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Fulgides for Memories and Switches

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Contents

I. Introduction

A. Scope and Limitation of This Review

Fulgides are famous as thermally irreversible photochromic compounds. However, fulgides were thermally reversible at the beginning of their history. Fulgides gained, slowly at first and rapidly recently, a variety of properties including the epoch-making “thermal irreversibility” through the 20th century. There have been some excellent review articles dealing with fulgides.[1−5] In this review, we will see the history and properties of fulgides; in particular research toward the application in photon-controlled memory devices and switching of functions are emphasized. The main period of research history of fulgides in this review is from 1981 through the end of 1998.

B. Definition of Structures of Fulgides and Their Photochromism

Stobbe, Universität Leipzig, stated in his article in 1905 that he named the derivatives of 1,3-butadiene-2,3-dicarboxylic acid and its acid anhydride as “fulgenic acid” and “fulgide”, respectively (Chart 1), after the Latin word “fulgere” (glitter or shine), because some derivatives exhibited a variety of characteristic colors by light, and they usually formed shiny crystals.[6] To be photochromic, fulgides should have at least one aromatic ring on the *exo*-methylene carbon atom, so that they form a 1,3,5-hexatriene structure that may undergo 6π-electrocyclization.

The photochromism of fulgide occurs between one of the colorless open forms (hereafter abbreviated as

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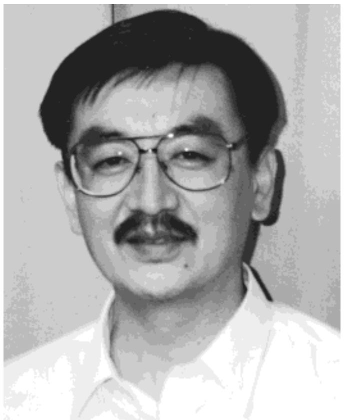
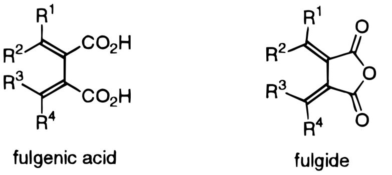


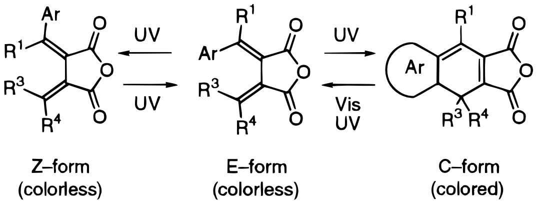
Yasushi Yokoyama was born in 1953 in Yokohama. He spent nine years at the University of Tokyo, from which he earned B.Sc., M.Sc., and Ph.D. degrees under the supervision of Professor Takeyoshi Takahashi. In 1980, immediately after receiving his Ph.D. degree, he was appointed as an Assistant Professor of the Department of Materials Chemistry, Yokohama National University. From 1985 to 1986, he worked as a postdoctoral research fellow with Professor Amos B. Smith, III, at the University of Pennsylvania. He was promoted to Associate Professor in 1991 and then to Professor in 1999. His current research interest is to elaborate photochromic molecules and systems with interesting and/or useful properties.

Chart 1



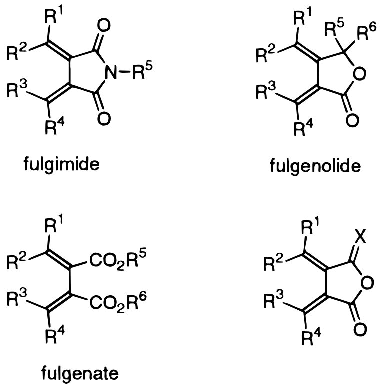
the "*E*-form" because the geometry of the double bond connecting the aromatic ring and the succinic anhydride is usually *E*) and the photocyclized *colored* form (abbreviated as the *C*-form) (Chart 2). However, there is an additional photochemical *E*−*Z* isomerization pathway. The "*Z*-form", the geometrical isomer of the *E*-form, is not considered as an important member of the photochromic system. There has been no report that the *Z*-form cyclizes directly by absorbing one photon to give the *C*-form. Therefore, *E*-to-*Z* photoisomerization, competing with the photochromic *E*-to-*C* isomerization, is an energy-wasting as well as system-complicating process in terms of the "photochromism of fulgides."

Chart 2



Although the name "fulgide" is given to bismethylenesuccinic anhydrides, this review deals with some related derivatives in addition to fulgides, such as the succinimides (fulgimide), butanolides (fulgenolide), diesters (fulgenate), and compounds having an anhydride ring with a modified carbonyl group instead of the genuine succinic anhydride ring (Chart 3).

Chart 3

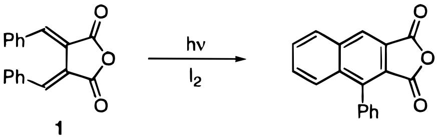


II. Narrative History of Fulgides before They Gained Thermal Irreversibility

Fulgides were first synthesized by Stobbe early in this century. He and co-workers prepared a vast number of fulgides; most of them had one to four substituted and unsubstituted phenyl groups as the aryl groups, but some had a furyl or a naphthalene ring. In 1911 he reported the chemistry of fulgides in an article which is over 100 pages.[7]

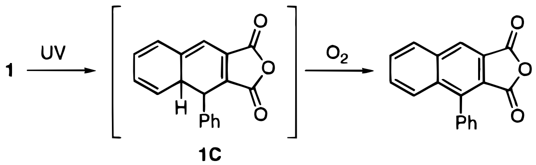
Although the photocoloration mechanism of fulgides was not known at that time, Stobbe noticed that 1-phenylnaphthalene-2,3-dicarboxylic anhydride was formed by photoirradiation of benzene or chloroform solution of bisbenzylidenefulgide **1** in the presence of iodine[8] (Chart 4).

Chart 4



Until the 1960s, the coloration was believed to occur by *E*−*Z* isomerization of a double bond.[9,10] Other hypotheses such as formation of colored radical intermediates during photocyclization[11] and photochemical change between the electronic mesomeric forms[12] were also considered. In 1968, Becker et al. confirmed that the colored form of **1** was oxidized, this time by dioxygen, to yield 1-phenylnaphthalene-2,3-dicarboxylic anhydride. Accordingly, the structure of the colored form was deduced to be 1,8a-dihydro-1-phenylnaphthalene-2,3-dicarboxylic anhydride **1C**[13] (Chart 5). Since then the coloration mechanism of fulgide has been well understood as the photochemical 6π-electrocyclization of the hexatriene moiety.

Chart 5



Later in 1984, Kaftory succeeded in the X-ray crystallographic analysis of the colored form of a thienylfulgide, **2C**[14] (Chart 6).This result determined

Scheme 1

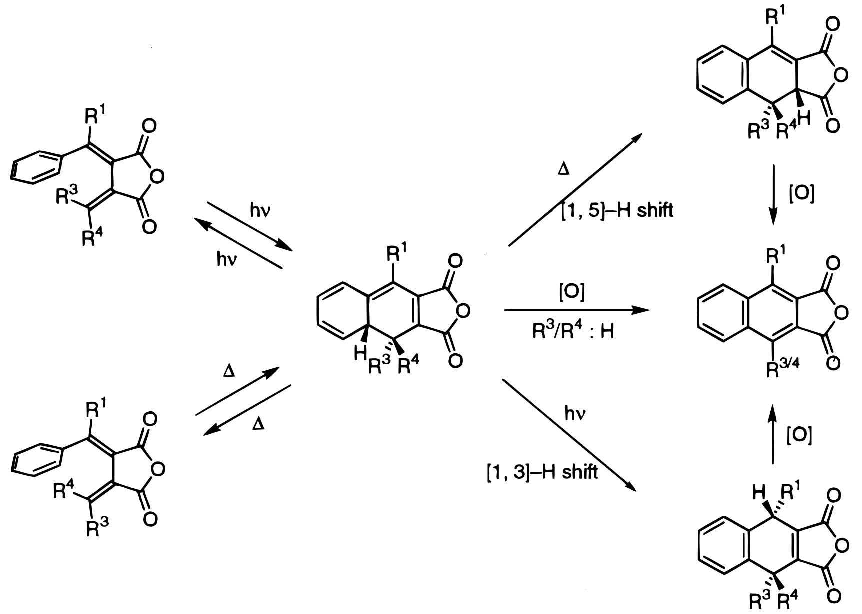
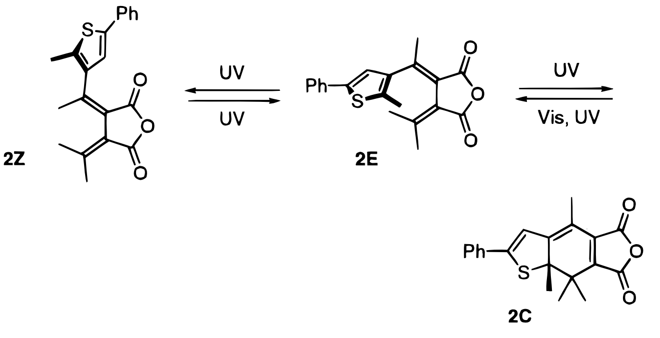


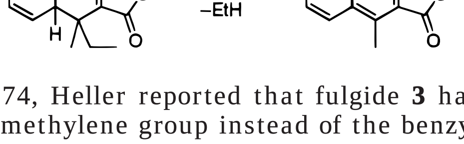
Chart 6



the structure of the colored form and the photocoloration mechanism unequivocally.

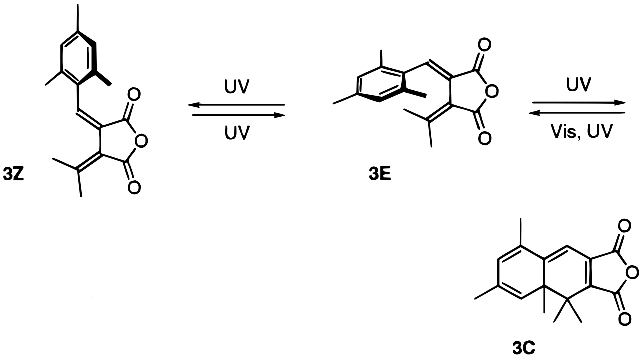
From the late 1960s through the 1970s Heller and co-workers published a series of articles entitled “Overcrowded Molecules”,[15−31] in which the chemistry of fulgides and closely related compounds was dealt with. They clarified the thermal reactions of the colored form of fulgides as depicted in Scheme 1.[3,30−32] Besides the thermal ring opening, the major thermal reactions are hydrogen rearrangement and (or followed by) dehydrogenative aromatization. They observed that even ethane was liberated by thermal treatment to gain aromaticity[28] (Chart 7).

Chart 7



In 1974, Heller reported that fulgide **3** having a mesitylmethylene group instead of the benzylidene group and an isopropylidene group prevented the side reactions in which the hydrogen atoms on the ring-closing carbon atoms were involved, since there was no hydrogen to rearrange or to be removed (Chart 8). In addition, the vicinal methyl groups on the ring-closing aromatic carbon atoms prevented the thermal

Chart 8



ring opening of the *C*-form that should occur by way of, different from the photochemical ring opening, the disrotatory pathway, by the steric repulsion between them. Indeed, they observed that the color did not fade at 160 °C. Unfortunately, the conversion ratio to the colored form at the photostationary state was so low that almost no colored form remained when the colorless form solution of **3E** was irradiated with 366 nm light until it reached the photostationary state.[23]

In 1981, Heller reported the photochromism of fulgide **4**, which had a 2,5-dimethyl-3-furyl moiety[32,33] (Chart 9). For the same reasons as the mesityl-substituted fulgide, **4** showed neither the side reactions nor the thermal back-reaction. Furthermore, because **4C** had a small molar absorption coefficient at 366 nm where **4E** had a large absorption, the photochemical back-reaction from **4C** to **4E** upon irradiation by 366 nm light was negligible. Therefore, the conversion of **4E** to **4C** was close to 100%. Figure 1 shows the absorption spectra of **4E** and **4C** in toluene.

This compound, **4**, is the monument of the long research history of the photochromism of fulgides. The thermally irreversible photochromism has been realized for the first time with **4**. The valuable information for the molecular design to append

Table 1. Quantum Yields of Photoreactions of Furylfulgides

compd	solvent	Φ_{EC}(366)	Φ_{CE}(366)	Φ_{EZ}(366)	Φ_{ZE}(366)	Φ_{CE}(492)	ref
4	toluene	0.18	(0.00)	0.13	0.11	0.048	68
5	chloroform	0.34		0.06	0.12	0.027	62
6	chloroform	0.45		0.04	0.10	0.044	62
7	toluene	0.58	0.00	0.00		0.043	68
8	toluene	0.79	0.082	0.00		0.034	65
9	toluene	0.12	0.06	0.10	0.10	0.21	68
10	toluene	0.51	0.28	0.02	0.05	0.26	68

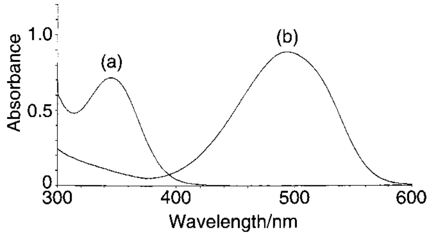
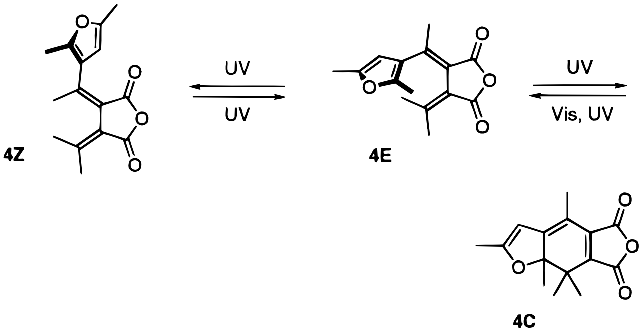


Figure 1. Absorption spectra of **4** in toluene (concentration 1×10^{-4} mol dm^{-3}): (a) **4E**; (b) **4C**. (Kindly provided by Professor Harry G. Heller, University of Wales, Cardiff, U.K.)

Chart 9



thermal irreversibility, i.e., (1) introduction of substituents other than hydrogen onto the ring-closing carbon atoms and (2) employing a heteroaromatic ring, was thus brought about.

The possible application of thermally irreversible photochromic compounds such as **4** is in rewritable optical recording media.[2,34,35] Roughly saying, the 1980s and early 1990s were devoted to improve the properties of **4**, while after the early 1990s to date, development of new fulgides rather than improvement has been the main research interest. In the following sections, improvement of thermally irreversible **4** and development of new fulgide derivatives in some different aspects will be described.

In the meantime, a series of independent studies on the photochromism of fulgides have been done by Paetzold and Ilge's group from the late 1970s through the early 1990s.[36−61] They mainly studied benzylidenefulgides by means of various spectroscopic methods, molecular orbital calculations, and ultrafast spectroscopic analyses. Their work will be introduced in the later sections.

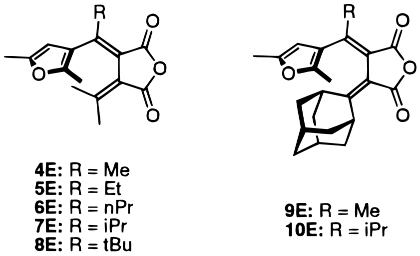
III. Substituent Effects on the Photochromism of Fulgides

A. Steric Effects

Photochromism of fulgide is a reversible photochemical electrocyclization. It requires that three conjugating double bonds are lying in an *s-cis*−*cis*−*s-cis* manner so that the carbon atoms that form the C−C single bond upon photoirradiation would come close. Therefore, the conformation of fulgides at their ground state influences the quantum yield of photocyclization. One of the factors that govern the conformation is steric bulkiness around the hexatriene moiety.

Yokoyama et al. examined the steric influence of the alkyl group on the methylene carbon next to the furan ring.[62−64] As summarized in Table 1, the ring-closing quantum yield upon UV irradiation (Φ_{EC}(UV)) became larger and the *E*-to-*Z* isomerization quantum yield (Φ_{EZ}(UV)) became smaller when the alkyl group became larger. For fulgides with an isopropyl (**7**)[62,63] or *tert*-butyl (**8**)[65] group as the substituent (Chart 10), the *E*-to-*Z* isomerization did not occur (Figure 2). By the way, the method of analysis of photoreactions to obtain quantum yields has been described.[63]

Chart 10



Heller found that the adamantylidene group of **9** (Chart 10) instead of the isopropylidene group of **4** increased the ring-opening quantum yield of visible-light irradiation (Φ_{CE}(vis)).[66,67] Yokoyama et al. synthesized furylfulgide **10** (Chart 10) that has an isopropyl group and an adamantylidene group. It showed 0.51 for Φ_{EC}(UV) and 0.26 for Φ_{CE}(vis), which are 3 times and 5 times, respectively, as large as those of **4**.[68] Similar effects were observed for thienylfulgides[69] and indolylfulgides.[70]

One exceptional result has been reported by Tomoda et al. Phenylfulgide **11** (Chart 11) showed 0.65 for Φ_{EC}(UV) in toluene, even though it possessed merely a hydrogen on the methylene carbon next to the aromatic ring.[71]

Theoretical approaches to explain the steric effects on quantum yields have been tried by several groups. Ilge et al. tried to explain the increase in Φ_{EC}(UV) with increasing steric bulkiness by the change of the sum of the π-free valence of the bond-forming carbon atoms at the singlet excited state.[61] Yokoyama et al. estimated the population of stable conformations of furylfulgides to explain the larger Φ_{EC}(UV) for larger alkyl substituents.[72] Yoshioka et al. reported, as the

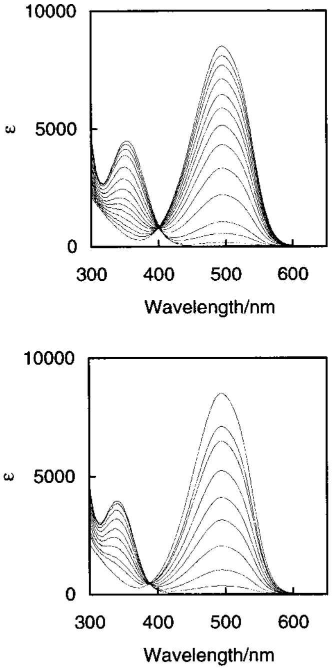
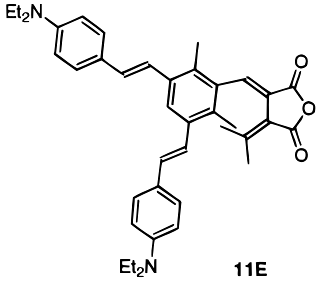


Figure 2. (a, top) Change in absorption spectra of **7** in toluene by 366 nm light irradiation, starting from **7Z**. (b, bottom) Change in absorption spectra of **7** in toluene by 505 nm light irradiation, starting from **7C**. Measured in the author's laboratory.

Chart 11



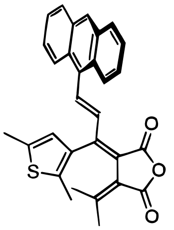
11E

results of ab initio calculations, that there was an intrinsic bond-forming interaction between the cyclization sites of *E*-forms of various furylfulgides in the LUMO.[73]

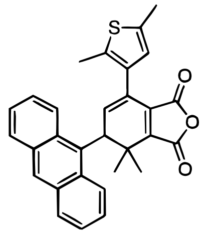
Thienylfulgides with different lengths of alkyl chains have been synthesized.[74]

A unique fulgide, **12**, that had a 9-anthrylvinyl group and a 2,5-dimethylthienyl group on the same methylene carbon of fulgide was synthesized.[75] Upon UV light irradiation, it showed cyclization onto the thienyl group, *E*−*Z* isomerization of two double bonds concerning the aryl groups, and the cyclization product of the hexatriene moiety involving the vinyl group next to the anthryl group. The last one, **12U**, was the ultimate product so that the amount kept increasing during photoirradiation (Chart 12).

Chart 12



12E



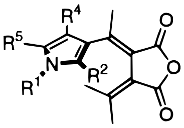
12U

B. Electronic Effects

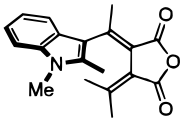
A change of the electronic state of fulgides mainly changes the position of the absorption bands of both isomers. The absorption wavelengths of the colored forms are usually more important, and attempts have been made to lengthen them. Early in the 1980s, only one usable diode laser (AlGaAs) emitted light at about 800 nm. A fulgide should have had the absorption at 800 nm when it would be used as the optical recording material. However, as the absorption maximum of the *C*-form ($\lambda_{max}(C)$) of **4** was about 500 nm and the molar absorption coefficient of **4C** was zero at 800 nm in toluene, improvement of the absorption property of **4C** was required. Because the absorption of the *C*-form in the visible region corresponds to $\pi\pi^*$ excitation, enhancement of the electron-donating ability of the furan ring of **4** may induce the shift of $\lambda_{max}(C)$ toward longer wavelength.

Several heteroaromatic fulgides were synthesized by Matsushima et al.[76] They synthesized 14 compounds, 11 of which were new. Among them, the *C*-form of pyrrylfulgides **13** showed absorption at longer than 600 nm (Chart 13). They also reported the thermal stability and photochemical fatigue resistivity of the fulgides in PMMA film. Although indolylfulgide **14** and thiazolylfulgide **15** were more fatigue-resistive than others, higher fatigue resistivity is required when fulgides are to be applied to devices with repeated use.

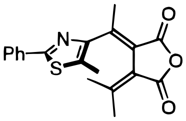
Chart 13



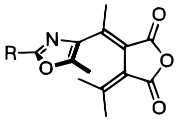
13E



14E



15E



16E

Tomoda et al. reported several oxazolylfulgides **16**[77,78] (Chart 13).

Fan et al. studied various pyrrylfulgides **13** extensively.[79−91]

Electronic effects of substituents on indolylfulgides were investigated in detail by Yokoyama et al. (Figure 3).[92,64] Introduction of electron-donating substituents such as methoxy, methylthio, and dimethylamino groups on the 5-position of the indole ring showed a remarkable shift of the absorption of the *C*-forms to longer wavelength. Especially, the *C*-form of dimethylamino-substituted indolylfulgide, **19C** (Chart 14), showed $\lambda_{max}(C)$ at 673 nm in toluene, and had certain absorption at 800 nm. Another effect of an electron-donating substituent was that Φ_{EC}(UV)

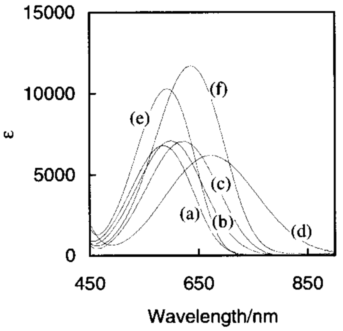
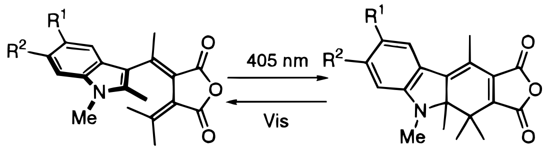


Figure 3. Absorption spectra of substituted indolylfulgides in toluene: (a) **14C**; (b) **17C**; (c) **18C**; (d) **19C**; (e) **20C**; (f) **21C**. Measured in the author's laboratory.

Chart 14



14E: R^1 = H, R^2 = H
17E: R^1 = SMe, R^2 = H
18E: R^1 = OMe, R^2 = H
19E: R^1 = NMe_2, R^2 = H
20E: R^1 = H, R^2 = OMe
21E: R^1 = OMe, R^2 = OMe

14C: R^1 = H, R^2 = H
17C: R^1 = SMe, R^2 = H
18C: R^1 = OMe, R^2 = H
19C: R^1 = NMe_2, R^2 = H
20C: R^1 = H, R^2 = OMe
21C: R^1 = OMe, R^2 = OMe

Table 2. Absorption Spectral Data and Quantum Yields of Photoreactions of Indolylfulgides in Toluene

compd	λ_{max}(C)/nm (ϵ_{max}/cm^{-1} dm^3 mol^{-1})	Φ_{EC}(405)	Φ_{CE}(405)	Φ_{CE}(608)	ref
14	584 (6810)	0.045	0.16	0.051	95
17	600 (7090)	0.028	0.027	0.011	92
18	625 (7060)	0.024	0.024	0.012	92
19	673 (6200)	0.015	0.001	0.00004	92
20	594 (10300)			0.038[a]	93
21	639 (11700)			0.010	93

[a] 612 nm irradiation.

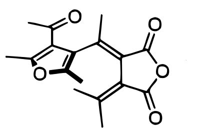
as well as Φ_{CE}(vis) became smaller when the electron-donating ability became stronger. For **19C**, Φ_{CE}(vis) was practically zero (Table 2).

Yokoyama et al. also examined the position effect of substitution on the indole ring. Different from **18C** on which the methoxyl group is substituted on the 5-position, which moved the absorption band toward longer wavelength compared to that of **14C**, substitution of a methoxy group on the 6-position of indole (**20C**) (Chart 14) resulted in a higher molar absorption coefficient (ϵ_{max}(*C*)). Interestingly, 5,6-dimethoxy-substituted **21C** (Chart 14) resulted in a shift of λ_{max}(*C*) toward longer wavelength as well as the enlargement of ϵ_{max}(*C*).[93]

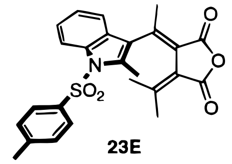
Introduction of a long conjugation with a strong electron-donating group to mesitylmethylene(isopropylidene)fulgide **3**[23] gave a drastic change.[71] At the photostationary state of 366 nm light irradiation for **11**, over 90% of the fulgide changed to the *C*-form in C_6D_6, while the *C*-form of **3** initially formed from the *E*-form did not remain because of formation of the stable *Z*-form at the photostationary state. In addition, this molecular modification gave rise to the remarkable red shift of λ_{max}(*C*) (633 nm) and the large ϵ_{max}(*C*) (24 300 mol^{-1} cm^{-1} dm^3) for **11**.

As the counterpart of the observation for electron-donating substituents, electron-withdrawing substituents gave rise to the shift of absorption of the *E*- and C-forms toward shorter wavelength, and the greater Φ_{CE}(vis). Additional substitution of an acetyl group on C-3 of the furan ring of **4** resulted in shortening of absorption from 345 nm (**4E**) to 318 nm (**22E**) (Chart 15) and from 495 nm (**4C**) to 472 nm (**22C**), as well as an increase in Φ_{CE}(vis) from 0.048 of **4C** to 0.39 of **22C**, in toluene.[94] Decreasing the electron-donating ability of the indole nitrogen by substituting methyl with *p*-toluenesulfonyl had similar effects. In particular, Φ_{CE}(vis) of **14** was 0.051 whereas that of **23** was 0.27.[95] Introduction of an electron-withdrawing group to the middle part of conjugation was somewhat different. Replacement of the CH_3 group of **14** on the methylene group next to the indole ring with a CF_3 group (**24**) (Chart 15) resulted in a shift of the absorption toward shorter wavelength for the *C*-form by 14 nm while toward longer wavelength for the *E*-form by 41 nm. Also, the CF_3 group brought about an increase in Φ_{EC}(UV) and decrease in Φ_{CE}(vis), as well as thermal stability of the *C*-form and photochemical repeatability.[96a] However, the thermal stability of the *E*-form was decreased.[96b]

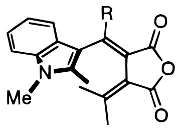
Chart 15



22E



23E



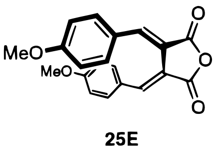
14E: R = CH_3
24E: R = CF_3
28E: R = iPr
29E: R = nPr

IV. Stereochemistry and Spectroscopy of Fulgides

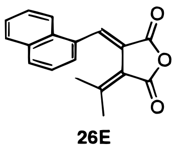
A. X-ray Crystallographic Analysis

Stereostructures of isomers of fulgides have been examined by X-ray crystallographic analyses frequently because of the structural interest that the open forms are sterically congested. The first study was carried out by Cohen in 1970 on bis(4-methoxybenzylidene)fulgide **25E**[97] (Chart 16).

Chart 16



25E



26E

The X-ray crystallographic analysis of the colored form was done in 1984 by Kaftory for **2C**.[14] This study unequivocally determined the structure of the colored

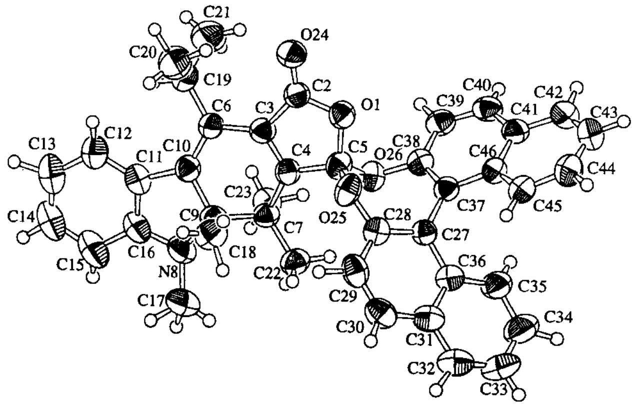


Figure 4. Stereostructure of the major isomer of **27C** ((9a*S*)-**27C**). (Reprinted from ref 104. Copyright 1996 American Chemical Society.)

form and hence the mechanism of photoreaction. Kaftory has also done X-ray crystallographic analyses for **2E** and **2Z**, and found that these isomers formed crystals with one enantiomer (vide infra), while **2C** formed crystals with racemic mixtures of enantiomers with regard to the quaternary chiral carbon atom. Kaftory irradiated a crystal of **2E** by UV light to try to induce photochromic reaction in the crystalline state, but only the surface of the crystal turned to the colored form.

X-ray crystallographic analyses of furylfulgides **4E** and **4Z**,[98] **7E**,[72] bisbenzylidenefulgide **1E** and the corresponding fulgenic acid,[99] substituted bisbenzylidenefulgides,[100−102] and naphthylmethylenefulgide **26E**[103] (Chart 16) have been done so far. The second example of X-ray crystallographic analysis of the *C*-form has been done on chiral derivative **27C** by Yokoyama et al.[104] The ORTEP diagram is shown in Figure 4.

The structural features of the *E*-form are (1) the distance between the bond-forming carbon atoms upon photoirradiation is between 3.3 and 3.9 Å, (2) the aromatic ring slants from the plane of the adjacent double bond by 25−50°, and (3) the two double bonds around the single bond on the succinic anhydride are twisted toward each other by 23−40°.

In relation to their X-ray crystallographic analysis, ab initio molecular orbital calculations of **4E**, **4Z**, and **4C** have been done by Yoshioka et al.[105] The results were in good agreement with the structures determined by X-ray crystallographic analysis. It should be pointed out that **4C** is calculated to be 10 kcal mol^{-1} more stable than **4E**.

B. NMR Spectroscopic Study of Fulgides

Several NMR spectroscopic analyses of fulgides have been reported. Cohen et al. reported the ^{1}H NMR data of bis(4-methoxybenzylidene)fulgide **25** in 1970.[97] Ilge et al. assigned the ^{1}H[54] and ^{13}C[46] NMR signals of a number of substituted phenylfulgides. Heller et al. reported ^{1}H NMR data of a variety of thienylfulgides.[106] Yamamoto et al. assigned the ^{13}C NMR signals of the furylfulgide **4E** by H−C COSY and 2D-INADEQUATE measurements.[107]

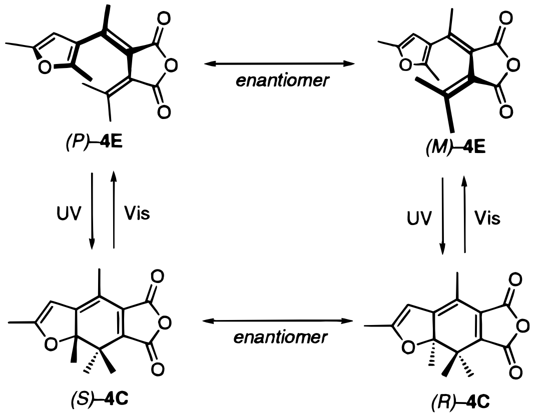
Kaptein et al. succeeded in following the photoreaction from **4E** to **4C** by ^{1}H NMR using newly developed nuclear spin coherence transfer pulse sequences, and correlated the signals of methyl protons of **4E** with those of **4C**.[108] This study confirmed the conrotatory ring-closing mode, which had been reported by Heller et al.,[33] upon UV-light irradiation.

Yonker et al. studied the pressure (up to 2 kbar) and temperature (up to 120 °C) effects on the photochromism of **4** in $CDCl_3$ by ^{1}H NMR.[109] No photocoloration of the *E*-form occurred at 2.0 kbar at 120 °C whereas little effect of high pressure was observed at 25 °C.

C. Chiral Properties of Fulgides and Derivatives

Because of the steric hindrance, it has been pointed out that the hexatriene moiety of the *E*-forms could not lie in a plane and generated chirality.[14] As the chirality of the *E*-form is derived from the helicity of the hexatriene moiety (the two enantiomeric helicities are abbreviated as *(P)* for plus and *(M)* for minus, which represent right-handed-screw-like orientation and left-handed-screw-like orientation, respectively, of the hexatriene moiety), photochromism of fulgides intrinsically involves the chiral nature. An *E*-form molecule with *(P)* helicity should generate the *(S)*-*C*-form, while the *(M)*-*E*-form generates the *(R)*-*C*-form, because the photochromic electrocyclization reaction obeys Woodward−Hoffmann rules.[33] The relationship between the helicity of the *E*-form and the asymmetry of the *C*-form is exemplified for **4** in Scheme 2.

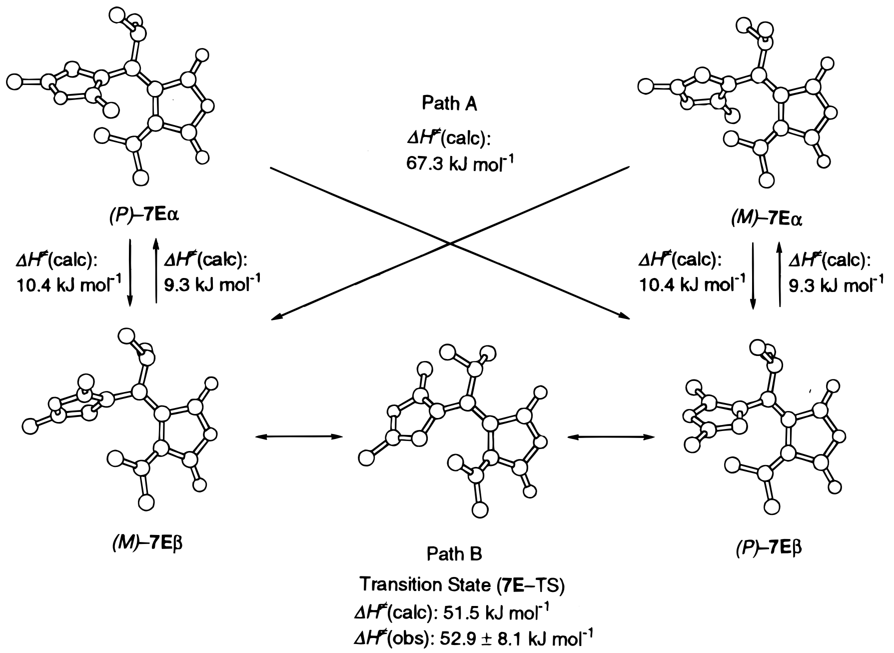
Scheme 2



The racemization of the helicity of an *E*-form fulgide in solution was first observed by Yokoyama et al. for **7E** by ^{1}H NMR.[72,110] They compared $\Delta H^{\ddagger}$ values of racemization of **7E** obtained by experiment with those of the possible racemization methods obtained by AM1 semiempirical MO calculations, and determined that the enantioisomerization process occurs by way of the highly congested transition state **7E-TS**, shown in Scheme 3.

As an extension of this work, Yokoyama et al. succeeded in optical resolution of indolylfulgide **28E** having an isopropyl group[111] (Chart 15). The resolved fulgide showed repeated change of circular dichroic (CD) spectra with photochromic reaction. Upon heating or prolonged irradiation of UV light, however, racemization occurred gradually. The activation en-

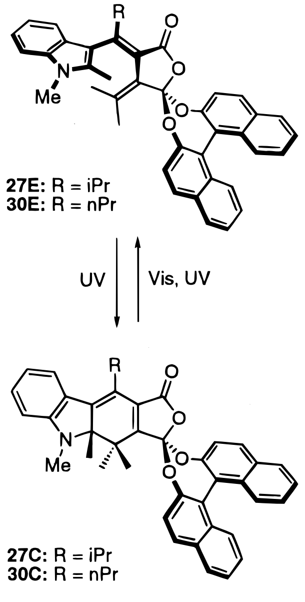
Scheme 3



ergy of thermal racemization was determined to be 107 kJ mol^{-1}.

By taking advantage of facile enantioisomerization of the helicity of fulgides having a rather small alkyl group such as *n*-propyl on the methylene carbon adjacent to the aromatic ring, Yokoyama et al. realized a diastereoselective photochromic system. They introduced *(R)*-binaphthol onto the succinic anhydride ring of fulgide **29E** in an acetal-like manner to give **30E**[104] (Chart 17). Because of steric repulsion between one of the naphthalene rings of binaphthol and one of the methyl groups of the isopropylidene group located outside the molecule, the hexatriene moiety of **30E** was forced to take *(P)*-helicity. Consequently, the diastereomeric ratio of the *C*-form generated by UV irradiation was 95/5 (90% de) for **30C** (Chart 17), in which the *(S)*-diastereomer was predominant.[112,113] The absorption spectra of **30E**, **30C**, and the potostationary state of UV irradiation are shown in Figure 5.

Chart 17



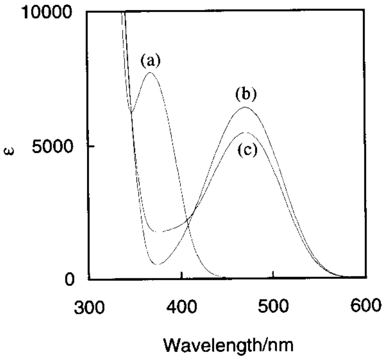


Figure 5. Absorption spectra of *(R)*-binaphthol-condensed indolylfulgide **30** in toluene: (a) **30E**; (b) **30C**. (c) Spectrum of the photostationary state of 366 nm light irradiation to **30E**. Measured in the author's laboratory.

V. Environmental Effects on the Photochromism of Fulgides

Fulgides exhibit photochromism in solution, in polymer films, or in glass solids. In crystals, however, they show photochromism only in the surface layers[14] or form [2+2] dimers.[114] Examining the effects of the environment on the photochromism of fulgides is important because when they are used as photoswitches they might be used in polymer films or in glass solids. However, in the fundamental study, photochromism in solution is also indispensable.

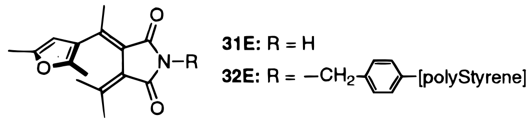
Several groups have reported medium effects on the photochromic behavior of furylfulgide **4**. Heller et al. reported the quantum yields of photoreactions in five solvents.[115] In all solvents used, $\Phi_{EC}(366)$ is about 0.20. They stated that it was useful as a convenient chemical actinometer. However, warnings on the use of **4** as an actinometer were reported by Gou et al.[116] that the recycling use of the same solution of **4E** was not recommended because of formation of **4Z**, and by Gauglitz et al.[117] that Φ_{CE}(366) was not zero as reported[33] but should be as large as Φ_{CE}(vis) so that the *E*- and *Z*-forms remained at the photostationary state of 366 nm light irradiation. The better properties of **7E** for the chemical actinometer than **4E**, i.e., no *E*-to-*Z* isomerization and large Φ_{EC}(UV), have been pointed out.[62]

Saito et al. developed the method to determine quantum yields of photoreactions in polymer films. By this method, they studied the temperature dependence of the ring-opening quantum yield Φ_{CE}(vis) of **4C** in a PMMA film.[118]

Horie et al. measured Φ_{CE}(vis) of **4** in PMMA film at 4 K.[119] There were "mobile sites" (in which **4C** can change its structure) and "immobile sites" in a PMMA film at 4 K, and Φ_{CE}(vis) for the molecules in the mobile sites was almost the same as those at 298 K in PMMA or in solvents at room temperature. However, the extent of decoloration reaction was only 13%, and the remaining **4C** molecules were in the immobile sites.

Smets et al. examined the dependence of quantum yields of **4** and fulgimide **31** (Chart 18) on the nature of polymers (PMMA and its family, and polystyrene).[120] They found that the quantum yields determined above T_g of polymers were close to those in solution, whereas those determined below T_g were smaller. The quantum yields showed dependence on solvents used, but showed little temperature dependence. They also examined the photochromic nature of the fulgimide-pendant styrene copolymer **32** (Chart 18). Below T_g, the quantum yields of it were smaller than those of the fulgimide dispersed in polymer films, but close to those in solution when measured above T_g.

Chart 18

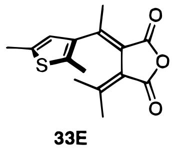

31E: R = H

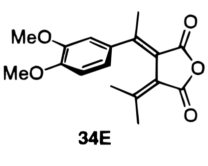
32E: R = —CH$_2$—⬡—[polyStyrene]

Yokoyama et al. studied the photochromism of **4** in solvents and polymer films.[121] In solution, Φ_{EC}(UV) and Φ_{CE}(vis) decreased slightly when the solvent polarity such as E_T(30) or dielectric constant increased. In polymer films, Φ_{CE}(vis) greatly depended on the polarity of the polymers used, and was larger when measured in less polar media. In general, quantum yields of photoreactions upon UV-light irradiation in solvents were larger than those in polymer matrix, but Φ_{CE}(vis) values in solvents were smaller than those in polymer films.

Port et al. studied thienylfulgide **33E** (Chart 19) in solvents and polymer films at different temperatures and determined the activation energy of decoloration at the excited state.[122]

Chart 19


33E


34E

Gou et al. studied the solvent effect on the ring-closing rate of phenylfulgide **34E**[123] (Chart 19).

Chaput et al. demonstrated that indolylfulgide **14E** doped in a hybrid organic–inorganic sol–gel matrix, prepared from methyltriethoxysilane, showed usual photochromism.[124] The absorption of **14C** shifted toward longer wavelength.

Kurita et al. investigated the photochromism of crystals of fulgide **7**, and showed that the transformation between the *E*- and *C*-forms occurs in crystals.[125]

VI. Photophysical Study of Photochromism of Fulgides

A. Ultrafast Analysis of Photoreactions of Fulgides

As the photochromism of fulgide belongs to the concerted electrocyclization, it occurs very fast. Several groups have been involved in determining the rate of photochromic reactions of fulgides.

Becker et al. examined the photocyclization of several phenylfulgides as well as **4** with nanosecond laser flash photolysis, and reported that the reaction was completed within 1 ns.[126] Judging from the data obtained in this study including the fact that dioxygen did not affect any of the photochemical properties, they concluded that photocyclization reactions of fulgides were initiated from the excited singlet state of $\pi\pi^*$ character. The same assumption was obtained by MNDO semiempirical molecular orbital calculations.[98] These results have been accepted to date rather than the previously proposed nπ^* excitation mechanism.[24]

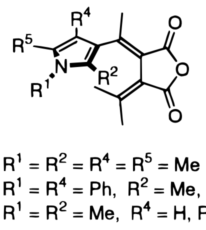
Ilge et al. reported that the cyclization of various fulgides was completed within a few picoseconds.[57] They interpreted the reason the cyclization and *E*–*Z* isomerization occurred so fast was that these processes required no activation energy on the excited-state energy surfaces because of the torsion of the bonds caused by the steric congestion.

Rentzepis et al. examined the transient spectra of furylfulgide **4**, and found the cyclization reaction occurred within 20 ps without any intermediate.[127]

Kurita et al. reported that the time constant of cyclization of **7E**, which did not show *E*-to-*Z* isomerization, was 10 ps. It was not affected by the kind of polymer matrixes used.[128]

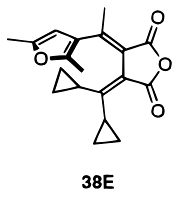
Fan et al. studied the photocyclization of pyrrylfulgides **35**,[79] **36**,[81] and **37**[82] (Chart 20) by nanosecond laser flash photolysis, and concluded that the cyclization reactions of pyrrylfulgides occurred mainly from the $\pi\pi^*$ excited singlet, but the $\pi\pi^*$ excited triplet state was also involved.

Chart 20


35E: R^1 = R^2 = R^4 = R^5 = Me

36E: R^1 = R^4 = Ph, R^2 = Me, R^5 = H

37E: R^1 = R^2 = Me, R^4 = H, R^5 = Ph


38E

The transient absorption of cyclization of furylfulgides **4E** and **9E** was measured by Port et al. recently with subpicosecond laser flash photolysis. They postulated a reaction model in which there were two pathways of reactions from the excited *E*-form, one of which included an intermediary state while the other a direct reaction.[129,130]

Rappon et al. observed the activation energy for the photocyclization reaction of **4E** in polymer matrixes at room temperature or higher,[131] which was inconsistent with the observations of other researchers.[122,132,128]

Kurita et al. reported that the lifetime of S_1 of **7C**, estimated from the time response of fluorescence, was 1 ns at 4.2 K in a PMMA film.[133,134] They also reported that energy transfer occurred from S_1 of **7C** to another **7C** molecule which had lower S_1 energy (caused by the difference of the environment in the polymer matrix) when the concentration of fulgide was high.[133] In a separate paper, they estimated that the nonradiative deactivation of **7C** occurred through the C−H vibration of methyl groups.[135]

Wallace et al. studied picosecond laser flash photolysis of furylfulgide **38E** (Chart 20) and concluded that the time constants of coloration reaction in solution was less than 20 ps and that in polymer films it was less than 50 ps.[136] They also demonstrated the formation of the holographic interference grating with polymer films containing **38**.

B. Fulgides as Probes of Detection of Environmental Situation

Wallace et al. studied the orientation of toluene at the air−liquid interface by second harmonic generation (SHG). Addition of the furylfulgide **38** to toluene weakened SHG intensity.[137]

Rappon et al. used **4** as the probe of association of pentanols in heptane.[138] The decoloration rate of **4C** was measured in the mixture of various molar ratios of pentanols and heptane and at various temperatures, and the apparent rate constants were obtained. From the data obtained, it was concluded that the associations of 1- and 2-pentanols formed linear multimers, whereas that of *tert*-pentanol (2-methyl-2-butanol) formed cyclic multimers.

C. Irradiation Wavelength Dependence of Decoloration Quantum Yield

Heller et al. reported that while Φ_{EC}(UV) of **2**, **4**, or **9** did not depend on the reaction temperature and irradiating wavelength, Φ_{CE}(vis) depended on both.[2,67] They proposed the equations which related Φ_{CE}(vis) with the temperature at which the experiment was carried out and the irradiating wavelength, for **2C**[2] and for **9C**[67] in toluene. An explanation of the wavelength dependence of photoreaction was given by Becker et al.,[126] though they observed wavelength dependence of Φ_{EC}(UV). They presented that photocyclization occurred more efficiently when excited to a higher vibrational level on the excited state, and photoreaction competed with internal conversion. Wavelength dependence of Φ_{CE}(vis) for other fulgides was also reported by Yokoyama et al.[139,140]

Table 3. Arrhenius Activation Energy of Decoloration Processes of Fulgides

compd	matrix	temp/K	E_a/cm^{-1} (λ/nm)	ref
4	PMMA	303−353	722 (500)	118
4	heptane	303−333	831 (540)	141
4	toluene	303−333	742 (540)	141
4	1-pentanol	303−333	382 (540)	141
4	ethanol	303−333	353 (540)	141
4	ethyl acetate	303−333	650 (540)	141
4	acetonitrile	303−333	952 (540)	141
7	PMMA	100−350	240 (426), 520 (546)	139
9	toluene	294−355	300 (426), 340 (546)	2
10	PMMA	100−350	200 (426), 230 (546)	139
32	polystyrene	100−300	50 (546)	122
2	toluene	294−356	385 (426), 580 (546)	2

D. Activation Energy of Decoloration Process on the Excited States

As described in part in the above section, several groups reported the temperature dependence of Φ_{CE}(vis) for different fulgides in different matrixes.[67,118,2,132,141] Since ln(Φ_{CE}(vis)) showed good linearity with regard to T^{-1},[122,139] the apparent activation energy values of ring opening on the excited-state energy surfaces have been calculated. These calculations were done on the understanding that the photochemical kinetic constant (and hence Φ_{CE}(vis)) showed the Arrhenius-type temperature dependence. Combined data are shown in Table 3.

VII. Application to Optical Recording Memory

A. Trial Preparation of Recording Media Employing Fulgides

Because of thermal irreversibility of fulgides, application of them to rewritable photon-mode optical memory media[142] was stated with reality by Heller when his group synthesized the furylfulgide **4**.[143,66] Several properties are required to be used for memories, such as (1) thermal stability, (2) fatigue resistivity, (3) nondestructive readout ability, (4) high efficiency of photoreactions (large quantum yields and large molar absorption coefficients), (5) high speed of photoreactions, (6) diode laser susceptibility, (7) solubility in the polymer matrix, and so on. Fulgides gained thermal irreversibility in 1981,[33] and most of the other requirements have largely been improved since then. While the most difficult problem may be to develop a nondestructive readout method, memory media with faint destruction of records by readout have been prepared by way of trial so far.

Tomoda et al. prepared optical memory disks as shown in Figure 6 using oxazolylfulgides **39**−**41** (Chart 21) and furylfulgides **4** and **9**.[144] The disk was first irradiated with UV light to make it entirely colored (unrecorded state) and then recorded on by decoloration to form pits by pulses of an Ar ion laser (514.5 nm). The best signal-to-noise (S/N) ratio, 49

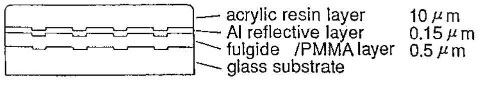
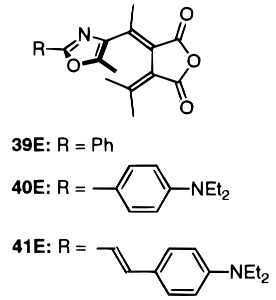


Figure 6. Disk structure employed for data storage using fulgides. (Reprinted with permission from ref 144. Copyright 1992 Chemical Society of Japan.)

Chart 21



dB, was obtained for a disk with 10 wt % **41** in PMMA. To characterize the performance of recording density, recording experiments with various frequencies of the laser pulse were done for the disk with **9**. Under the experimental conditions, a good S/N ratio (ca. 38 dB) was maintained under a 1.5 MHz laser pulse. Readout of the record was done by the difference of reflection using a 514.5 nm Ar ion laser. As shown in Figure 7, **41** showed high stability toward readout. Fatigue resistivity was also tested for a disk of **41**. Figure 8 shows that only a small decrease of the S/N ratio of readout was observed after 20 cycles of write and erase.

Matsui et al. prepared a recording disk using 5-dimethylaminoindolylfulgide **19**.[140] As described in the previous chapter, Φ_{CE}(vis) depended on the irradiation wavelength. They found that the inclination of relation is quite steep (Figure 9) so that Φ_{CE}(vis) became zero at the area of longer wavelength inside the absorption band of **19C**. This means that irradiation of light of long wavelength inside the absorption band to a disk containing **19C** will not induce photoreaction, even though it shows absorption. They applied this finding to the nondestructive readout method of recording on the disks containing **19.** The schematic diagram of the cross section of the disk is shown in Figure 10. Recording was done by a 325 nm He−Cd laser, and readout was done by detecting the reflecting light intensity of a AlGaAs 784 nm diode laser. The remarkable result was that, after 10^5 readouts, the recorded pit had more than 80% of the initial absorption.

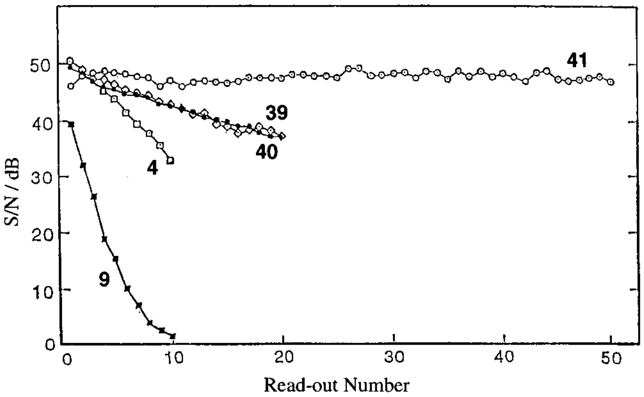


Figure 7. Read-out stability of various fulgide disks. (Reprinted with permission from ref 144. Copyright 1992 Chemical Society of Japan.)

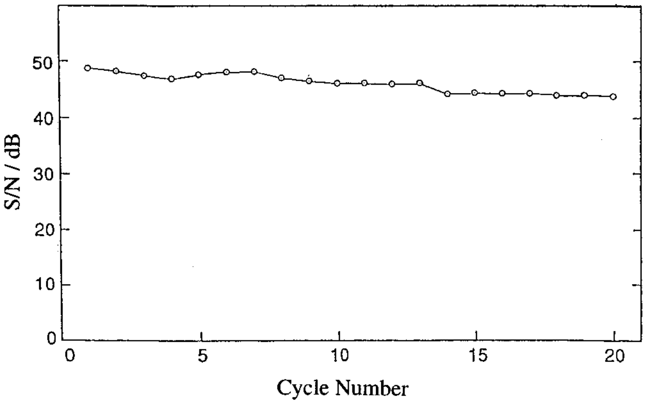


Figure 8. Change of the read-out signal from a disk containing fulgide **41** with recording and erasing cycles. Recording: line velocity, 3.8 m/s; laser, Ar^+ 514.5 nm, 18 mW, 300 kHz. Read-out: line velocity, 7.5 m/s; laser, Ar^+ 514.5 nm, 3 mW. (Reprinted with permission from ref 144. Copyright 1992 Chemical Society of Japan.)

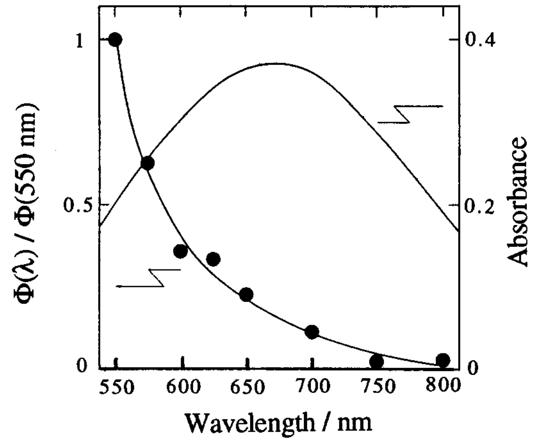


Figure 9. Relative decoloration quantum yield of **19C** in a PMMA film (ca. 10 μm). Dots: Ratio of decoloration quantum yield with regard to the quantum yield at 550 nm. Line: Absorption spectra of **19C** in PMMA. (Reprinted with permission from ref 140. Copyright 1994 Chemical Society of Japan.)

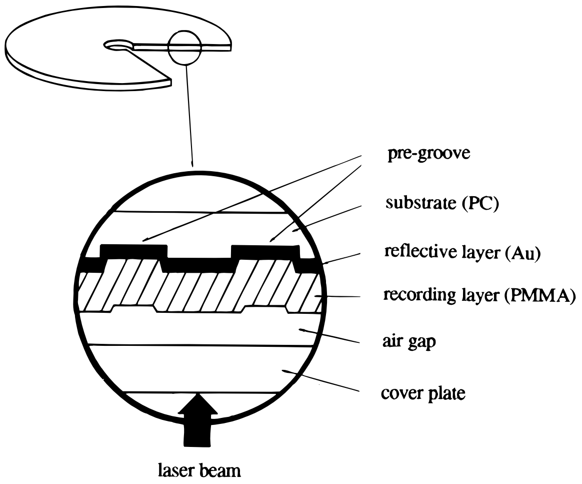


Figure 10. Schematic diagram of the cross-section of a sample disk containing **19**. (Reprinted with permission from ref 140. Copyright 1994 Chemical Society of Japan.)

Fan et al. prepared a recording disk with pyrrylfulgide **42** (Chart 21) by spin-coating it with PMMA or by vacuum evaporation.[90] Over 500 write−erase cycles were possible without any observable change of disk performance.

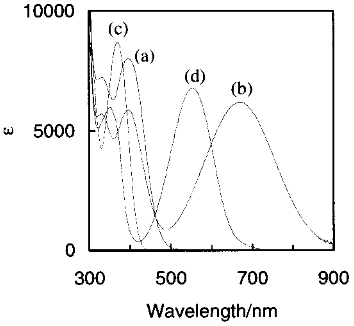
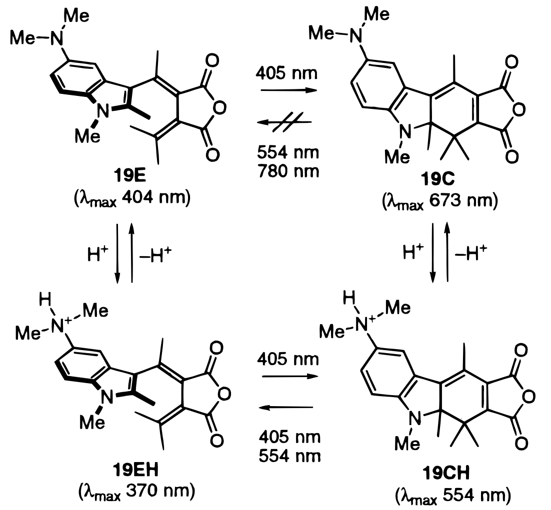


Figure 11. Absorption spectra of dimethylaminoindolylfulgide **19** in the absence and presence (excess amount) of trichloroacetic acid in toluene: (a) **19E**; (b) **19C**; (c) **19EH**; (d) **19CH**. Measured in the author's laboratory.

B. Nondestructive Readout Possibility of Recorded Memory

As described before, development of the nondestructive readout method is a challenging problem. Matsui's method[140] is one of them. Using the same compound **19**, Yokoyama et al. proposed another and completely different nondestructive readout method. In the section Electronic Effects, it was introduced that **19C** did not go back to the *E*-form by visible-light irradiation. However, protonation to nitrogen of the dimethylamino group restored the ability of decoloration upon visible-light irradiation, together with a large shift of absorption toward shorter wavelength in toluene (Figure 11). When a small amount of acid was present in solution, an acid–base equilibrium was maintained, even when the photochemical isomerization proceeded (Scheme 4). This result gave rise to the application to the memory media using three different light sources. At 800 nm, only **19C** absorbs light, but no photoreaction occurs. Therefore, it can be used as the readout light. At 550 nm, both **19C** and **19CH** absorb light, but only **19CH** changes to **19EH**, perturbing the acid–base equilibrium. To restore equilibrium, **19C** was protonated to **19CH**, which then changes to **19EH** under the illumination of 550 nm light. This is regarded as the erase procedure. Irradiation with 405 nm or shorter wavelength light generates a mixture of **19C** and **19CH**. This is the writing procedure.[145] These phenomena were also observed in a PMMA film containing CCl_3COOH or in a copolymer of PMMA–PMA.[146]

Scheme 4



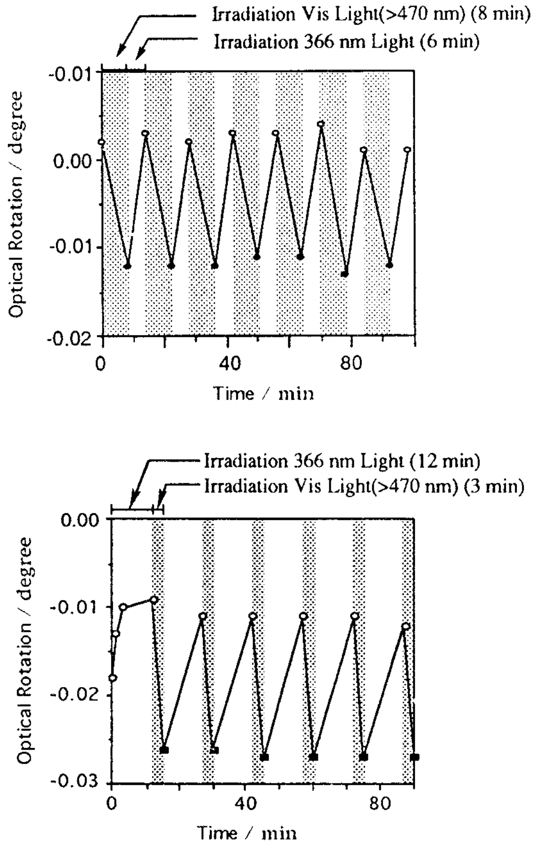
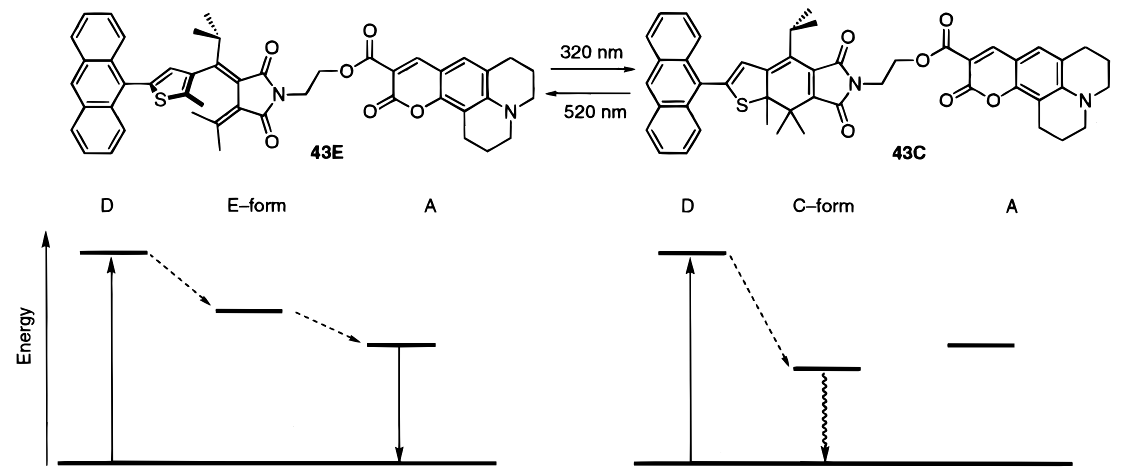


Figure 12. Reversible changes of optical rotation of **27** (top) and **30** (bottom) in PMMA films. (Reprinted from ref 104. Copyright 1996 American Chemical Society.)

As far as the photochromic reaction is applied to the memory media, write–erase procedures require two different wavelengths of light. Readout should be done by either "readout of the locked memory with write or erase light" or "readout of the memory with the third light, the wavelength of which should locate outside the absorption band". The latter trial has been demonstrated by Yokoyama et al. by detecting the change in optical rotation of chiral fulgide derivatives.[104,112,113] They prepared PMMA films containing **27** or **30**, and examined the change of optical rotation of the film at 589 nm (sodium D-line). The optical rotation values changed repeatedly with photochromic reactions by ca. 0.01° (Figure 12). Because neither *E*-forms nor *C*-forms had absorption at 589 nm, readout procedures did not induce photochromism.

If the memory, recorded by UV- or visible-light irradiation, is read out by the change of vibrational spectra in the IR region, it is a nondestructive readout method. Port et al. demonstrated that it is possible.[147,148,130] While **7E** has a small absorption at 1523 cm^{-1}, **7C** has a medium one there. Irradiation of 366 nm light on **7E** in dichloroethane decreased the transmittance of the IR laser at 1534 cm^{-1}, and irradiation of 546 nm light to the resulting solution increased the transmittance of the IR laser. Since the IR diode laser never induces photochromic reaction, this finding can be a nondestructive readout method.

Scheme 5



VIII. Switching of Functions

Photochromism induces a restorable change of structure of molecules by photoirradiation. As a result, its color (location of the absorption band) changes drastically. However, the third property of the molecule itself or the effect imposing on the surrounding environment may be altered repeatedly by the photochromic reactions. In other words, some properties of the molecules (other than absorption) or the properties of the system that includes the photochromic molecules can be switched by photoirradiation.

A. Fluorescence

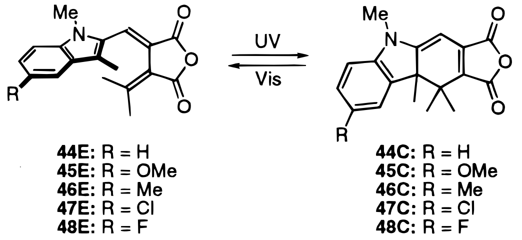
While *C*-forms of fulgides often fluoresce at lower temperature,[13,133,134] no fulgide has been believed to be luminescent at room temperature unless it has a luminescent substituent.

Port et al. synthesized fulgimide **43** possessing an anthracene ring as the light antenna (energy donor, D) on the far side of thiophene ring, and an aminocoumarin ester moiety as the luminescent group (energy acceptor A) on the fulgimide nitrogen.[149,148] When the fulgimide part took the *E*-form, excitation of the anthracene moiety at 400 nm resulted in emission of fluorescent light from the coumarin part. The energy transfer from the excited anthracene to the coumarin occurred through the *E*-form core of fulgimide **43**. On the contrary, after irradiation of 320 nm to induce photocyclization of **43E** to reach the photostationary state, the fluorescence intensity decreased. This was explained by the fact that because the energy level of the excited state of the *C*-form core of fulgimide **43** was lower than that of the coumarin, it worked as the energy trap between D and A, and **43** returned to the ground state by radiationless deactivation. Therefore, the intensity of fluorescence changed between strong and weak repeatedly by photoirradiation (Scheme 5).

Yokoyama et al. found that the fluorescent property of *(R)*-binaphthol-condensed fulgide **30** was changed by photochromic reaction.[150,113] While **30E** did not emit light when excited at any wavelength longer than 300 nm in toluene, **30C** did. This was the first example of complete on/off of fluorescence because no light-emitting species remained after visible-light irradiation. Although **27** showed the same phenomenon, the intensity of fluorescence of **27** was about one-tenth that of **30**.

Rentzepis et al. synthesized five indolylfulgides, **44**−**48**[151] (Chart 22), with which the connecting position of substituted indole rings with the succinic anhydride moiety were not ordinary C-3 but C-2.[152] They found the *C*-forms of these compounds were fluorescent at room temperature while the *E*- and *Z*-forms were not fluorescent.[151]

Chart 22

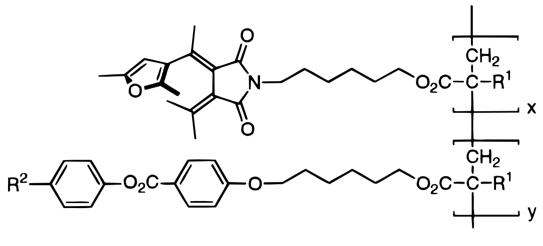


B. Liquid Crystalline Properties

Because of the reversible change of structure, the ability of interaction of photochromic compounds with their environments can be changed. When the environment is the liquid crystal which takes the stable ordered molecular orientation, the doped photochromic molecules act as the perturbing factor of molecular order, and their ability to disorder the arrangement of liquid crystalline molecules changes reversibly by the photochromic structure change. Although these studies have been done extensively with azobenzenes, fulgides have also been used by taking advantage of the property of thermal irreversibility.

Ringsdorf et al. prepared liquid crystalline methacrylic and acrylic copolymers **49** and **50** (Chart 23), prepared from the monomers having a fulgimide unit and the monomers having a phenyl benzoate mesogen unit.[153] Both polymer films showed normal photochromism. Irradiation of UV light to induce cyclization caused the clearing point to be higher. The optically stored image of a photomask was reported to be observed with the polarizing microscope.

Chart 23

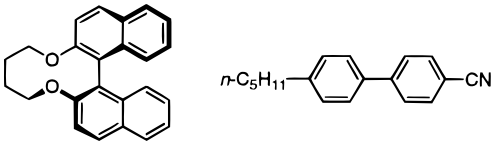


49: R^1 = H, R^2 = CN
50: R^1 = Me, R^2 = OMe

Gleeson et al. mixed furylfulgide **4** or thienylfulgide **33** (less than 2% w/w) with a nematic liquid crystal (E7, Merck) which is composed of several biphenyl derivatives.[154] Although they had expected a large change of clearing point by photochromism, little change was observed. They also examined the change of dielectric constants and elastic constants by photoirradiation to the mixture of **33** and E7.[155] The difference arose mostly from the change of clearing points, and no significant change was observed when they were compared on the basis of "reduced temperature", the deviation from the clearing point.

Schuster et al. demonstrated that the photochromism of a fulgide was able to alter the helical pitch length of a cholesteric liquid crystal.[156] They added indolylfulgide **14** (5.2% w/w) to a cholesteric liquid crystal which was generated by adding 1.35% (w/w) of chiral cyclic ether **51**, prepared from *(R)*-binaphthol, to 4-cyano-4′-pentylbiphenyl **52** (5CB) (Chart 24). The cholesteric pitch length was changed reversibly between 30 and 42 μm, for colored and colorless states, respectively.

Chart 24



(R)-**51** **52** (5CB)

Yokoyama et al. reported that the binaphthyl derivatives of indolylfulgides **27** and **30** acted as chiral dopants to generate cholesteric phases by addition to nematic liquid crystal **52**. Photochromism of them induced a dramatic change of cholesteric pitch.[157,113] Thus, addition of only 1.1 mol % **27** showed a change of pitch length between 15.8 and 2.6 μm, for the *E*-form and the photostationary state of UV irradiation, respectively. The iterative change was possible as shown in Figure 13.

C. Fulgides with a Crown Ether Moiety

Combination of crown ethers with photochromic molecules has been extensively studied on azobenzenes because of the large change of molecular shape upon *E*−*Z* photoisomerization.[158] Because of a relatively small structural change induced by photoirradiation for fulgides, little study has been done on this topic.

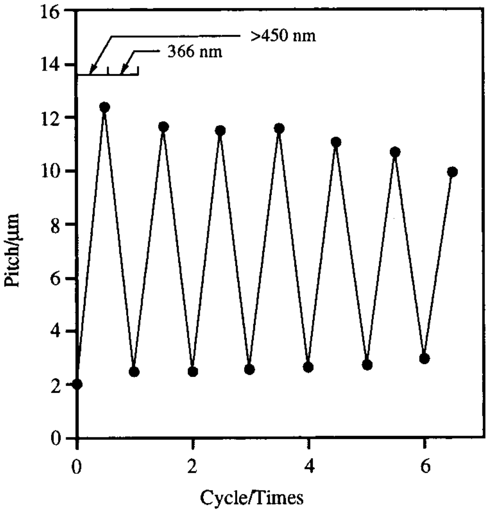
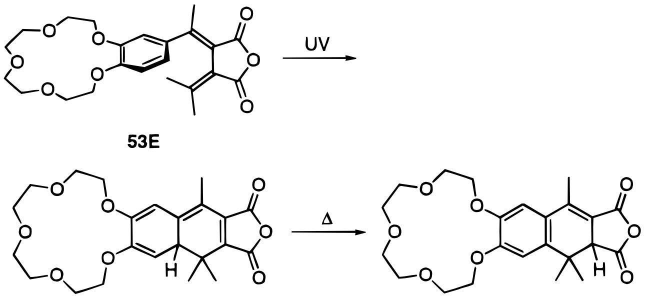


Figure 13. Reversible changes of the cholesteric pitch of a mixture of 5CB (**52**) and **30**, by photochromism of **30**. Concentration: 1.22 × 10^{-2} mol dm^{-3}. Starting with **30C** at 30 °C. Irradiation time: >450 nm, 5 min; 366 nm, 60 min. (Reprinted with permission from ref 157a. Copyright 1997 Chemical Society of Japan.)

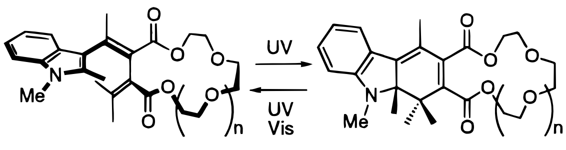
Guo et al. prepared phenylfulgide **53** bearing a benzo-15-crown-5 moiety, and compared the photochromic properties in the presence and absence of metal cations.[159] The absorption of both colored and colorless forms shifted by 28 nm toward shorter wavelength in the presence of sodium cation, while it shifted only 12 nm in the presence of potassium cation. More than 40 nm shifts were observed for alkaline-earth-metal cations. Addition of sodium cation also inhibited the thermal 1,5-sigmatropic rearrangement of the colored form to yield the photochemically inert species **54** (Chart 25).

Chart 25



Yokoyama et al. synthesized some cyclic diesters (fulgenates), **55**−**57** (Chart 26), from indolylfulgide **13** and the diol having crown-ether-like structures.[160] Because of the larger flexibility, the binding con-

Chart 26



55E: n = 1
56E: n = 2
57E: n = 3

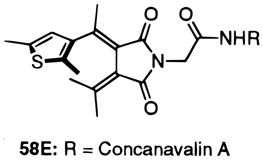
55C: n = 1
56C: n = 2
57C: n = 3

stants with the alkali-metal cations were larger for the *E*- and *Z*-forms than the *C*-form. No cyclization upon irradiation of UV light occurred in the cases of combination of **56E** and Na^+ and **57E** and K^+.

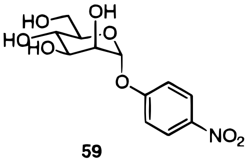
D. Control of Biological Activities by Photochromism of Fulgides

Fulgimide **58** (Chart 27), synthesized by Willner et al., was attached to lysine nitrogen of concanavalin A, a protein that forms complexes with specific pyranoses such as α-D-mannopyranoside through the substituent on the imide nitrogen of **58**. Upon photoirradiation, the structural change of fulgimide induced a change of the association constant with 4-nitrophenyl α-D-mannopyranoside **59**. The largest change of association constant was observed when nine fulgimide molecules were attached to one protein molecule. The association constant changed from 0.78×10^4 M^{-1} for the colorless state to 1.21×10^4 M^{-1} for the colored state.[161]

Chart 27



58E: R = Concanavalin A
60E: R = α–Chymotrypsin



59

Willner et al. prepared fulgimide-modified α-chymotrypsin **60** (Chart 27), possessing nine fulgimide units on one protein through the lysine residues.[162] The protein was active toward esterification of *N*-acetylphenylalanine in cyclohexane. Together with the bioimprinting of the substrate, light-induced control of the esterification rate was performed.

E. Control of Nonlinear Optics Properties

Nakatani et al. demonstrated the photoswitching of secondary harmonic generation (SHG) of fulgide-doped PMMA films. When the PMMA film doped with furylfulgide **4** was irradiated by UV light under the dc electric field, the molecules were likely to arrange in such a manner that the transition moment of the molecule pointed in the same direction as the dc field. In such a situation, the SHG signal ($I_{2\omega}$) was observed at 1064 nm (Nd:YAG laser). On irradiation of visible light, the SHG signal disappeared. This cycle was repeatable by alternative irradiation of UV and visible light, although the orientation of molecules was disordered gradually.[163]

F. Control of Transmittance of Visible Light

When both UV light (coloring) and visible light (decoloring) are applied to a polymer matrix doped with fulgide, it should reach a photostationary state in which the ratio of the *E*- and *C*-forms may be controlled by the intensities of applied lights. Francini et al. prepared PMMA and polystyrene blocks containing the furylfulgide **38**. When the transmittance of the visible light was monitored during the two-light-beam application experiment, it changed nonlinearly with regard to the intensity of the applied visible light when the intensity of UV light was sufficient. They also prepared holographic recording material with the PMMA block containing the fulgide with 7 μm resolution of the grating.[164]

Mitsuhashi reported that the rapid change of transmission of **4** in the visible light region by light irradiation was applied to the nonlinear, real-time optical image processing.[165] The spatial resolution was more than 10 lines/mm over a 30 mm diameter aperture.

IX. Modification of Structure of Fulgides

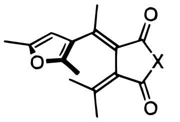
As the photochromism of fulgides is photochemical 6π-electrocyclization, the carbonyl groups as well as the aromatic rings are not inevitable. Although replacement of the aromatic ring with other functional groups has not been reported, replacement of the acid anhydride moiety with other functional groups has been carried out.

A. Fulgimides (Imides)

The name "fulgimide" was first introduced by Heller et al. for the succinimide of the corresponding fulgide,[166] though fulgimides had been synthesized much earlier.[167] Fulgimides have widely been prepared so far, because it is convenient to attach another substituent onto the fulgide core without a significant change of photochromic properties. For example, they were used for attaching the fulgide moiety to side chains of polymers,[120,153] attaching to a fluorescent group for control of fluorescence,[149] and attaching to proteins for regulation of substrate binding.[161,162]

Comparison of various heteroaromatic fulgides and fulgimides was undertaken by Tomoda et al. and Matsushima et al., and superior resistivity toward hydrolysis of the imide ring in protic solvents was shown.[168,169] That *N*-benzylfulgimide **61** (Chart 28) was less fatigue resistive than the corresponding fulgide **4** was also shown.

Chart 28



4E: X = O
61E: X = NCH_2Ph

B. Fulgenolides (Lactones)

Replacement of one of the two carbonyl groups of the anhydride group with an alkyl group yields two isomers of lactones. Heller et al. prepared some bisbenzylidenelactones in relation to the elucidation of the biosynthetic route of apolignan lactones.[24,170] They also reported that bisbenzylidenelactone **62EE** cyclized to give **62C$_A$**, in which the phenyl group remote from the remaining carbonyl group took part in cyclization[24] (Chart 29).

Yokoyama et al. studied which one of the carbonyl groups was more important for photochromism of heteroaromatic fulgides.[171,64] They carried out the photoreactions of two kinds of indolylfulgenolides, **63E**/**64E** and **65E** (Chart 30), with unambiguous regiochemistry, and concluded that the carbonyl

Chart 29

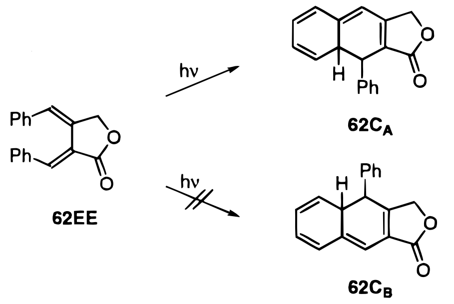
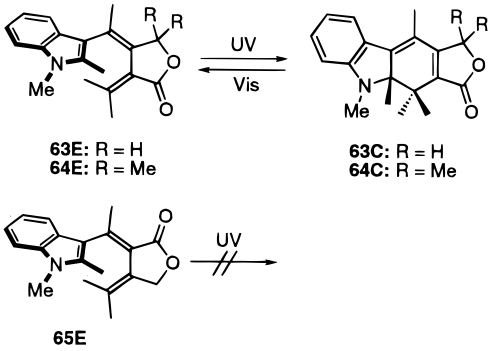


Chart 30

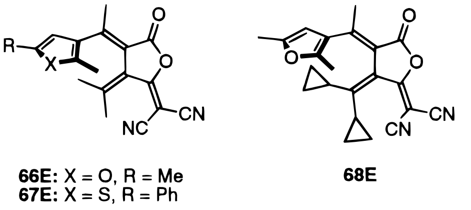


group remote from the indole ring was indispensable. The result obtained was in accord with Heller's observation.[24] In addition, the fulgenolides had the following properties: much larger quantum yields of Φ_{EC}(UV) and Φ_{CE}(vis) and shorter $\lambda_{max}(E)$ and $\lambda_{max}(C)$ than those of the corresponding indolylfulgide **14**.

As described in the previous sections, Yokoyama et al. synthesized *(R)*-binaphthol-condensed indolylfulgides **27** and **30**.[104] These compounds could be regarded as a kind of lactone derivatives. Interestingly, the remaining carbonyl group was located on the closer position to the aromatic ring. Their diastereoselective photochromism,[104,112] application to nondestructive readout method,[104,112] control of fluorescent ability by photochromism,[150,113] and control of cholesteric pitch by photochromism[157,113] were described.

Condensation of active methylene compounds such as malononitrile to one of the carbonyl groups also yields a lactone derivative. Heller et al. prepared several such compounds, **66**–**68**[172] (Chart 31). The major notable feature was that $\lambda_{max}(C)$ shifted more than 100 nm toward longer wavelength compared to the original fulgide (Figure 14). Similar compounds were reported by Hosmane et al.[173,174]

Chart 31



As a notable extension of these compounds, Heller et al. synthesized lactones in which the central double bond was incorporated in a phenyl ring, such as **69**[175] (Chart 32). After UV irradiation, the resulting *C*-form lost the aromaticity of the relevant phenyl group to take an *o*-quinodimethane structure. However, an intramolecular charge transfer from the lone pair of the sulfur atom of the thiophene ring to the lactone carbonyl oxygen rescued the *o*-quinodimethane group to restore the aromaticity. Consequently, $\lambda_{max}(C)$ was located in the near-IR region (Figure 15).

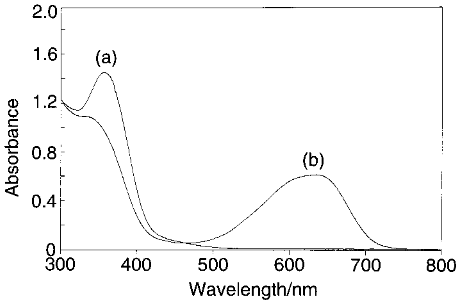


Figure 14. Absorption spectra of malononitrile-condensed fulgide **68** in toluene (concentration 1 × 10^{-4} mol dm^{-3}): (a) **68E**; (b) **68C**. (Kindly provided by Professor Harry G. Heller, University of Wales, Cardiff, U.K.)

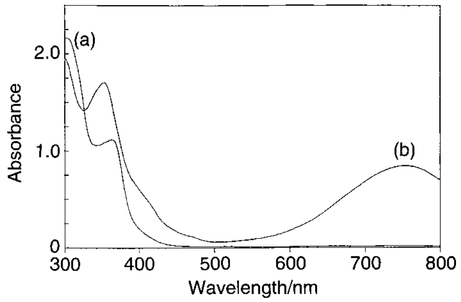
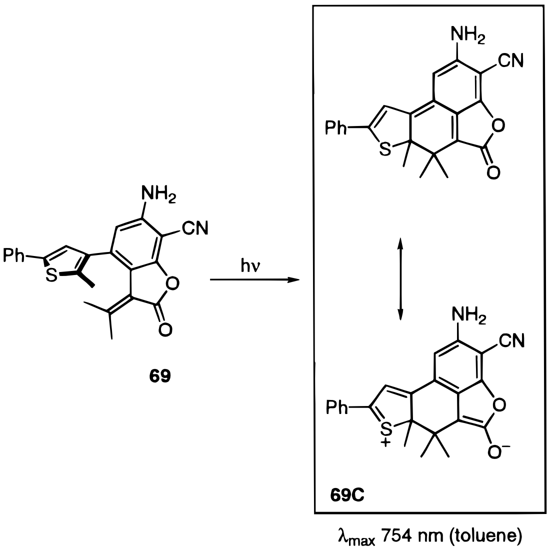


Figure 15. Absorption spectra of near-IR-absorbing fulgide **69** in toluene (concentration 1 × 10^{-4} mol dm^{-3}): (a) **69**; (b) **69C**. (Kindly provided by Professor Harry G. Heller, University of Wales, Cardiff, U.K.)

Chart 32

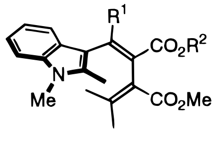


C. Fulgenates (Diesters)

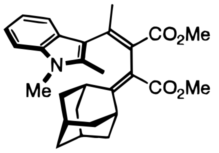
Heller et al. synthesized some diesters from the intermediate of the synthesis of fulgides.[176] However, photochromic properties were not reported.

Yokoyama et al. examined the photochromic properties of indolylfulgenates **70**−**73**[177,64] (Chart 33).

Chart 33



70E: R1 = R2 = Me
71E: R1 = Me, R2 = Et
72E: R1 = nPr, R2 = Me

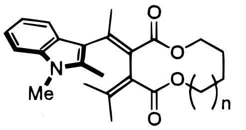


73E

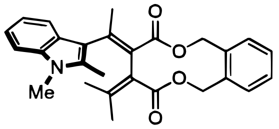
Notable features were small Φ_{EC}(UV), large Φ_{CE}(UV) and Φ_{CE}(vis), and shift of $\lambda_{max}(E)$ and $\lambda_{max}(C)$ toward shorter wavelength. The percentage of *C*-forms at photostationary states of UV irradiation was about 10%. Despite such poor photochromic properties, fulgenates were still attractive because two functional groups could be appended to the photochromic core of fulgides, and different from fulgides, they were inert toward hydrolysis in protic solvents.

Later, Yokoyama et al. reported the improvement of this inferior property of fulgenates to that of the corresponding fulgide. They inhibited the free rotation of the central C−C single bond connecting the two acrylate parts, to restore the planarity of the *E*-form by employing butane- or pentanediols.[178] Consequently, Φ_{EC}(UV) of **74**−**76** (Chart 34) became more than 5 times as large as that of **70**, and the percentage of the *C*-forms at UV photostationary states was about 40%.

Chart 34



74E: n = 1
75E: n = 2



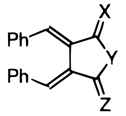
76E

Fulgenates with crown ether diesters **55**−**57** were prepared.[160]

D. Other Fulgide Derivatives

Fulgides possessing the thioanhydride group, **77**,[179] or mono- or dithioimide group, **78**, **79**[180] (Chart 35), were synthesized from the corresponding bisbenzylidenefulgide **1** by Dillen et al. For **77**, slight bathochromic shifts of absorption for the *E*,*E*- and *C*-forms compared to the corresponding fulgide **1** and *N*-phenylfulgimide were observed, and they showed similar photochromic properties.[179] However, **78** and **79** did not cyclize by photoirradiation but isomerized between the olefinic geometrical isomers.[180]

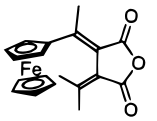
Chart 35



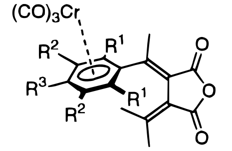
77EE: X = Z = O, Y = S
78EE: X = Z = S, Y = NPh
79EE: X = S, Y = NPh, Z = O

McCabe et al. synthesized ferrocenylfulgide **80** (Chart 36), in which one of the ferrocene rings served as the aromatic ring of fulgide.[181] Unfortunately, it merely showed *E*−*Z* isomerization upon UV irradiation. McCabe also prepared $Cr(CO)_3$ complexes of substituted phenylfulgides **81** and **82** (Chart 36). Instead of cyclization, E−Z isomerization and decomposition of the complexes occurred upon UV irradiation.[182]

Chart 36



80E



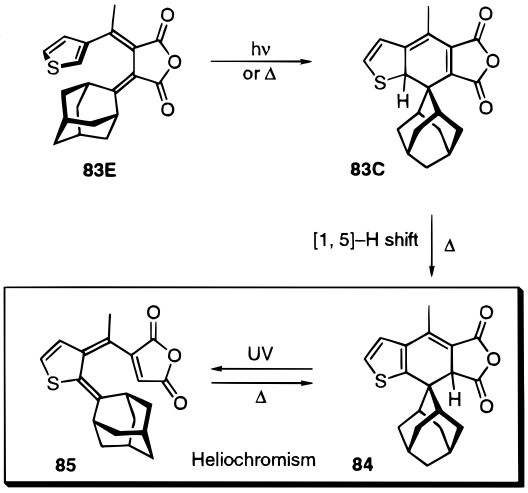
81E: R1 =H, R2 = R3 = OMe
82E: R1 = R3 = Me, R2 = H

X. Heliochromism

When a thermally reversible photochromic compound possesses a large Φ_{EC}(UV), small Φ_{CE}(UV) and Φ_{CE}(vis), and a quick thermal fading rate yet does not prevent coloration by sunlight, it can be applied to ophthalmic lenses with automatic regulation of light transmission. Heller et al. discovered such a new thermally reversible photochromic system based on fulgides,[2,3,34] and named this kind of photochromism "heliochromism". Some spiropyrans, spirooxazines, and naphthopyrans also show heliochromism.

Heller et al. observed that a fulgide such as **83E**, possessing a hydrogen atom on the C−C bond forming carbon atom of aromatic ring and an adamantylidene group on the other end of the molecule, underwent cyclization by UV irradiation or thermal treatment to form the usual colored C-form **83C**, which in turn restored the aromaticity by thermal 1,5-hydrogen shift to become the colorless compound **84**. Upon irradiation of UV light, a reverse electrocyclization occurred to generate a colored hexatriene, **85**, which lost the aromaticity again. This compound returned to the aromatic cyclohexadiene **84** thermally (Chart 37; Figure 16).

Chart 37



The structural feature of heliochromic fulgides, known so far, is that they should have an adamantylidene group.

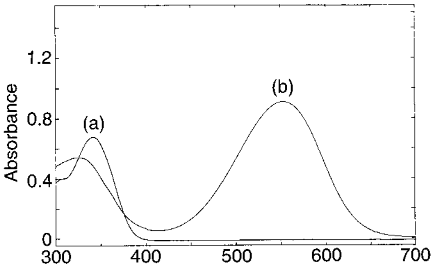
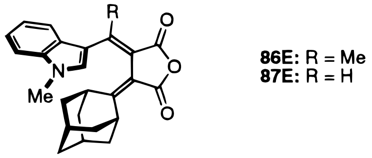


Figure 16. Absorption spectra of heliochromic fulgide **84**/**85** in toluene (concentration 1.17 × 10^{-4} mol dm^{-3}): (a) **84**; (b) **85** (after exposure to a flashgun; the half-life by thermal treatment ($t_{1/2}$) is 130 s at 25 °C). (Kindly provided by Professor Harry G. Heller, University of Wales, Cardiff, U.K.)

However, the corresponding indolylfulgides **86** and **87** (Chart 38) were not reported to produce heliochromic species.[183]

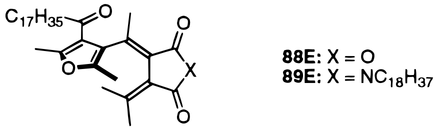
Chart 38



XI. Other Studies of Photochromic Fulgides

Hibino et al. synthesized fulgide **88** and fulgimide **89** (Chart 39) possessing a long alkyl chain[184] to prepare Langmuir–Blodgett films, to know whether aggregates would be formed, such as spiropyrans,[185] or not after UV irradiation. However, no aggregation was observed.

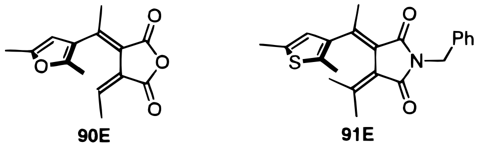
Chart 39



Fan et al. showed, by ESR, that pyrrylfulgide **42** formed a charge-transfer complex with TCNQ, and UV irradiation generated a radical ion pair. Irradiation with visible light restored the CT complex.[186]

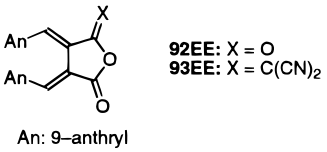
When Fox et al. reduced a few furyl- and thienylfulgides and a thienylfulgimide electrochemically, some of them (**4E**, **33E**, **90E**, **91E**) (Chart 40) gave the *C*-forms from the one-electron-reduced anion radical.[187]

Chart 40



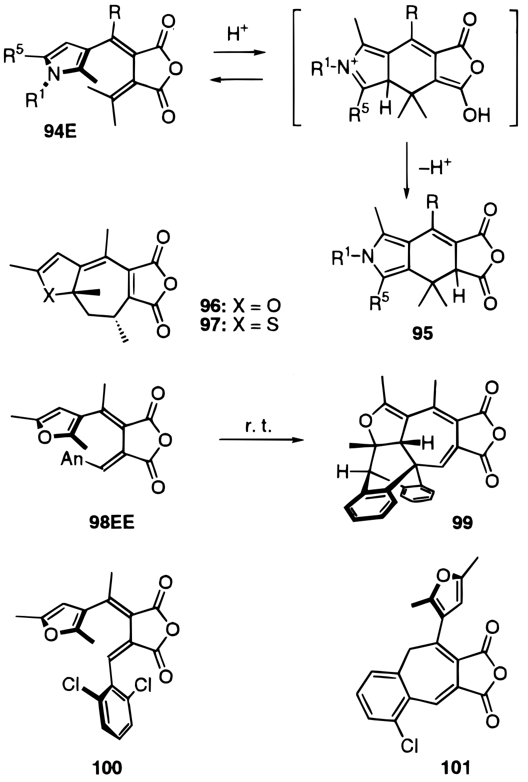
Heller et al. reported that bis(9-anthrylmethylene)fulgide **92EE** and its dicyanomethylene derivative **93EE** (Chart 41) underwent photochemical [4+4] cycloaddition in the manner of anthracene dimerization.[188]

Chart 41



Heller et al. reported several ground-state reactions (Chart 42). Some pyrrylfulgides such as **94E** underwent acid-catalyzed cyclization to give dihydroisoindole derivatives **95**.[189] In boiling pyridine, furyl- and thienylfulgides **4** and **33** cyclized to yield **96** and **97** possessing a seven-membered ring, respectively.[190] The *E*,*E*-form of a furylfulgide having the 9-anthrylmethylene group, **98**, underwent thermal Diels–Alder reaction between the central phenyl ring of anthracene as the diene and the furan double bond as the dienophile to afford **99** at room temperature.[191] Condensation of 2,6-dichlorobenzaldehyde with diethyl isopropylidenesuccinate afforded the corresponding fulgide **100** in addition to benzocycloheptatriene derivative **101**.[192]

Chart 42



Güsten et al. observed the change of absorption spectra by photoirradiation to **4** adsorbed on silica gel by photoacoustic spectroscopy.[193]

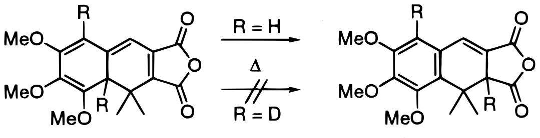
Adams et al. examined the thermal reactions of **4** in the presence of smectite clay in refluxing toluene.[194] They found that (1) absorption of the *E*- and *C*-forms shifted their absorption toward longer wavelength, (2) clay-catalyzed *Z*-to-*E* reaction occurred rather quickly, and (3) acid-catalyzed colored form formation took place slowly, while this colored form did not go back to the *E*-form by visible-light irradiation. It should be noted that the identity of the colored form obtained here with the photochemically obtained **4C** was not confirmed in that paper.

Anjaneyulu et al.[195] and Satyanarayana et al.[196] carried out, in relation to the synthesis of lignans (plant natural products), photochemical electrocyclization of substituted bisbenzylidene- and naphthylmethylenefulgides, respectively.

Scaiano et al. used **4E** as an actinometer of laser flash photolysis.[197]

Different from the *C*-form of fulgide **102-H** that underwent a thermal 1,5-hydrogen shift, the *C*-form of deuterated analogue **102-D** did not give the 1,5-deuterium shift but just showed thermal ring opening[198] (Chart 43).

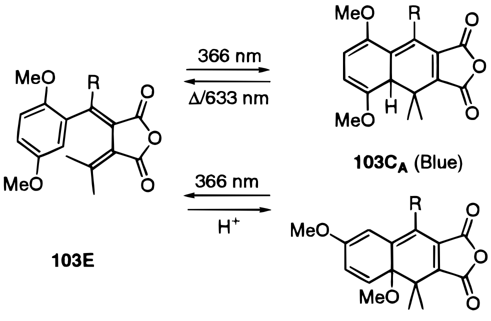
Chart 43



102E **102C**

Dimethoxyphenylfulgide **103E** gave a mixture of two *C*-forms, **103C$_A$** and **103C$_B$** (Chart 44). The former, exhibiting blue color, was removable by either the thermal or photochemical ring-opening reactions, while the latter could be eliminated by the addition of a trace amount of acid to promote the acid-catalyzed ring opening. Thus, **103** can exhibit red, blue, and purple colors.[199]

Chart 44



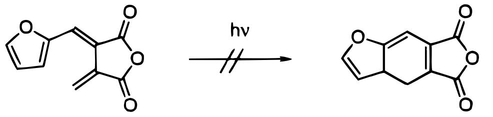
103E

103C$_A$ (Blue)

103C$_B$ (Red)

Minkin et al. reproduced the lack of photocyclization of 2-furylmethylenefulgide, which had been reported by Heller et al.,[32] by AM1 semiempirical MO calculations for **104E**[200] (Chart 45).

Chart 45



104E **104C**

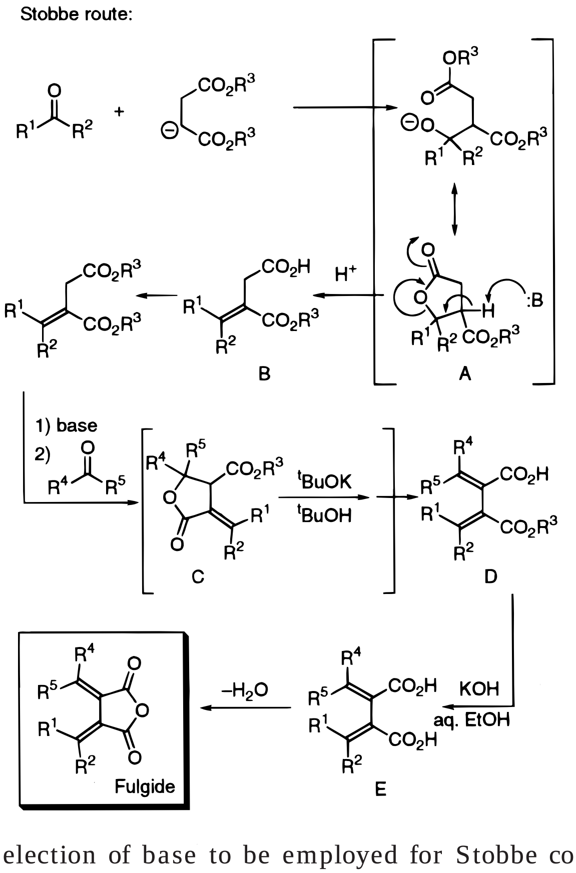
Kardinal et al. examined the change in refractive index of PMMA films doped with fulgide **4** by photoirradiation.[201]

XII. Synthetic Methods of Fulgides

A. Stobbe Condensation Route

As the final section of this review, the synthetic methods are introduced. The general and most frequently used route employs "Stobbe condensation reaction", which was first carried out by Stobbe, the pioneer of fulgide chemistry.[202] This aldol-type reaction produces a 2-alkylidenesuccinic half-ester from dialkyl succinate and a ketone or an aldehyde. The notable feature is that the second ester moiety which did not participate in the condensation forms a lactone, **A**, with the alkoxide anion generated by the nucleophilic attack of the enolate of succinate to the carbonyl compound. While this lactone **A**, usually formed as a mixture of diastereomers, can be isolated when the reaction conditions are mild, the successive base-assisted lactone ring opening may occur in situ to yield the half-ester **B** under rather stronger reaction conditions of condensation. Esterification followed by the second Stobbe condensation yields the lactone **C** or the half-ester **D** possessing two *exo*-methylene functional groups. The lactone **C**, when isolated, can be converted to the half-ester **D** by tBuOK/tBuOH. The half-ester **D** is then hydrolyzed by KOH in aqueous EtOH to give the diacid **E**, which in turn is treated by a dehydrating reagent such as acetic anhydride, acetyl chloride, trifluoroacetic anhydride, trifluoroacetylimidazole, *N*,*N′*-dicyclohexylcarbodiimide, etc. to produce fulgide, usually as a mixture of *E*- and *Z*-forms.[5,63] Some fulgides with a strongly electron-donating aromatic ring such as indole, can be isolated as the *E*-form after silica gel column chromatography because of facile *Z*-to-*E* isomerization (Scheme 6).[70,95]

Scheme 6

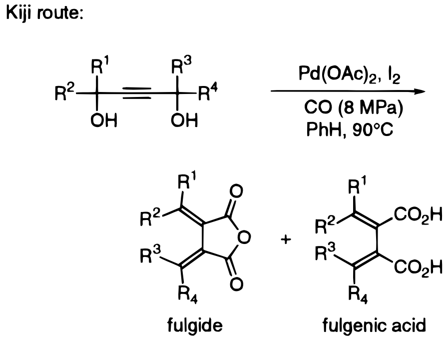


Selection of base to be employed for Stobbe condensation is important. For the synthesis of fulgides such as **4**, the first step is the condensation of acetone with diethyl succinate. Usually tBuOK in tBuOH is used for this purpose.[203] After esterification of the half-ester with suitable alcohol and sulfuric acid, tBuOK in tBuOH or EtONa in toluene is usually used for the second condensation with aromatic ketones or aldehydes such as 3-acetyl-2,5-dimethylfuran. When the reaction does not proceed smoothly because of steric bulkiness of substituents, use of lithium diisopropylamide (LDA) in THF as the base to be employed is recommended.[62,63] For preparation of fulgides with strongly electron-donating character, such as **19**, Yokoyama et al. used cerium enolate[204] of diethyl isopropylidenesuccinate in THF, where LDA did not give any condensation product because of smaller positive charge on the carbonyl carbon atom.[92,93]

B. Pd-Catalyzed Carbonylation Route

Kiji et al. reported that the reaction of substituted 1,4-butynediol with carbon monoxide in the presence of Pd catalyst, under elevated temperature and high pressure, afforded fulgide and the corresponding fulgenic acid.[65,95,205] This method is useful for the synthesis of sterically congested fulgides. While Stobe condensation of 2,5-dimethyl-3-pivaloylfuran with diethyl isopropylidenesuccinate using LDA as base failed to react,[62] the Pd-catalyzed route gave the corresponding fulgide in 59% yield, together with the diacid in ca. 20% yield.[65] One limitation is that this reaction was not effective for the synthesis of fulgides with a strongly electron-donating aryl group such as indolylfulgides with an *N*-methyl group. However, *N*-tosylindolylfulgide **23E** was synthesized in ca. 30% yield by this method (Scheme 7).[95]

Scheme 7



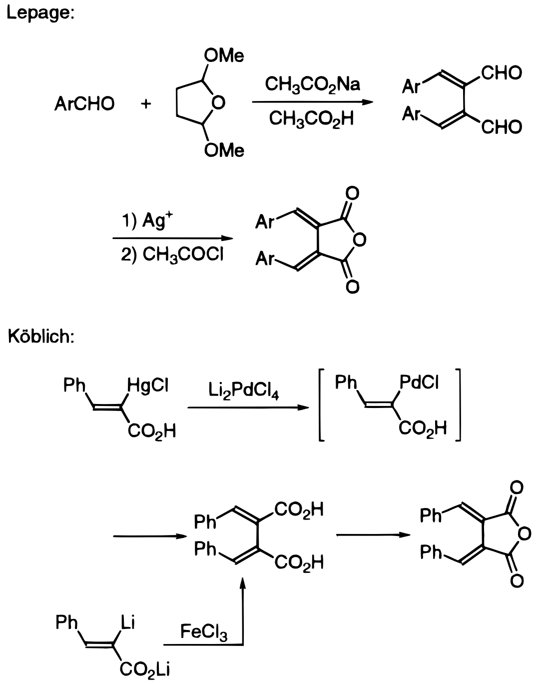
An improved method was introduced recently.[206]

C. Other Methods

Lepage et al. synthesized fulgides by condensing two substituted benzaldehyde molecules with 2,5-dimethoxytetrahydrofuran in the presence of sodium acetate, and by the subsequent oxidation and dehydration reactions (Scheme 8).[207]

Köbrich et al. synthesized bisbenzylidenefulgide **1** by Pd-catalyzed dimerization reaction of organomercury compound, and by oxidative dimerization of 2-lithiocinnamic acid catalyzed by $FeCl_3$ (Scheme 8).[208]

Scheme 8



XIII. Concluding Remarks

Since the synthesis of thermally irreversible fulgide **4** by Heller et al. in 1981, the study of heteroaromatic fulgides has been carried out with enormous efforts in many universities, research institutes, and companies. Some of the fulgides prepared so far exhibited superb properties—the properties intrinsic to themselves or the properties they impose on their environment—as optical recording materials and photofunctional switches. The compilation of the long history of study on fulgides will produce, in the "era of photonics" that we are approaching so closely, further photofunctional fulgides or related derivatives which would satisfy all the requirements for each of the applications.

XIV. Acknowledgments

I thank Professor Harry G. Heller, University of Wales, Cardiff, U.K., the pioneer of the chemistry of the fulgides of the second generation, for providing me with valuable spectra. I am also indebted to the former Professor Yukio Kurita, Yokohama National University, Yokohama, Japan, who allowed me to initiate the research of fulgide chemistry.

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