October, 1988] Bull. Chem. Soc. Jpn., 61, 3569—3573 (1988)

Photochemical Fatigue Resistances and Thermal Stabilities of Heterocyclic Fulgides in PMMA Film[1)]

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(Received April 14, 1988)

Thermal stabilities of the colored forms at 80 °C and photochemical fatigue resistances against coloration-discoloration cycles were measured in PMMA thin film, using 14 derivatives of fulgide with different heterocyclic structures. The indolyl (**12**), oxazolyl (**13**), and thiazolyl (**14**) derivatives showed very low thermal degradabilities (TD≦1.5%/day) while **12** and pyrazolyl derivative (**9**) showed low photochemical fatigues (PF≦0.2%/cycle), as compared with the furyl (**1**), thienyl (**2**), and pyrrolyl (**3**) derivatives. However, many of them featured low photo-responsiveness and low absorptivities for coloration on UV irradiation.

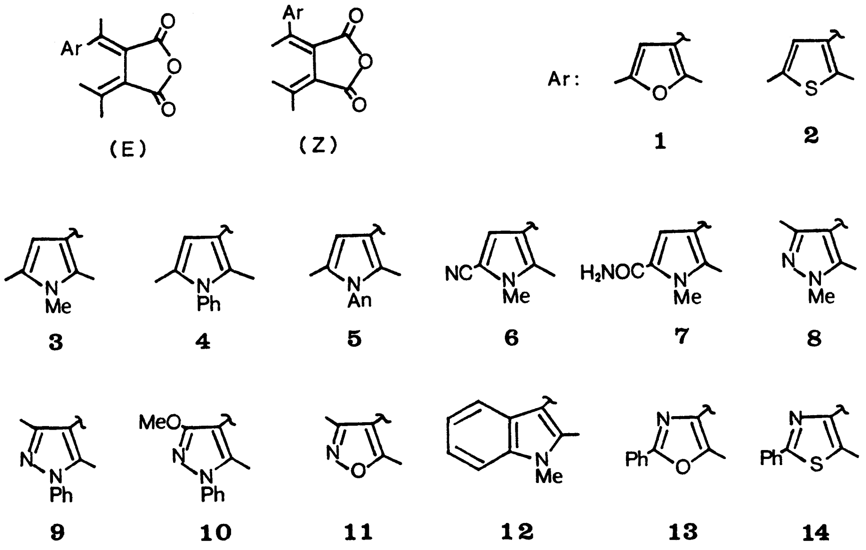
Molecular-structural modifications are powerful and interesting methods for research and development of photochromic materials, e.g., thermally stable and photochemically fatigue-resistant 1,2-diarylethenes,[2)] spiropyrans,[3)] and highly photoresponsive heterocyclic fulgides[4—6)] and spiropyrans.[7)]

Though furyl (**1**),[8)] thienyl (**2**),[9,10)] and pyrrolyl (**3**)[4)] derivatives have been studied in some detail in solution as well as in polymeric media,[5,10)] other heterocyclic fulgides seem to have been scarcely studied. Nor has been the relationship between the heteroaromatic ring structure and the photochromic properties clarified. In order to realize the potential utility of photochromic organic compounds in optical memory devices, extensive studies in solid polymers are needed,[11)] clarifying the medium effects as well as the structure-activity relationships.

This work has been undertaken to investigate the effects of the heteroaromatic ring structure (Ar) on the photochromic properties, particularly thermal stabilities and photochemical fatigue resistances, in PMMA[††] thin film as compared in dilute solution, using a wide variety of fulgides **1**—**14** (Scheme 1).

Results and Discussion

Absorption Spectra and Photochromic Properties. Figure 1 illustrates the spectra of **1** and their changes on alternative irradiations of UV and visible light in dilute toluene solution (a) and PMMA thin film (b). A photostationary state (pss) of coloration was attained by irradiation of **1E** (curve 0) with UV light in 30—60 s, hereafter the absorbance value in the visible band (A_0, curve 1) was no more increased on further UV irradiation. Subsequent irradiation with visible light led to rapid discoloration (in ca. 60 s). Similar colora-



Scheme 1.

Heterocyclic fulgides. Methyl substituents on carbon atoms are denoted by bars for simplification.

[††] PMMA=poly(methyl methacrylate).

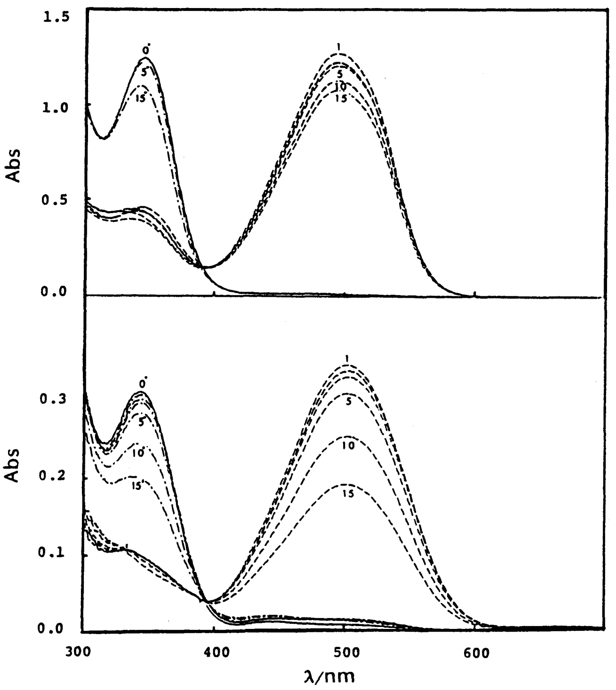


Fig. 1. Reversible changes in the absorption spectra of **1** on alternative irradiations with UV and visible light. (a) 2.0×10^{-4} mol dm^{-3} solution in toluene, (b) 15 wt% in PMMA film of 1.0 μm thickness. Curve 0: **1E** before irradiation, curve 1: after UV irradiation for 30 s. Absorption curves around 500 nm refer (from the top) to the colored forms after 2, 3, 5, 10, and 15 cycles of repeated coloration–discoloration reaction, while curves around 340 nm refer to the uncolored forms.

Table 1. Absorption Properties of Fulgides in PMMA Film[a]

Fulgide	Uncolored form[b]		Colored form[c]	
	λ_E/nm	A_E	λ_C/nm	A_0
1	344	0.31	503	0.40
2[d]	335(Z 340)	0.31(Z 0.33)	526	0.20
3	370 sh	0.26	662	0.10
4	379	0.32	635	0.20
5	380	0.14	636	0.10
6	345	0.50	579	0.16
7	355	0.10	629	0.05
8[e]	336	0.35	546	0.04
9[e]	336	0.38	539	0.04
10			545	0.06
11[e]	304	0.27	435	0.04
12[e]	392	0.35	589	0.07
13	338	0.52	462	0.45
14[d]	305(Z 310)	0.55(Z 0.70)	486	0.29

a) PMMA film of 1.0 μm thickness containing 15 wt% of fulgide. b) Values in parentheses refer to *Z*-isomers. c) A_0 refers to the absorbance value at photostationary state attained on UV irradiation. d) Initial form was *Z*-isomer, which rapidly isomerized into *E*-isomer on UV irradiation. e) Initially a mixture of *E*/*Z* isomers, which rapidly changed into *E*-isomer on UV irradiation.

tion–discoloration cycles were repeated a number of times (curves *n*). The absorption properties of the colored forms (λ_C and A_0), obtained at the initial pss of coloration, are summarized in Table 1 together with those of the uncolored (*E*)-isomers (λ_E and A_E). The absorption maxima of the colored forms tend to red shift with the electron-donating ability of the heterocyclic groups, e.g., the λ_C increases in the order **1C**<**2C**<**3C**, **6C**<**7C**<**3C**, and **9C**<**8C**≪**4C**<**3C**, respectively. This suggests that the electronic transitions of the colored forms involve intramolecular electron migration from the heteroatoms to the carbonyl groups.

The absorbance values (A_0) attained at pss for coloration are low with **7**—**12**. The ^{1}H NMR spectra of the photolyzed mixtures (pss) of **9**, **12**, and **14** in $\mathrm{CDCl_3}$ implied that the mole fractions of the colored forms were in the range of 15—40%. Also, a molecular model suggests that the steric repulsions between the 4-methyl groups and the 3-substituents of **8**—**12C** should hinder the coplanar configuration. Such poor coplanarity would lead to a poor overlapping of the pertinent orbitals and lower the transition probability (or extinction coefficient) for light absorption.[12] Further, **9**, **12**, and **14** featured rather low photo-responsiveness for coloration, thus their quantum yields (below 0.1) were significantly lower compared with 0.20 of **1**.[5,8]

It is speculated that the steric hindrance of the substituents (**9**, **12**) and/or the higher stabilities of the heteroaromatic groups depress the rate of the cyclization reaction as well as the C/E ratio at pss.

Photochemical Fatigues. As illustrated in Fig. 1 the reversibilities of the absorption spectra of **1**, on repeated coloration–discoloration cycles, are rather poor in PMMA film (b) while moderate in dilute toluene solution (a). This implies a significant effect of the medium and/or concentration of the solute on the photochemical fatigue. As a numerical measure for relative photochemical fatigue, a quantity $\mathrm{PF}=(A_0-A)/nA_0$ was evaluated where A_0 and A are the absorbance values at pss attained on the 1st and *n*th cycles of coloration, respectively. Table 2 lists the PF values of various fulgides obtained within half-lives, while Fig. 2 illustrates the plots of the fatigue resistance A/A_0 over a wide range of cycles. Fulgides **8**, **9**, and **12** show excellent fatigue resistances compared with **1**—**3**. The PF values of **4**—**12** are little affected by the medium and/or concentration. The high fatigue resistances and low medium dependences of **8**—**10**, **12**, and **13** are attributable to the high chemical stabilities of the heterocyclic groups.

Thermal Stabilities of the Colored Forms. Figure 3 illustrates thermal degradations of the colored forms in PMMA film at 80 °C in the dark. Similar tendence was obtained at 50 °C though more stable. As a measure for relative thermal degradability of the colored forms, a quantity $\mathrm{TD}=(A_0-A)/dA_0$ has been evaluated, where A_0 refers to the initial absorbance value of the colored form and A is that measured after *d* days of

Table 2. Photochemical Fatigues and Thermal Degradabilities of Fulgides in PMMA Film[a)]

Fulgide	Photochemical fatigue[b)]			Thermal degradability[c)]		
	Cycle	$(A_0-A)/A_0$	PF/%	Time/day	$(A_0-A)/A_0$	TD/%
1	18(15)	0.50(0.10)	2.8(0.7)	1	0.90	90
2	16(15)	0.50(0.22)	3.1(1.4)	10	0.35	3.5
3	12(15)	0.50(0.42)	4.2(2.8)	1	0.70	70
4	20(15)	0.42(0.38)	2.1(2.6)	1	0.55	55
5	17(15)	0.50(0.36)	3.0(2.4)	1	0.60	60
6	6(8)	0.50(0.50)	8.3(6.2)	5	0.50	10
7	10(9)	0.50(0.50)	5.0(5.5)	1	0.50	50
8	20(15)	0.03(0.02)	0.2(0.2)	6	0.50	8.3
9	20(15)	0.03(0.03)	0.2(0.2)	10	0.35	3.5
10	(15)	(0.05)	(0.3)	10	0.45	4.5
11	15(15)	0.20(0.10)	1.3(0.7)	1	0.95	95
12	20(15)	0.02(0.02)	0.1(0.1)	10	0.13	1.3
13	50	0.40	0.8	10	0.07	0.7
14	10(10)	0.25(0.10)	2.5(1.0)	10	0.05	0.5

a) Experimental conditions are shown in the legends of Figs. 2 and 3. b) $PF=(A_0-A)/n\,A_0$, as a measure for photochemical fatigue, where n is the number of repeated cycles. Values in parentheses refer to the data in dilute toluene solution (2×10^{-4} mol dm^{-3}). c) $TD=(A_0-A)/d\,A_0$, as a measure for thermal degradability of colored forms, where d refers to the heating time (day) at 80 °C in the dark.

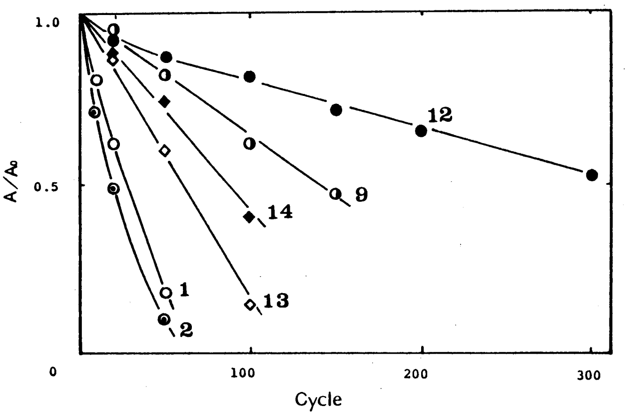


Fig. 2. Photochemical fatigues of fulgides by repeated coloration-discoloration cycles in PMMA film. PMMA film was of 1.0 μm thickness containing 15—20 wt% of fulgide.

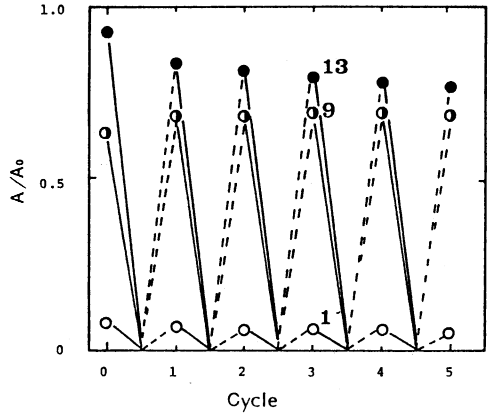


Fig. 4. Photochromic properties of the fulgides which had previously been heated at 80 °C for 10 days in PMMA film. Irradiated with visible (——) and UV (----) light at room temperature; **1** (○), **9** (◑), **13** (●).

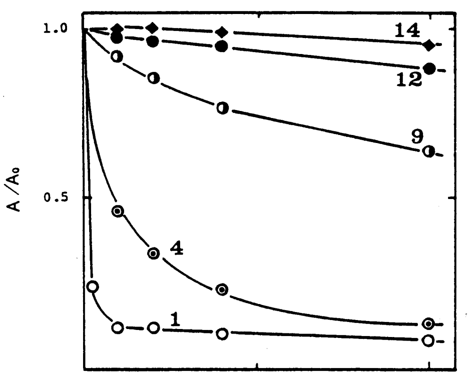


Fig. 3. Thermal degradations of the colored forms in PMMA film at 80 °C. PMMA film containing fulgide (15—20 wt%) had been previously irradiated with UV light leading to the photostationary state for coloration.

heating at 80 °C. The TD values of different fulgides are listed in Table 2. Figure 3 and Table 2 show a wide variation in the thermal stability: excellent stabilities with **12—14C**, fairly good with **2C** and **8—10C**, but poor with **1C** and **3—5C**.

Figure 4 shows the photochromic properties of the colored forms which had been heated at 80°C for 10 days in PMMA film. While **1** show little, **9** and **13** show substantial retainments of their photochromic properties, demonstrating their excellent thermal and photochemical fatigue resistances. With the fused benzene ring (**12**) or electronegative heteroatoms (**9**, **13**, **14**), the heterocyclic double bonds (both in the colored and uncolored forms) are considered to be stabilized and resistant to photochemical and thermal side reactions such as bimolecular cycloadditions[6)] and oxida-

Table 3. Physical Constants and Analytical Data of Heterocyclic Fulgide[a)]

Fulgide	Mp	^{1}H NMR, δ in $CDCl_3$		Found (Calcd)/%				m/z
	θ_m/°C	-CH_3(3H, s)	-CH= and others	C	H	O	N	M^+
5E	120—123	1.32 1.65 1.97	5.90(1H, s)	72.02	6.46	17.75	3.77	
		2.28 2.60 3.85	7.00(4H, s)	(72.30	6.36	17.51	3.83)	
6E	172—176	0.93 1.08 2.23	6.92(1H, s)	67.44	5.78	17.05	9.73	
		2.57 3.67		(67.58	5.68	16.89	9.85)	
7E	208—222	1.22 2.02 2.22	6.31—6.72(2H, br. s)	60.90	5.98	24.51	8.61	
	(decomp)	2.53 3.80	6.78(1H, s)	(63.59	6.02	21.12	9.27)	
8E[b)]	106—110	1.21 2.04 2.15		63.83	6.71	18.52	10.58	274
		2.26 2.56 3.21		(65.68	6.61	17.50	10.21)	
9E[b)]	164—166	1.32 2.08 2.20	7.20—7.40(5H, m)	70.70	6.03	14.61	8.19	336
		2.32 2.65		(71.41	5.99	14.27	8.33)	
10Z	188—192	1.95 2.15 2.25	7.20—7.23(5H, m)	67.94	5.97	18.50	7.59	
		2.40 3.95		(68.14	5.73	18.18	7.95)	
12E[b)]	154—158	0.92 2.18 2.78	7.17—7.28(4H, m)	74.13	6.28	15.13	4.56	309
		3.65 3.65		(73.77	6.19	15.52	4.53)	
13E	157—160	1.40 2.13 2.37	7.38—8.07(5H, m)	70.56	5.34	19.99	4.31	323
		2.73		(70.57	5.30	19.79	4.33)	
14E[c)]	166—168	1.32 2.15 2.30	7.30—7.93(5H, s)	66.68	5.09	14.26	4.02	339
		2.73		(67.24	5.06	14.14	4.13)	

a) Melting points and ^{1}H NMR spectra of **1E**—**4E** were consistent with those reported in the literature. **11** was out-of-stock. b) *E*-isomers were obtained by UV irradiation of the *E*/*Z* isomeric mixtures. c) *E*-isomer was obtained by photochemical isomerization of the *Z*-isomer with UV light.

tions. The higher chemical stabilities of the heterocyclic groups, however, would inevitably feature lower photochemical responsiveness as described above. Thus we are now put into a dilemma in molecular architecturing of *highly-responsive and highly-resistant* photochromic compounds.

Contrary to the high thermal stability in PMMA film, **14** (both colored and uncolored forms) underwent substantial degradations in hydroxylic solvents at room temperature in the dark, as readily as **1**. A major degradation product of **14C** in ethanol solution, isolated on silica gel, showed UV spectrum and R_f value (TLC on silica gel) different from those of **14E** or **Z**. From its UV (λ_{max}410, $\varepsilon \approx 5500$) and ^{1}H NMR spectra (e.g., methylene protons of the ethyl ester group at 3.6 ppm), the half-ester of the colored form was implied. Thus, it is assumed that the anhydride groups of both colored and uncolored forms are subject to rapid solvolysis in hydroxylic solvents, regardless of the structure of the heterocyclic groups.

Experimental

Melting points were uncorrected. UV and ^{1}H NMR spectra were recorded on a Hitachi U-3200 spectrophotometer and a JEOL JNM-PMX 60 NMR spectrometer, respectively. Solvents were freshly distilled before use. PMMA film (ca. 1.0 μm thickness) was prepared on a glass plate by spin-coating of a deaerated cyclohexanone solution containing fulgide and PMMA (15—20:85—80 by weight). For the measurement of the thermal stability, the surface of the PMMA film was coated with acrylic polymer (SD-17 Dainihon-Inki) in 4—5 μm thickness to protect from sublimation. This treatment did not affect the photochromic properties, except that some intermixing appeared to take place and the absorbances of fulgides were somewhat reduced. The UV light beams of 310—380 nm isolated through a glass filter (Toshiba UV-D36C), were irradiated at a 50-cm distance from a 80-W cm^{-1} metal halide lamp (Ushio Electric). Visible light beams were irradiated at a 15-cm distance from a 50-W halogen lamp (Philips) through a glass filter (Toshiba Y-50, Y-45, or L-39). The incident light intensities were in the range of 10—40 mJ cm^{-2} s^{-1} both with UV and visible lights. Absorption spectra were measured at 10-s intervals during coloration and discoloration reactions.

Materials. Heterocyclic fulgides were prepared by the Stobbe condensation reaction of diethyl isopropylidenesuccinate with 3-(or 4-)acetyl derivatives of heteroaromatic compounds, according to the methods described in the literature.[8,9)] The analytical data and other physical constants are summarized in Table 3.

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