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Diastereoselective Photochromism of an (*R*)-Binaphthol-Condensed Indolylfulgide

Yasushi Yokoyama,[*,†] Soichi Uchida,[†,‡] Yayoi Yokoyama,[§] Yoko Sugawara,[‖] and Yukio Kurita[†]

Contribution from the Department of Materials Chemistry, Faculty of Engineering, Yokohama National University, Yokohama 240, Japan, Faculty of Home Economics, Tokyo Kasei Gakuin University, Machida, 194-02, Japan, and School of Science, Kitasato University, Sagamihara 228, Japan

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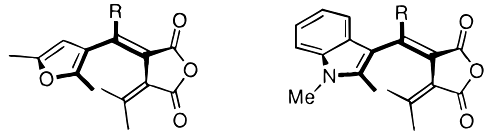
Abstract: Two new thermally irreversible photochromic (*R*)-binaphthol-condensed indolylfulgides (with a 1-(1,2-dimethyl-3-indolyl)-2-methylpropylidene group and with a 1-(1,2-dimethyl-3-indolyl)butylidene group, **6** and **7**, respectively) were synthesized. Because of rapid thermal equilibration between the conformational isomers of **7E** at room temperature, photocyclization of a substantial portion of **7E** occurred through (*P*)-**7E**α to give (9a*S*)-**7C** selectively. On the other hand, as thermal equilibration requires a long time for **6E** at room temperature, its photochromic interconversion occurs only between (*P*)-**6E**α and (9a*S*)-**6C**, and the photocyclization-inert **6E** remained unchanged. The thermal stability and fatigue resistivity toward the iterative photochromic interconversion of **7** have been proved to be excellent among the fulgide derivatives. The photochromic reactions were accompanied by large changes of specific rotation values. The X-ray crystallographic analysis of a visible-light-sensitive colored form, (9a*S*)-**6C**, was carried out.

Since Heller's synthesis of 3-[1-(2,5-dimethyl-3-furyl)ethylidene]-4-isopropylidenedihydrofuran-2,5-dione (**1E**), which undergoes mutual conversion with the red-colored isomer **1C** only by photoirradiation,[1] fulgides have been regarded as representative of thermally irreversible photochromic organic compounds. Although this compound was gradually decomposed either by iterative photoconversion or by heating, indolylfulgide **2** was reported to be much more durable.[2] Fulgides were first regarded as candidates for materials of photon-mode optical recording media.[3] Recent interests, however, moved to the application to photoswitchable functional materials, including photoregulation of binding of proteins with carbohydrates,[4] photoswitching of liquid crystalline properties of either polymeric[5] or monomeric[6,7] states, and photoswitching of emission of fluorescence.[8] These are all induced by the structural interconversion of fulgide derivatives between the colorless but flexible *E*-form (sometimes accompanied by the *Z*-form) and the photostationary state of UV irradiation composed of the *E*- and *Z*-forms and the rigid and colored *C*-form, in which the *C*-form is usually the main component (Charts 1 and 2).

Chart 1



1E R = Me
3E R = *i*-Pr

2E R = Me

That the *E*-, *Z*-, and *C*-forms of fulgides are chiral has been known from several X-ray crystallographic analyses of fulgides.[9] The *E*- and *Z*-forms have helical chirality, whereas the *C*-form has an asymmetric center. Evidence for enantiotopomerization of the *E*-form of fulgides in solution, however, was not witnessed until very recently, when we observed the coalescence of the signals of two methyl groups of the isopropyl group of **3E**.[10] With the aid of AM1 molecular orbital calculations, we elucidated the mechanism of enantiotopomerization of the furylfulgide **3E**. In that study, we also found that there are two conformational isomers, **3E**α (*s-cis*-like with regard to the C−C single bond between the aromatic ring and the furylalkylidene group) and **3E**β (*s-trans*-like), in solution, whose heat-of-formation values obtained by AM1 are quite close (Chart 3). The former is cyclizable, while for the latter cyclization is impossible. On the basis of these results, we have succeeded in obtaining an indolylfulgide, **4E**, that hardly enantiotopomerizes.[11]

Through the studies described above, we have clarified that the chirality of fulgides, which comes from the helicity of the

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[†] Yokohama National University.

[‡] Fellow of JSPS Fellowships for Japanese Junior Scientists.

[§] Tokyo Kasei Gakuin University.

[‖] Kitasato University.

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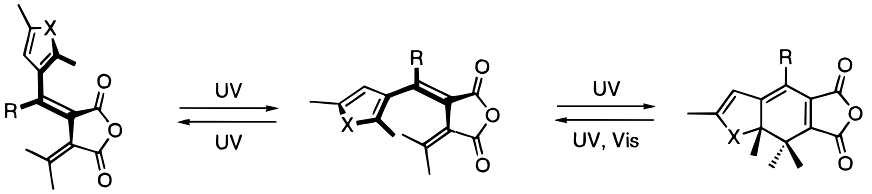
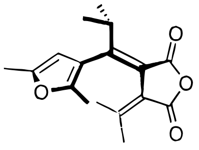
Chart 2

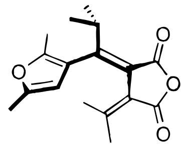


Z E C

Chart 3



3Eα



3Eβ

bis(methylene) substituents on the dihydrofurandione moiety, is not rigid and changes the mode of helicity thermally. If a chiral auxiliary with rigid chirality is introduced to the fulgide molecule, it should have two chiral units: one, the chiral unit of the auxiliary, being rigid, the other, that of the helical array of the bis(methylene) substituents on the dihydrofurandione moiety, being flexible. Accordingly, this kind of compound generates a set of diastereomers. In the case of fulgides, as they have another set of diastereomeric factors, **E**α and **E**β, they should exist as a mixture of four diastereomers if the introduced auxiliary is optically pure. As each diastereomer has a different reactivity toward photoirradiation (in particular, for **E**β cyclization is impossible), fulgides may show a diastereoselective photochromic reaction that may induce large changes in chiroptical properties. In this article, we report the *first* diastereoselective photochromic reaction of a fulgide derivative possessing a binaphthol unit as the chiral auxiliary.

Results and Discussion

Classification of Chiral Photochromic Molecules. An enantiomer of a photochromic compound with one chiral unit (either of an asymmetric center, a helical chirality, or a C_2 chirality) may show an enantiospecific photochromic reaction if the chirality is maintained during the mutual conversion. The resolved indolylfulgide **4E**[11] and Feringa's highly crowded stilbene derivatives[12] are representative of this category (category I).

Introduction of an optically active auxiliary to an achiral photochromic compound generates an enantiomer, which shows a photochromic interconversion between the corresponding enantiomers, if the auxiliary is inert toward the photochromic reaction. Although this compound may induce a change in the properties of the chiral auxiliary such as the mode of helicity of the polypeptide chain or a change in chiroptical properties of the bulk material by the photochromic interconversion, it is nothing more than an extension of a photochromic reaction of an achiral molecule: neither stereochemical specificity nor stereochemical selectivity is required during the photochemical interconversion. Studies of polypeptides with azobenzene units as the pendant functionalities are classified in this category,[13] if each amino acid linked photochromic unit is considered to be independent of the others (category II).

Photochromic molecules that have two chiral units, in which one is rigid and the other is flexible, may show stereoselective photochromism (category III). If one of the diastereomers is rich in population or highly reactive, and the thermal equilibration between the diastereomers is considerably fast, we may see a highly biased diastereomer ratio of the products. The acetal of 2,2′-dihydroxy-1,1′-binaphthyl (binaphthol) of a tetralonecarbaldehyde showed photochemical diastereotopomerization to cause different photostationary states by irradiation with different wavelengths of light, although the spectral change of the diastereomers was small.[14] It should be noted that spiropyran derivatives attached to the polypeptide chain could be included in this category,[15] if diastereoselective ring closure from the open forms is induced either thermally or photochemically by the influence of chirality of the auxiliary such as the polypeptide chain. However, no information about the *R/S* ratio of the asymmetric center of the closed form of this kind of spiropyran derivative has been reported so far.

On the basis of the background described above, we here report the construction of the *first* highly *diastereoselective* photochromic system.[16] The ring-closing reaction of a colorless photochromic fulgide derivative, which exists as a mixture of diastereomers, gave one diastereomer of the colored species with high diastereoselectivity. The photochemical ring-opening reaction afforded the initial mixture of colorless diastereomers.

Synthesis of Binaphthol-Condensed Indolylfulgides. Syntheses of indolylfulgides having a 2-propyl or a propyl group as a substituent on the indolylmethylene group, **4E** and **5E**, respectively, have been described elsewhere.[17] Starting with them, reaction of the sodium salt of (*R*)-2,2′-dihydroxy-1,1′-binaphthyl ((*R*)-binaphthol) followed by the treatment with trifluoroacetic anhydride gave the desired **6E** (R = *i*-Pr) and **7E** (R = Pr) (Scheme 1). As **4E** and **6E**, and **4C** and **6C**, respectively, showed similar behavior on column chromatography, a mixture of **4E** and **6E**, obtained by the synthesis, was irradiated by 366-nm light in toluene to give a mixture of **4E**, **4C**, **6E**, and **6C**. This mixture was then irradiated with red

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[16] We define the term *stereoselective reaction* as *a reaction that yields predominantly one stereoisomer of several possible diastereomers.* In contrast, the term *stereospecific reaction* is defined as *a reaction in which stereochemically different molecules react differently.* (a) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 6th ed.; Prentice-Hall: Englewood Cliffs, 1992; pp 367−386. (b) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; John Wiley & Sons: New York, 1994; pp 835−990.

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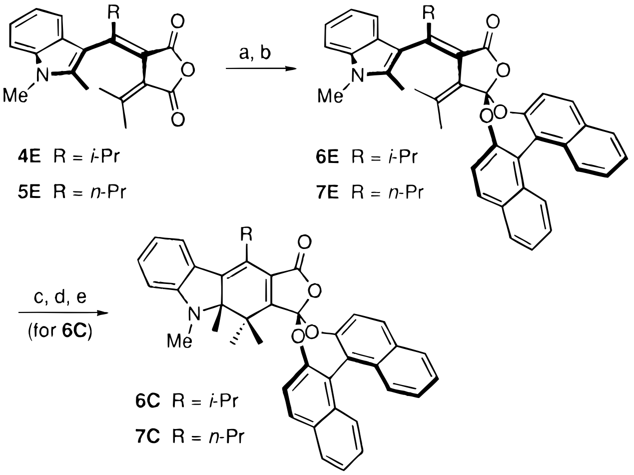
Scheme 1. Synthesis and isolation of (*R*)-binaphthol-condensed indolylfulgides **6** and **7**[a]



[a] (a) (*R*)-binaphthol (1.2 equiv), NaH (*ca.* 2 equiv), THF, 0 °C; (b) trifluoroacetic anhydride (2.4 equiv for **6** and *ca.* 10 equiv for **7**), THF, room temperature; (c) 366-nm-light irradiation, dichloroethane; (d) visible-light (>660 nm) irradiation, dichloroethane; (e) flash column chromatography (hexane/EtOAc = 95/5).

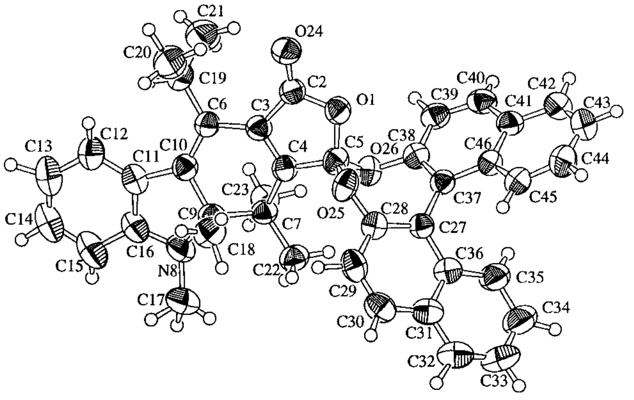


Figure 1. Stereostructure of the major isomer of **6C** ((9a*S*)-**6C**).

light (>660 nm) to induce the photoreaction of only **4C** to **4E**. Thus, after this procedure, a mixture of **6E**, **6C**, and **4E** was obtained, from which **6C** was easily separated by column chromatography. It was further purified by recrystallization from acetone twice. On the other hand, **7E** was isolated without event.

X-ray Crystallographic Analysis of 6C. As high-pressure liquid chromatography (HPLC) and ^{1}H NMR proved that **6C**, obtained by the procedure described above, was composed of two diastereomers in a 98/2 ratio, the X-ray crystallographic analysis of **6C** on a crystal recrystallized from acetone was carried out. The absolute configuration at the asymmetric quaternary carbon atom of **6C** induced by the cyclization was determined to be the *S* configuration with reference to the (*R*)-2,2′-binaphthyl group. The stereostructure of **6C** is shown in Figure 1. The carbon and oxygen atoms of the conjugated double bonds of the indolylfulgide moiety are nearly coplanar, *i.e.*, the deviations of these atoms from the least-squares plane through them are less than 0.1 Å (Table 1). This result proved that the photochemical electrocyclization occurred from the (*P*)-conformational isomer of **6E** ((*P*)-**6E**) to afford (9a*S*)-**6C** selectively, because the photoreaction of fulgides obeys the Woodward−Hoffmann rules[1] (Chart 4).

Chart 4

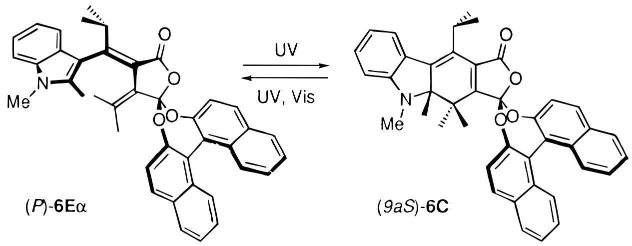


Table 1. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) of (9a*S*)-**6C**

atom	*x*	*y*	*z*	*U*(eq)
O1	0.7712(2)	0.8618(2)	0.3483(2)	0.0608(5)
O24	0.9055(2)	0.9525(2)	0.2822(2)	0.0733(7)
O25	0.5802(2)	0.8902(2)	0.3777(2)	0.0631(6)
O26	0.6358(2)	0.7325(2)	0.3384(2)	0.0569(5)
O85	1.0897(6)	0.6109(8)	0.1539(5)	0.224(4)
O89	1.0440(5)	0.9880(4)	0.6461(5)	0.160(2)
N8	0.3914(3)	0.8743(2)	−0.0467(2)	0.0708(8)
C2	0.8073(3)	0.9119(2)	0.2685(2)	0.0561(7)
C3	0.7088(3)	0.9024(2)	0.1757(2)	0.0539(6)
C4	0.6165(3)	0.8510(2)	0.2046(2)	0.0529(6)
C5	0.6463(3)	0.8297(2)	0.3185(2)	0.0553(7)
C6	0.7055(3)	0.9390(2)	0.0709(2)	0.0546(6)
C7	0.5047(3)	0.8166(2)	0.1279(2)	0.0520(6)
C9	0.4763(3)	0.9016(2)	0.0500(2)	0.0571(7)
C10	0.5935(3)	0.9344(2)	0.0092(2)	0.0531(6)
C11	0.5524(3)	0.9581(2)	−0.1007(2)	0.0598(7)
C12	0.6060(4)	1.0075(3)	−0.1739(3)	0.0691(9)
C13	0.5404(5)	1.0179(3)	−0.2733(3)	0.0843(12)
C14	0.4247(5)	0.9802(3)	−0.3002(3)	0.0885(13)
C15	0.3665(4)	0.9318(4)	−0.2286(3)	0.0900(13)
C16	0.4329(3)	0.9202(3)	−0.1284(3)	0.0670(8)
C17	0.2587(4)	0.8662(5)	−0.0510(4)	0.112(2)
C18	0.4253(4)	0.9907(3)	0.0991(4)	0.0757(10)
C19	0.8188(3)	0.9790(4)	0.0340(3)	0.0801(12)
C20	0.8440(5)	1.0831(4)	0.0742(5)	0.108(2)
C21	0.9335(4)	0.9152(6)	0.0538(4)	0.106(2)
C22	0.3949(3)	0.7871(3)	0.1795(3)	0.0653(8)
C23	0.5465(3)	0.7256(3)	0.0737(3)	0.0624(7)
C27	0.4994(3)	0.7791(2)	0.4921(2)	0.0502(6)
C28	0.4847(3)	0.8556(2)	0.4238(2)	0.0550(6)
C29	0.3740(3)	0.9094(3)	0.4036(2)	0.0661(8)
C30	0.2748(3)	0.8830(3)	0.4478(3)	0.0704(9)
C31	0.2805(3)	0.8006(3)	0.5130(3)	0.0652(8)
C32	0.1783(3)	0.7716(4)	0.5591(4)	0.0813(11)
C33	0.1853(4)	0.6913(4)	0.6189(4)	0.0966(15)
C34	0.2912(4)	0.6357(4)	0.6344(4)	0.0906(13)
C35	0.3938(3)	0.6610(3)	0.5926(3)	0.0723(9)
C36	0.3932(3)	0.7471(2)	0.5331(2)	0.0571(7)
C37	0.6208(3)	0.7304(2)	0.5180(2)	0.0490(6)
C38	0.6842(3)	0.7061(2)	0.4406(2)	0.0523(6)
C39	0.7938(3)	0.6496(2)	0.4563(3)	0.0591(7)
C40	0.8425(3)	0.6208(2)	0.5534(3)	0.0611(7)
C41	0.7888(3)	0.6508(2)	0.6386(3)	0.0572(7)
C42	0.8439(3)	0.6253(3)	0.7406(3)	0.0704(9)
C43	0.7971(4)	0.6594(4)	0.8231(3)	0.0822(11)
C44	0.6949(4)	0.7219(4)	0.8080(3)	0.0796(11)
C45	0.6348(3)	0.7449(3)	0.7103(2)	0.0629(8)
C46	0.6794(3)	0.7086(2)	0.6222(2)	0.0521(6)
C82	0.8838(6)	0.6548(7)	0.1643(5)	0.126(2)
C83	1.0236(5)	0.6590(5)	0.1972(4)	0.106(2)
C84	1.0727(7)	0.7209(7)	0.2864(6)	0.138(2)
C86	0.8306(9)	0.9627(11)	0.5874(6)	0.184(4)
C87	0.9475(5)	0.9493(4)	0.6556(4)	0.0956(13)
C88	0.9429(8)	0.8845(7)	0.7429(6)	0.147(3)

Crystals of **7C**, 95/5 by HPLC and ^{1}H NMR, were obtained in a manner similar to that for **6C**. The X-ray crystallographic analysis of **7C**, however, was unsuccessful at the present stage. It is quite natural to assume that the replacement of the 2-propyl group with a 1-propyl group does not upset the selectivity of photoreaction completely. Therefore we assigned the absolute configuration of **7C** to be (9a*S*)-**7C**. This conclusion was supported by semiempirical molecular orbital calculations (*vide infra*).

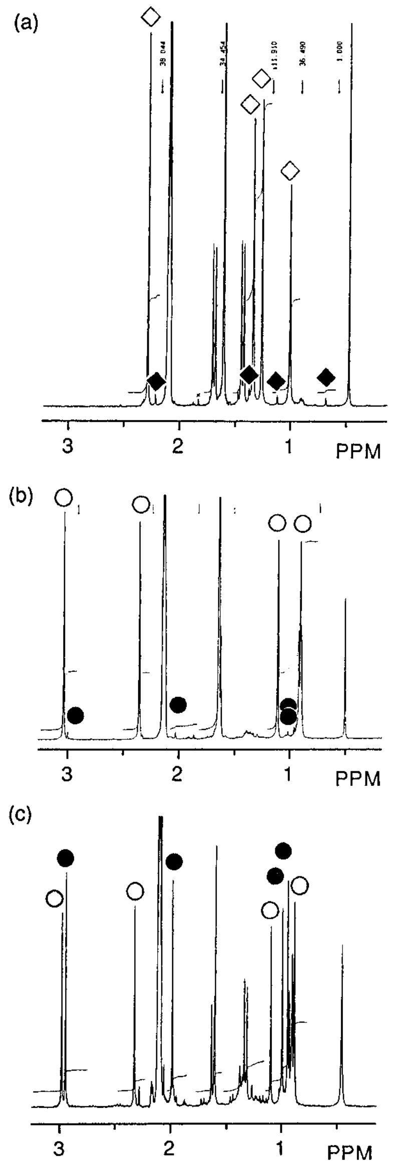


Figure 2. ^{1}H NMR spectra of **6** in toluene-d_8 (270 MHz, 20.1 °C): (a) before irradiation (*C*-form: ◇, major conformer, ◆, minor conformer); (b) after 495-nm irradiation (*E*-form: ○, major conformer; ●, minor conformer); (c) **6E** at thermal equilibrium (○, major conformer; ●, minor conformer).

Photochromic Behavior of 6 and 7. Irradiation with 495-nm light of a 1.40 × 10^{-4} mol dm^{-3} toluene solution of **6C** (98/2 conformer ratio, Figure 2a) produced **6E** (96/4 conformer ratio, Figure 2b). The quantum yield of decoloration was 0.17. The thermal equilibrium ratio of the diastereomers of **6E** (125 days at about 6 °C) was found to be 48/52 (Figure 2c). Diastereoisomerization to reach thermal equilibrium also occurred within 30 min in refluxing toluene.

Irradiation with 366-nm light of a toluene solution of colorless **6E** obtained immediately after visible-light irradiation of **6C** ("fresh" **6E**, Figure 3a) afforded the photostationary state (pss), where **6C**/**6E**, determined by HPLC, was 82/18 (Figure 3b). The diastereomeric ratio of **6C** was 99.7/0.3. On the contrary, coloration of the thermally equilibrated ("matured") **6E** gave a **6C**/**6E** mixture, where the diastereomeric ratio of **6C** (about 45% conversion) was 95/5, and the amount of the cyclization-inert conformer of **6E** changed only a little. Prolonged UV irradiation resulted in decomposition of the cyclization-inert **6E**. Thus, this system was proved to show poor photochromism: **6** exhibits the photochromic transformation between (*P*)-**6E**α (and

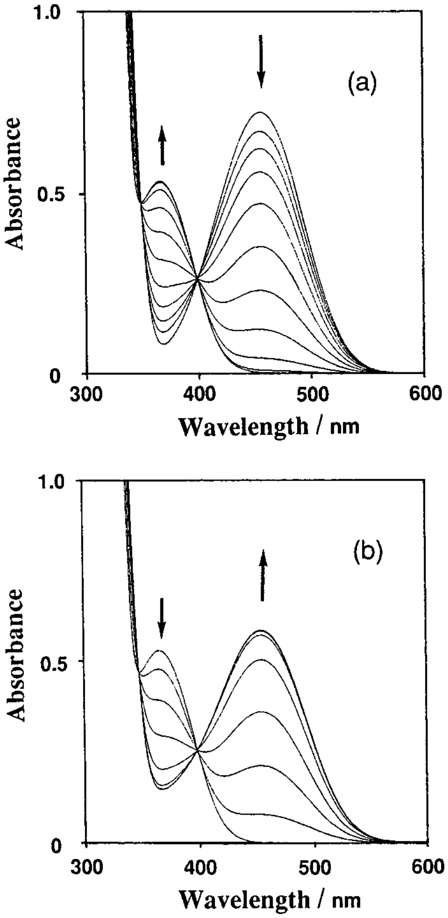


Figure 3. Absorption spectral change of **6** (1.40 × 10^{-4} mol dm^{-3} in toluene; cell length, 1 cm): (a) 495-nm-light irradiation to **6C** (irradiation, 495-nm light from 500-W xenon lamp; light intensity, 8.07 × 10^{-1} mW cm^{-2}; irradiation time/min, 0, 0.5, 1.0, 1.7, 2.8, 4.5, 6.8, 10, 15, 23, 40 (pss)); (b) 366-nm-light irradiation to **6E** (irradiation, 366-nm light from 500-W high-pressure Hg lamp; light intensity, 4.37 mW cm^{-2}; irradiation time/min, 0, 0.2, 0.5, 1.0, 1.8, 3.0, 4.8, 7.5, 11.5 (pss)).

(*M*)-**6E**β, which isomerizes to (*P*)-**6E**α easily; *vide infra*) and (9a*S*)-**6C** (category II), and the rest of the conformers of **6E** do not participate in the photochromism.

The ^{1}H NMR of **7E** at 24.7 °C showed that it exists as a 57/43 mixture of conformers in toluene-d_8 (Figure 4a). Irradiation with 366-nm light of a 1 × 10^{-4} mol dm^{-3} solution of **7E** in toluene afforded the pss, where **7C**/**7E** was 86/14 (Figures 4b and 5a,b). The HPLC and ^{1}H and ^{13}C NMR proved that the diastereomeric ratio of **7C** was 95/5.

Irradiation with 495-nm light of a 366-nm-pss toluene solution reproduced the mixture of conformers of **7E** with a conformer ratio of 57/43. The quantum yield of decoloration by 495-nm light was calculated to be 0.18, by regarding that **7C** consisted of only one diastereomer.

As the conformer ratio did not change significantly when "fresh" **7E** was heated up to 100 °C for 30 min in toluene-d_8, the conformers of **7E** are concluded to be in a thermal equilibrium above room temperature. This means that isomerization from the photocyclization-inert **7E** to photocyclizable (*P*)-**7E**α occurred fairly quickly to maintain thermal equilibrium during UV irradiation. Thus, the photochromic coloration of **7E** was proved to occur diastereoselectively (category III).

It should be noted that while the UV−vis spectral change from **6E** to its UV-pss by irradiation with 366-nm light has isosbestic points (Figure 3b), that from **7E** does not (Figure 5a). As described previously, because the photochromic col-

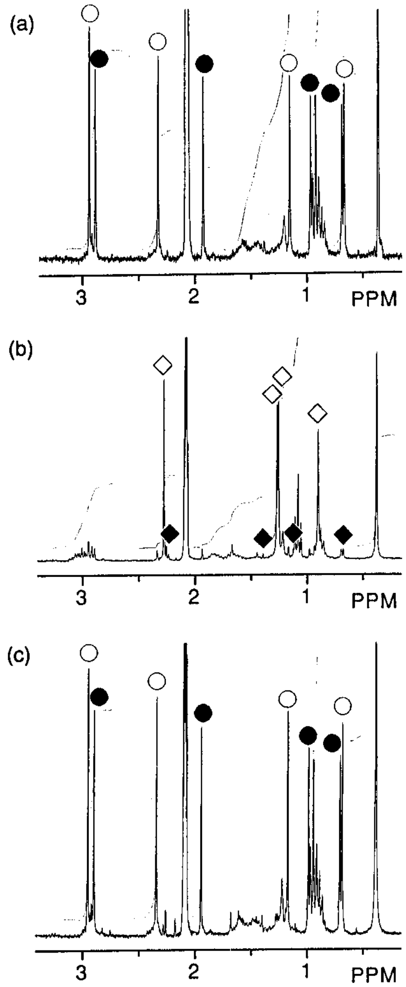


Figure 4. ^{1}H NMR spectra of **7** in toluene-d_8 (270 MHz, 24.7 °C): (a) **7E** at thermal equilibrium (○, major conformer; ●, minor conformer); (b) at pss of 366-nm-light irradiation to **7E** (*E*-form, ○, major conformer, ●, minor conformer; *C*-form, ◇, major conformer, ◆, minor conformer); (c) at pss of 495-nm-light irradiation.

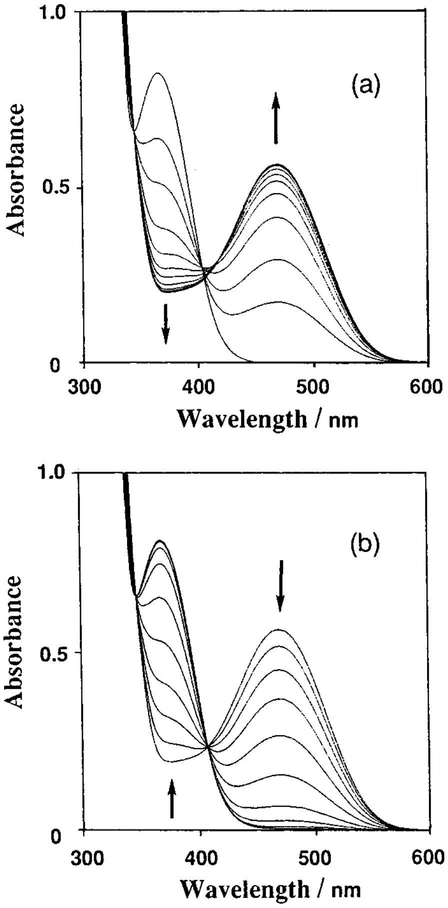


Figure 5. Absorption spectral change of **7** (1.00×10^{-4} mol dm^{-3} in toluene; cell length, 1 cm): (a) 366-nm-light irradiation to **7E** (irradiation, 366-nm light from 500-W high-pressure Hg lamp; light intensity, 2.23 mW cm^{-2}; irradiation time/min: 0, 0.5, 1.0, 1.8, 3.0, 5.0, 8.5, 15, 25, 35, 50, 75 (pss)); (b) 495-nm-light irradiation to pss (irradiation, 495-nm light from 500-W xenon lamp; light intensity, 5.38 $\times$ 10^{-1} mW cm^{-2}; irradiation time/min, 0, 0.5, 1.2, 2.2, 3.7, 6.0, 9.3, 13.3, 20, 35, 70 (pss)).

oration of **6** occurred only between the photocyclizable **6E** and (9a*S*)-**6C**, the isosbestic points appeared. On the contrary, the photocoloration of **7E** was accompanied by thermal isomerization from the photocyclization-inert conformers to photocyclizable (*P*)-**7E**α. As it took about 10 min for the mixture to become almost thermally equilibrated at room temperature,[18] no isosbestic points appeared. To the contrary, decoloration reactions caused by visible light irradiation of both **6C** and **7C** showed isosbestic points clearly (Figures 3a and 5b). Thermal equilibration of **7E** might have occurred at the vibrationally excited ground state of **7E** produced at the last phase of photodecoloration.

AM1 Semiempirical Molecular Orbital Calculations and Elucidation of the Remarkable Diastereoselectivity of the Coloration of 6E. In order to explain the results obtained by the photochromic reactions, the heat-of-formation values of possible conformers of the model compound **8E** (for simplification of the calculation, the C_3-alkyl groups of **6** and **7** were replaced by a methyl group) with regard to the helical array of the substituents (*P* or *M*) and the conformation of the indole ring (α or *β*) were obtained by AM1 semiempirical molecular orbital calculations.[19] The differences of heat-of-formation values (ΔH_f) compared to that of the most stable conformer, (*P*)-**8E**α, are shown in Figure 6.[20]

While (*P*)- and (*M*)-**E**α conformers can undergo cyclization upon UV-light irradiation, (*P*)- and (*M*)-**E***β* cannot.[21] This premise, the calculation, and the experimental results lead to the following conclusions: (i) The two conformers observed for both **6E** and **7E** by ^{1}H NMR were essentially (*P*)-**E**α and (*P*)-**E***β*, where only the former can give the cyclized product. The calculated population ratio of (*P*)-**8Eα** and (*P*)-**8E*β*** at 298 K at equilibrium was 67/33. These results are in good accord with the experimental results. (ii) Judging from the previous results for a furylfulgide,[10] the energy barriers of the processes that change both the helical chirality (*P* or *M*) and the indole conformation (α or *β*) in Figure 6 (*i.e.*, the isomerization between the conformers in the same square in Figure 6) are much lower than those of other processes. That **7E** reaches its thermal equilibrium much faster than **6E** implies that the conformational isomerization between the conformers belonging to different squares in Figure 6 for **7E** is much faster than the

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[18] The absorption spectra and the HPLC chromatogram changes of **7E** obtained immediately after visible-light irradiation in toluene proved that the diastereoisomerization of the components occurred with the sum of the thermal diastereoisomerization rate constants of about 7×10^{-3} s^{-1} at 21 °C.

[19] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

[20] All of the frequencies were positive for optimized ground-state conformations. Neither abnormal atom distances nor bond angles were observed.

[21] If (*P*)- or (*M*)-**E***β* would give the cyclized products, they should contain an extremely unstable *trans,cis*-1,3-cyclohexadiene unit.

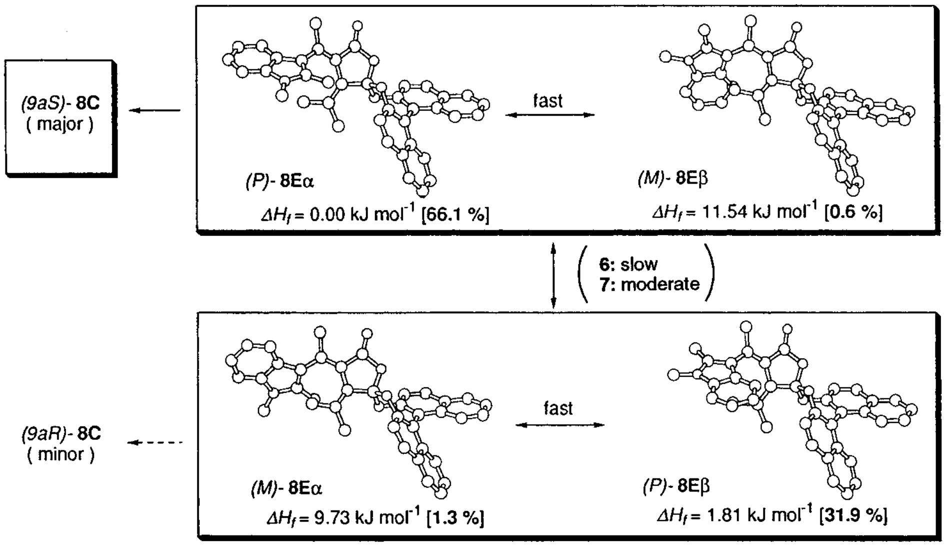

Figure 6. Structures and differences of heat-of-formation values of stable conformers of **8E** at 298 K obtained by AM1 molecular orbital calculations.

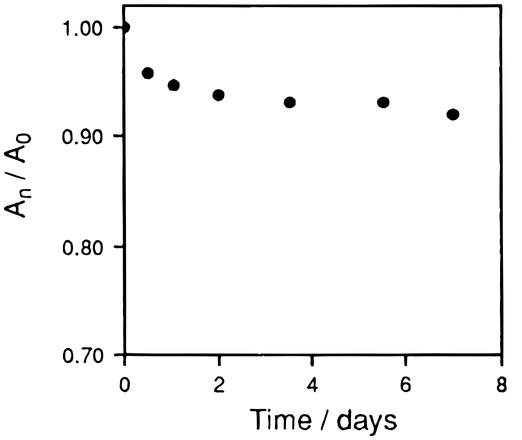

Figure 7. Thermal stability of **7C** in a PMMA film at 80 °C.

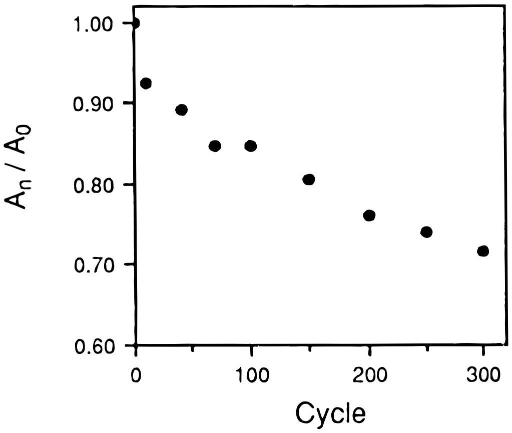

Figure 8. Fatigue resistivity of **7** during alternative irradiation of 366-nm light and visible light (>470 nm) in a PMMA film.

corresponding isomerization for **6E**. This assumption is in good accord with our previous results that while **4E**, the isopropyl-substituted indolylfulgide, does not enantiotopomerize at room temperature,[11] **5E**, the propyl-substituted indolylfulgide, enantiotopomerizes easily.[22]

Among the four possible conformers of **7E**, the most dominant one, (*P*)-**7E**α, can undergo photocyclization to afford (9a*S*)-**7C**, while the second dominant one, (*P*)-**7E**β, cannot. Other conformational isomers, including photocyclizable (*M*)-**7E**α, are energetically unfavorable, and their population is small. Therefore, the photoreaction of **7** is regarded as a diastereoselective photochromic system in which a mixture of diastereomers of **7E** gives the diastereomers of the product **7C** in a highly biased ratio by UV-light irradiation. Irradiation with visible light changed (9a*S*)-**7C** to the original mixture of diastereomers of **7E** by way of the vibrationally excited (*P*)-**7E**α.

Thermal Stability of the Colored Form 7C. We examined the thermal stability of **7C** (obtained as the pss of UV irradiation on **7E**) in a PMMA film when kept at 80 °C in air. The result is shown in Figure 7. Kaneko *et al.* defined the TD value in percentage as $(A_0 - An)/nA_0$,[2] where A_0 and An are the initial absorbance and the absorbance after *n* days of heating. The TD value 0.48%, calculated from the slope of the decrease of relative absorbance values of the experimental data from after 1 day of heating through the seventh day, is the best of the known fulgides so far. The relatively large decrease of absorbance in the first 24 h is probably due to the deformation of the PMMA film. After 7 days at 80 °C, **7C** showed photochromic decoloration.

Fatigue Resistivity of the Iterative Photoreaction of 7. The fatigue resistivity of **7** in a PMMA film toward the iterative photochromic reaction was studied. The ratio of absorbance at the absorption maximum of the colored form at UV-pss versus the initial absorbance at UV-pss was measured, and the result is shown in Figure 8. After about 300 iterations, the absorbance had been reduced to 70% of the initial absorbance. As indolylfulgide **2** reduced its absorbance to 50% of the initial absorbance after 300 iterations,[2] **7** holds a better fatigue resistivity than **2**.

Change in Optical Rotation of 6 and 7 in Solution and in PMMA Films. The photochromic reversible change was followed by the measurement of optical rotation in toluene. The specific rotation ($[\alpha]_D$) of "fresh" **6E** changed from −543° (before UV irradiation) to −122° (at pss). A similar change of $[\alpha]_D$ was observed for **7E**, from −572° to −186° (at pss). After visible-light irradiation, the $[\alpha]_D$ value recovered to −569°, practically the same value as that before UV irradiation.

Reversible changes of optical rotation of **6** and **7** in PMMA films were also observed as shown in Figures 9 and 10. As the change in optical rotation can be detected at wavelengths out of the absorption (*e.g.* the D-line of sodium (589 nm) is just out of the absorption bands of the *C*-forms), this phenomenon

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[22] Yokoyama, Y.; Shimizu, Y.; Uchida, S. Unpublished results.

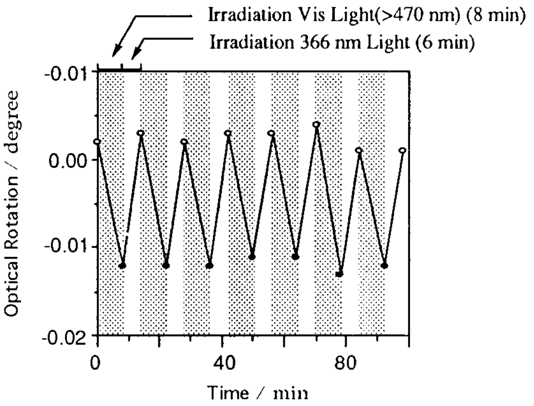

Figure 9. Reversible changes of optical rotation of **6** in a PMMA film.

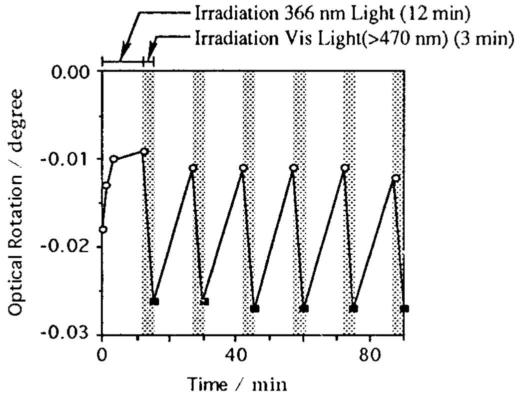

Figure 10. Reversible changes of optical rotation of **7** in a PMMA film.

can be used as a nondestructive readout of the records of photon-mode optical memory media using these photochromic compounds.

Conclusion. We have synthesized the thermally irreversible photochromic (*R*)-binaphthol-condensed indolylfulgides **6** and **7**. Because of the rapid thermal equilibration between the conformational isomers of **7E** at room temperature, photocyclization of a substantial portion of **7E** occurred through (*P*)-**7E**α to give (9a*S*)-**7C** selectively. On the other hand, as thermal equilibration requires a long time for **6E** at room temperature, its photochromic interconversion occurs only between (*P*)-**6E**α and (9a*S*)-**6C**, and the photocyclization-inert **6E** remained unchanged. Thermal stability and fatigue resistivity toward iterative photochromic interconversion of **7** have been proved to be excellent among the fulgide derivatives. The photochromic reactions were accompanied by large changes of specific rotation values. The X-ray crystallographic analysis of a visible-light-sensitive (9a*S*)-**6C** was also carried out.[23]

The diastereoselective mutual transformation caused by light irradiation associated with a large change of absorption spectra observed for **7** is a new class of photochromism. As light itself has a chiral nature, the introduction of chirality to photochromic materials should provide a number of ways of application.

Experimental Section

General Methods. IR spectra were measured using a Perkin-Elmer 1650 FT-IR or a JASCO A 202 IR spectrometer. ^{1}H NMR spectra were recorded with a JEOL JNM-EX-270 (270 MHz) spectrometer in toluene-d_8. The signals are expressed as ppm downfield from tetramethylsilane, used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; sep, septet; and m, multiplet. The low- and high-resolution mass spectra were taken with a JEOL JMS AX-500 mass spectrometer. UV−vis spectra were recorded on a JASCO Ubest-50 UV−vis spectrophotometer. The emission line of 366 nm of a 500-W high-pressure mercury lamp (Ushio Electric) was separated by filters (Toshiba UV-35, UV-D35, a 1-cm-thick aqueous $CuSO_4$ (50 g dm^{-3}), and a 5-cm water filter). A monochromatic light beam of 495 nm was taken out from a 500-W xenon lamp (Ushio Electric) using filters (a 5-cm water filter and Toshiba Y-47, IRA-25S, and KL-50 glass filters). The irradiation light intensities were determined by a photometer (IL-1350, International Light) with detectors (SED038 for 495-nm light and SED400 for 366-nm light), calibrated with a tris(oxalato)ferrate(III) chemical actinometer. Measurements of the concentration of components during the photoreactions were done using a high-pressure liquid chromatograph (Shimadzu LC-6A) and a detector (Shimadzu SPD-6AV) using a silica gel column (Wakosil 5-sil, 4.6 mm × 150 mm, Wako) with a mixture of ethyl acetate and hexane as an eluent. The silica gel column chromatography separations were carried out with Merck Kieselgel 60 (230−400 mesh) with a mixture of ethyl acetate and hexane as an eluent. The thin-layer chromatography analyses were performed on Merck precoated silica gel 60 F-254, 0.25-mm thick TLC plates. All of the synthetic reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl, and diethyl ether and dichloromethane were distilled from CaH_2 immediately before use.

Synthesis and Separation of 6C (Colored Form of (*R*)-Binaphthol-Condensed Isopropyl-Substituted Indolylfulgide). To a suspension of sodium hydride (60% in oil, 20.9 mg, 0.52 mmol) in THF (10 mL) was added (*R*)-2,2′-dihydroxy-1,1′-binaphthol ((*R*)-binaphthol) (100.8 mg, 0.352 mmol), and the mixture was stirred for several minutes until the evolution of hydrogen gas ceased. To the resulting solution was added a THF (10 mL) solution of indolylfulgide **4E** ((*E*)-3-[1-(1,2-dimethyl-3-indolyl)-2-methylpropylidene]-4-isopropylidenedihydro-2,5-furandione) (99.5 mg, 0.295 mmol), and the resulting mixture was stirred for 2 h. Diluted hydrochloric acid was added to the mixture, and it was extracted with ether three times. The combined organic layer was washed with saturated aqueous sodium chloride, and it was dried with anhydrous Na_2SO_4. After the drying agent was filtered off, the solvent was removed *in vacuo*. Addition of hexane to the residue yielded a grayish white powder, which was collected by filtration. This material, mainly composed of the half ester, was used for the next reaction without further purification.

To the THF (10 mL) solution of the material obtained above was added trifluoroacetic anhydride (ca. 0.1 mL), and the mixture was stirred for 10 min. To it was added saturated aqueous Na_2CO_3, and it was extracted with ether three times. The combined organic layer was washed with saturated aqueous sodium chloride, and it was dried with anhydrous Na_2SO_4. After the drying agent was filtered off, the solvent was removed *in vacuo*. The residue was purified by column chromatography, to give a mixture of **4E** and **6E**, which moved together in the silica gel chromatography (see text). The mixture was dissolved in 1,2-dichloroethane and then irradiated with 366-nm light to give a mixture of **4E**, **4C**, **6E**, and **6C**. The mixture in 1,2-dichloroethane was then irradiated with red light (>660 nm) to give a mixture of **4E**, **6E**, and **6C**, from which **6C** was separated by column chromatography (34.0 mg, 0.056 mmol, 19% yield). The colorless **6E** was obtained only in a small amount, for NMR and UV−vis spectral measurements, by irradiating the solution of **6C** with visible light.

6C: red cubes, mp 262−263 °C (acetone); IR 3056, 1789, 1213, 965, 751 cm^{-1}; ^{1}H NMR (toluene-d_8) (values in brackets are those of the minor diastereomer that appeared separately) δ 0.97 [0.63], 1.23 [1.08], 1.31 [1.45], 2.28 [2.21] (each 3H, s), 1.41 (3H, d, $J = 6.93$ Hz), 1.67 (3H, d, $J = 6.93$ Hz), 3.66 (1H, sep, $J = 6.93$ Hz), 6.8−8.1 (16H); UV λ_{max} 456 nm (ϵ_{max} 5200 mol^{-1} dm^3 cm^{-1}, toluene); exact mass (EI, 70 eV) calcd for $C_{41}H_{35}O_4N$ (M) 605.2566, found 605.2564.

6E (as a mixture of conformers): ^{1}H NMR (toluene-d_8) (values in brackets are those of the minor diastereomer that appeared separately) δ 0.83 [0.89], 1.05 [0.95], 2.32 [1.98], 3.01 [2.97] (each 3H, s), 0.84 (3H, d, $J = 6.59$ Hz) [0.90, d, $J = 6.50$ Hz], 1.58 (3H, d, $J = 6.96$ Hz)

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[23] It should be noted that to date there has been only one report of the X-ray crystallographic structural determination of the visible-light-sensitive colored form of a fulgide.[9a]

[1.28 (3H, d, $J = 6.92$ Hz)], 4.67 (1H, m), 6.9−7.7 (16H); UV λ_{max} 367 nm (ϵ_{max} 3800 mol^{-1} dm^3 cm^{-1}, toluene).

X-ray Structure Determination of 6C (Colored Form of (*R*)-Binaphthol-Condensed Isopropyl-Substituted Indolylfulgide). A crystal of approximate size 0.5 × 0.5 × 0.4 mm^3 was mounted on a Rigaku AFC7R four-circle diffractometer, and reflection data were collected with graphite-monochromatized Mo Kα radiation (0.710 69 Å) under dark to avoid photoreaction. Crystal data: monoclinic $P2_1$, $a = 10.941(9)$ Å, $b = 13.861(10)$ Å, $c = 13.141(8)$ Å, $\beta = 99.89(5)°$, and $Z = 2$. Intensity data of 4924 reflections up to a θ value of 27.5° were collected using the ω-scan mode. The structure was solved by direct methods using SHELXS-86 and refined by the full-matrix least-squares method using SHELXL-93.[24] The absolute configuration at the quaternary carbon atom induced by photocyclization was determined with reference to that of the (*R*)-2,2′-binaphthyl group. Two acetone molecules were located on a difference Fourier map. Hydrogen atoms except for those of the acetone molecules were also located on a difference Fourier map, and their isotropic displacement parameters except for those of *N*-methyl hydrogen atoms were refined. $R(F) = \sum||F_o| - |F_c||/\sum|F_o| = 0.049$, $R(wF) = (\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^{1/2})^{1/2} = 0.15$ with $w = 1/[\sigma^2(F_o{}^2) + (0.1135P)^2 + 0.0420P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ for 3682 observed reflections ($F_o{}^2 > 2\sigma(F_o{}^2)$). The final positional parameters are listed in Table 1.

Synthesis of 7E (Colorless Form of (*R*)-Binaphthol-Condensed Propyl-Substituted Indolylfulgide). Reaction of the indolylfulgide **5E** ((*E*)-3-[1-(1,2-dimethyl-3-indolyl)butylidene]-4-isopropylidenedihydro-2,5-furandione) (208.7 mg, 0.619 mmol) and (*R*)-binaphthol (213.6 mg, 0.755 mmol) with sodium hydride (60% in oil, 54.5 mg, 1.3625 mmol) in THF (20 mL) in a similar manner to the synthesis of **6E** gave the half ester (307.1 mg, 0.492 mmol, 80%). The half ester (30.5 mg, 0.0489 mmol), treated with trifluoroacetic anhydride (*ca.* 50 μL), gave a mixture of **5E** and **7E**. Although **5E** and **7E** moved together in silica gel column chromatography, pure **7E** was successfully obtained from this mixture by recrystallization from ethyl acetate (17.5 mg, 0.0289 mmol, 59%).

7E (as a mixture of conformers): colorless needles, mp 236−238 °C (ethyl acetate); IR (KBr) 3054, 1771, 1580, 1223, 990, 742 cm^{-1}; ^{1}H NMR (toluene-d_8) (values in brackets are those of the minor diastereomer) δ 0.68 [0.70], 1.17 [0.99], 2.34 [1.94], 2.95 [2.89] (each 3H, s), 0.94 (3H, t, $J = 7.34$ Hz) [0.94 (3H, t, $J = 7.34$ Hz)], 1.4−1.7 (2H, m), 2.9 (1H, m) [2.4 (1H, m)], 4.3 (1H, m) [4.3 (1H, m)], 7.0−8.1 (16H); UV (as a mixture of conformers) λ_{max} 368 nm (average ϵ_{max} 8200 mol^{-1} cm^3 cm^{-1}, toluene); exact mass (EI, 70 eV) calcd for $C_{41}H_{35}O_4N$ (M) 605.2566, found 605.2571.

With the procedures described for the preparation of **6C**, **7C** was obtained from 105.5 mg of **5E** (48.3 mg, 0.0797 mmol, 25%).

7C (25% yield, obtained similarly to **6C**): red cubes, mp 263−266 °C (ether); IR (KBr) 3055, 1787, 1599, 1473, 1292, 1236, 1201, 955, 747 cm^{-1}; ^{1}H NMR (toluene-d_8) (values in brackets are those of the minor diastereomer that appeared separately) δ 0.90 [0.69], 1.26 [1.18], 1.28 [1.45], 2.28 [2.23] (each 3H, s), 1.09 (3H, t, $J = 7.43$ Hz), 1.70, 1.86 (each 1H, m), 3.0 (2H, m), 6.8−8.1 (16H); UV (as a 95/5 mixture of diastereomers) λ_{max} 471 nm (average ϵ_{max} 6600 mol^{-1} dm^3 cm^{-1}, toluene); exact mass (EI, 70 eV) calcd for $C_{41}H_{35}O_4N$ (M) 605.2566, found 605.2554.

Preparation of the PMMA Film Containing the Fulgide Derivatives. A 3.0-mL dichloromethane solution of PMMA pellets (Wako) (279 mg) and a 4-mL toluene solution of **7C** (3.40×10^{-4} mol dm^{-3}) was mixed thoroughly, and the mixture was poured into a flat Petri dish. After the solvent was evaporated at room temperature under atmospheric pressure and finally *in vacuo*, the PMMA film was removed from the Petri dish. The thickness of the film was 32 μm.

For the thermal stability experiment, the film was irradiated with visible light and UV light successively, to attain the UV-pss. The film was put onto the wall of a quartz cell, and it was held in an oven (80 °C).

For the fatigue-resistivity experiment, the film was put onto a cell wall, and the film was irradiated alternately with UV and visible light, with occasional measurements of UV−vis spectra.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research, The Ministry of Education, Science, and Culture of Japan, Iketani Science and Technology Foundation, and Tokuyama Science Foundation.

Supporting Information Available: Tables of anisotropic thermal parameters of non-hydrogen atoms and positional parameters of hydrogen atoms of (9a*S*)-**6C** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9523045

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[24] Scheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.