl)-2,6-dimethyl-5-styrylbenzaldehyde. The bromide above (1.50 g, 3.3 mmol) was formylated by reaction with butyl lithium and DMF, and gave 3-(*p*-diethylaminostyryl)-2,5-dimethyl-5-styrylbenzaldehyde (0.70 g, 1.7 mmol, 52%). Mp 155—156 °C; ^{1}H NMR ($CDCl_3$) δ=1.19 (t, 6H), 2.54 (s, 6H), 3.35 (q, 4H), 6.63—7.86 (m, 14H), 10.7 (s, 1H).

2-[2,6-Dimethyl-3-(*p*-diethylaminostyryl)-5-styrylbenzylidene]-3-isopropylidenesuccinic Anhydride; Fulgide 3. A Stobbe condensation of the aldehyde (0.70 g, 1.7 mmol) and diethyl 2-isopropylidenesuccinate (0.50 g, 2.3 mmol) by the method described for fulgide **1** gave 0.12 g of fulgide **3**.

2-Bromo-4,6-bis[3-(1,3,3-trimethyl-2,3-dihydro-2-indolylidene)-1-propenyl]-*m*-xylene. A Wittig reaction of the diethy phosphate derivative (8.4 g, 20 mmol) and 2-(1,3,3-trimethyl-2,3-dihydro-2-indolylidene)acetaldehyde (8.0 g, 40 mmol) gave 4 g (6.9 mmol, 35%) of 2-bromo-4,6-bis[3-(1,3,3-trimethyl-2,3-dihydro-2-indolylidene)-1-propenyl]-*m*-xylene. Mp 245—248 °C; ^{1}H NMR ($CDCl_3$) δ=1.65 (s, 12H), 2.49 (s, 6H), 3.14 (s, 6H), 5.50 (d, 2H), 6.43—7.55 (m, 13H).

2,6-Dimethyl-3,5-bis[3-(1,3,3-trimethyl-2,3-dihydroindolylidene)-1-propenyl]benzaldehyde. The bromide above (3.50 g, 6.0 mmol) was formylated by reaction with 5.1 ml of a hexane solution of butyl lithium and 2 ml of DMF, and gave 2,6-dimethyl-3,5-bis[3-(1,3,3-trimethyl-2,3-dihydro-2-indolylidene)-1-propenyl]benzaldehyde (1.20 g 2.3 mmol, 38%). Mp 237—239 °C; ^{1}H NMR ($CDCl_3$) δ=1.66 (s, 12H), 2.49 (s, 6H), 3.15 (s, 6H), 5.50 (d, 2H), 6.56—7.76 (m, 13H), 10.7 (s, 1H).

Fulgide 4. A Stobbe condensation of the aldehyde above (1.70 g, 3.2 mmol) and diethyl 2-isopropylidenesuccinate (0.76 g, 3.5 mmol) by the method described for fulgide **1** gave 0.29 g of fulgide **4**.

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