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Photochromism of 4-Oxazolyl Fulgides[1)]

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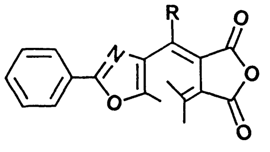
The thermal and photochemical stabilities of 2-[1-(2-phenyl-5-methyl-4-oxazolyl)]alkylidenesuccinic anhydrides (**1**) and (**2**) were studied. These compounds showed good thermal stabilities in PMMA film and low photochemical fatigue ($PF \leq 0.03\%$ /cycle) in a dilute toluene solution in the presence of air, compared with 3-furyl fulgide (**3**). Although in PMMA film the photochemical fatigue resistance property of the fulgides was poor, in comparison with that in solution, the addition of an organo-nickel stabilizer improved the property.

In order to use an optical memory device based upon a photochromic system, knowledge concerning the thermal stabilities of the colored and uncolored form (i.e. erase and write modes) is essential.

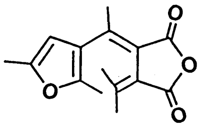
Heller et al.[2)] reported that heterocyclic fulgides, such as 3-furyl and 3-thienyl derivatives, showed good thermal stabilities. With this as a starting point, the possibility of organic photochromic compounds as data storage media have again been elevated as matters of chemical interest, and various investigations have been initiated.

Recently, Irie[3)] reported that diarylethene derivatives were thermally stable photochromic compounds, and more recently Tamaki and Ichimura[4)] showed that chelation of spiroindolinonaphthoxiazine was effective in improving thermal fatigue resistance.

On the other hand, in a previous paper[5)] we showed that 4-pyrazolyl, 3-indolyl, 4-oxazolyl, and 4-thiazolyl fulgide possesses good thermal and photochemical stabilities in comparison with 3-furyl fulgide **3**. However, it seemed that the photo-responsiveness and/or the conversion of these fulgides to the colored form in the photostationary state were too low, except for 4-oxazolyl fulgide. In this study we report on the responsiveness and the photochemical and thermal fatigue resistances of 4-oxazolyl fulgide in detail, and also on the effect of a long alkyl chain substituent.



1 R = CH_3
2 R = $C_{17}H_{35}$



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Results and Discussion

The absorption spectra of colored and uncolored forms of **1** in dilute toluene solutions (1.0×10^{-4} mol dm^{-3}) and PMMA thin films (ca. 1.0 μm thickness) are illustrated in Fig. 1.

A photostationary state (pss) for coloration, i.e. cyclization reaction, was attained by irradiation with UV light (366 nm) for 40 s. After subsequent irradiation for 40 s with visible light (>390 nm), it underwent discoloration, i.e. disclosure reaction.

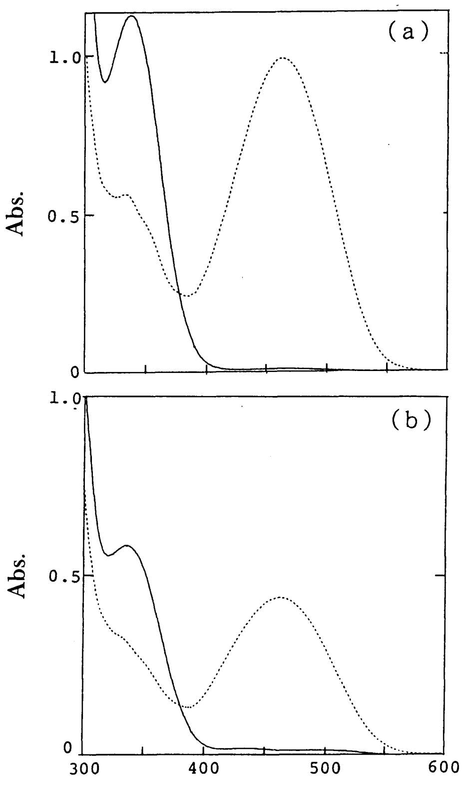

Fig. 1. Absorption spectra of uncolored and colored forms of **1**.
(a) In dilute toluene solutions (1.0×10^{-4} mol dm^{-3}).
(b) PMMA thin films (1.0 μm thickness, 20 wt%).

The absorption maximum and its intensity of color are similar, even when a methyl substituent is replaced with a long alkyl chain. Further, 0.20 mol dm^{-3} deuteriochloroform solutions of **1** and **2** in NMR tubes were exposed to UV light. The NMR measurements showed that these were converted nearly quantitatively into colored forms (**1C** and **2C**) in 84 and 91%, respectively.

Photo-responsiveness for coloration and bleaching of **1** and **2** are shown in Fig. 2. It was noticeable that

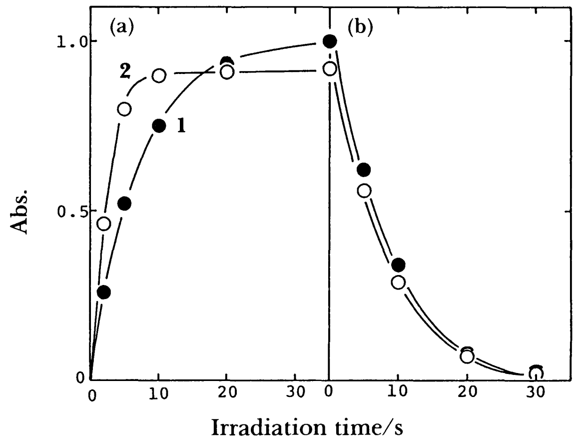

Fig. 2. Photo-responsiveness for coloration (a) and discoloration (b) of **1** and **2** in dilute toluene solutions (1.0×10^{-4} mol dm^{-3}) with UV and visible light irradiation.

fulgide **2** exhibited rapid coloration. The quantum yield (ϕ_c) for coloration of **2** was 0.42. The ϕ_c of **1** was 0.18, which was nearly the same as that for **3**. Kurita et al.[6] reported the relationship between the ϕ_c and the steric interaction for 3-furyl fulgides. According to their study, the introduction of a propyl substituent, instead of a methyl substituent, caused an increase in the ϕ_c, 0.19 to 0.45. They explained that the high efficiency of this cyclization reaction was due to a steric repulsion between the isopropylidene group and the alkyl substituent, which did not favor *E-Z* isomerization.

In our study, the ϕ_c of 3-furyl fulgide substituted with a long alkyl chain was 0.45. These results showed us that the introduction of a bulky alkyl substituent is also effective at improving ϕ_c of oxazolyl fulgide, similar to **3** .

Figure 3 illustrates the photochemical fatigue resistances of **1**, **2** and **3**. 4-Oxazolyl fulgides showed good resistances in a dilute toluene solution in the presence of air. The relative photochemical fatigue PF=$(A_0-A_n)/nA_0$ was evaluated, where A_0 and A_n are the absorbance values at pss attained on the lst and *n*th cycles of coloration. The values of **1**, **2**, and **3** are 0.03, 0.02, and 0.76%. Similar values were also obtained in an ethyl acetate solution. The photochemical stability of 4-oxazolyl fulgide is attributable to its heteroaromatic structure deactivated by electronegative nitrogen, though photochemical reactions of oxazole, such as photorearrangement[7] or photosensitized oxidation,[8] are known.

Irie et al.[9] evaluated the photochemical fatigue resistances of some photochromic compounds, and indicated that naphthoxazine showed the best stability. It is noteworthly that the excellent durability of naphthoxazine was caused by a slight modification of spiropyran, which showed little resistance. The only structural difference is that C=C bond in the pyran ring is replaced by a C=N bond. This modification improved the resistance remarkably; naphthoxazine could be photo-cyclized more than 2000 times.

As shown in Fig. 3, the replacement of the C=C bond with a C=N bond in the furan ring also improved the fatigue resistance markedly. These facts suggest that the C=N bond plays an important role in reducing photodegradation in a photochromic reaction.

On the other hand, further improvement caused by long alkyl chain substituent seemed to be due to the high ϕ_c of **2**, which reduces the possibility of side reactions.

As shown in Fig. 4, the fatigue resistance in PMMA thin film containing fulgide (20 wt%) was markedly decreased in comparion with that in a dilute solution. The PF values of **1**, **2**, and **3** are 0.63, 0.42, and 2.80%. This undesirable fact suggests the considerable effects of the medium and the concentration of the fulgides on photochemical fatigue.

Chu[10] reported on the photochromic performance

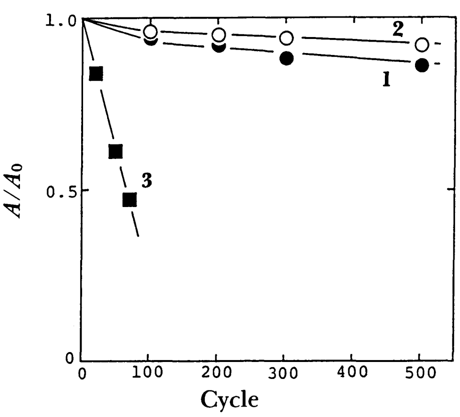

Fig. 3. Photochemical fatigues of fulgides by repeated coloration and discoloration cycles in dilute toluene solutions (1.0×10^{-4} mol dm^{-3}). A_0 and A_n are the absorbance values at pss attained on the 1st and *n*th cycles of coloration.

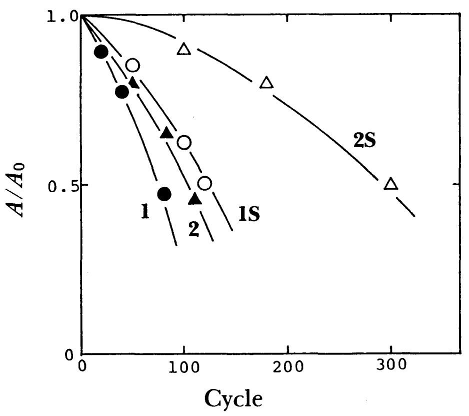

Fig. 4. Photochemical fatigues of fulgides in PMMA thin film (1.0 μm thickness, 20 wt%) and effect of organo-nickel stabilizer. 1 wt% Nickel stabilizer was added into PMMA thin film containing fulgides **1** and **2**; **1S**, **2S**.

of naphthoxazine in plastics. In his study he found that the excellent light fatigue resistance of naphthoxazine could be further improved by an organo-nickel stabilizer. From a practical view point, we also investigated the effect of some nickel stabilizers so as to improve it. Among the various derivatives, the nickel dithiophenolate derivative (bis(1,2,3-trichloro-5,6-dithiophenolate)Ni(II) tetrabutylammonium) which is known as being a light stabilizer for a near-infrared absorbing dye,11) had the greatest effect on the fatigue resistance. As illustrated in Fig. 4, only 1 wt% of the stabilizer in PMMA film exhibited this effect on the light fatigue resistance.

The thermal degradation of the fulgides in PMMA film at 80 °C in the dark are shown in Fig. 5. Colored forms (**1C** and **2C**) showed good fatigue resistance. Degradation after 11 days was only 7%, and the residues showed a same photochromic performance. Uncolored forms (**1** and **2**) were also investigated. PMMA film containing fulgide had been previously heated for various periods and then irradiated with UV light for coloration. These showed little fatigue, 24% and 18%, respectively, indicating their slight inferiority to colored forms.

Thermal stabilities of fulgide in solution had been investigated in some detail by Heller et al.12) According to their paper, the colored form of 3-furyl fulgide **3C** was stable below 100 °C. The uncolored form **3** in deuteriochloroform solution (0.20 mol dm^{-3}) on heating at 180 °C turned red, which was not reversible upon exposure to visible light.

As illustrated in Fig. 5, the thermal stability of **3C** in PMMA was much lower than that of **1C** and **2C**, and thermally bleached **3C** showed no photochromism. The uncolored form **3** also showed a similar tendency to the colored form, but thermally colored species were not detected in the absorption spectrum. On the other hand, the photocolorability of **3** in a dilute toluene solution was completely maintained after boiling at 80 °C for 24 h. These facts mean that the degradation in a polymer matrix, such as PMMA, differs from that in solution, and the introduction of a C=N bond is also effective in reducing thermal fatigue in PMMA film because of its higher chemical satability.12)

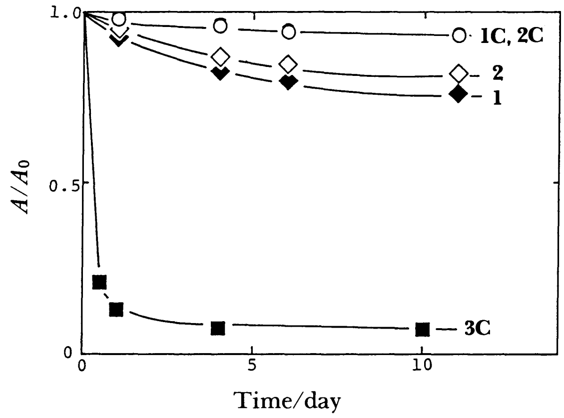

Fig. 5. Thermal degradations of the fulgides in PMMA film at 80 °C in the dark. PMMA films of 1 μm thickness containing fulgides (20 wt%) had been irradiated with UV light leading to the photostationary state for coloration after heating; **1**, **2**. The film had been previously irradiated with UV light for coloration before heating; **1C**, **2C**, **3C**.

Experimental

Materials. 4-Oxazolyl fulgide (**2**). A solution of 5-methyl-2-phenyl-4-stearoyloxazole13) (4.4 g, 0.010 mol) and diethyl isopropylidenesuccinate (2.7g, 0.012 mol) in *t*-butyl alcohol (10 ml) was added dropwise to a refluxing solution of potassium *t*-butoxide (1.2 g) in *t*-butyl alcohol (15 ml), and the solution was refluxed for 3 h. After removing the solvent, the reaction mixture was poured into water, and extracted with ether. The aqueous layer was acidified, and the liberated half ester was extacted with toluene and dried over anhydrous magnesium sulfate; the solvent was then removed. The residue, yellow oil (6.4 g), was hydrolyzed with 5% ethanolic potassium hydroxide and a solid potassium salt filtered off and acidified. The resulting diacids (4.8 g) were boiled with acetic anhydride. After the solvent was removed, **2** was isolated in 9% yield as *Z*-isomer by column chromatography on silica gel and recrystalized from hexane. Mp 65—67 °C; ^{1}H NMR ($CDCl_3$) δ=0.83 (t, 3H) 1.26 (s, 32H), 2.07 (s, 3H), 2.33 (s, 3H), 2.43 (s, 3H), 7.36—8.13 (m, 5H); mass spectrum, *m*/*z* 547 (M$^+$). Calcd for $C_{35}H_{49}NO_4$: C,76.52; H,9.02; N, 2.56; O, 11.68%. Found: C,76.52; H, 9.14; N, 2.61; O, 11.73%.

The *Z*-isomer of this fulgide in toluene solution or PMMA film rapidly isomerized into an *E*-isomer upon UV irradiation.

4-Oxazolyl fulgide (**1**) and 3-furyl fulgide (**3**) were prepared as described above and in the literatures.2)

Measurements. A mercury lamp (Ushio, 250 W) and a xenon lamp (Ushio, 300 W) were used as light sources for coloration and discoloration reactions. A mercury line, 366 nm (ca. 50 mJ) and visible light beams (>390 nm) were isolated by passing the light through glass filters (Toshiba UV-D36C, UV-35 and L-39). PMMA film (ca. 1.0 μm thickness) was prepared on a glass plate by spin coating a cyclohexanone solution containing fulgide and PMMA (20 : 80 by weight). For the measurement of thermal stability, the surface of the PMMA film was coated with acrylic polymer (SD-17 Dainihon-inki) in 4—5 μm thickness to protect them from sublimation. Quantum yields for coloration were determined by measuring the rate of the photoreaction, which was carried out in a toluene solution (6×10^{-4} mol dm^{-3}) by irradiation of the 311 nm mercury line, using a Quantum Yield Reactor (Model 2001 Applied Photophysics). The light intensity was measured with a potassium iron(II) oxalate actinometer.

The photochemical fatigue of fulgides was investigated by measurements of the absorption spectrums of the colored forms. In the presence of air toluene solution (1×10^{-4} mol dm^{-3}) and PMMA films were irradiated with UV and visible light, alternatively, using a photo-irradiater cycle test system (OMROM).

For evaluating the effect of various organo-nickel stabilizers in improving the fatigue resistance, PMMA films containing 3-furyl fulgide **3** and 4-oxazolyl fulgides **1** and **2** (20 wt%) were used as test samples. These films were prepared as described in the above, except for the addition of the stabilizers to the cyclohexanone solution. Nickel stabilizers such as Cyasorb 1084, AM105 and AM205 (evaluated by Chu) and a nickel dithiophenolate derivative were commercially available from American Cyamid, Ferro. Corp. and Mitsui Toatsu. However, the three stabilizers tested by Chu showed no effect in improving the fatigue resistance of fulgide.

The thermal degradation of PMMA film containing fulgide was carried out in an oven at 80 °C and was monitored by measuring the absorption spectrum of colored forms at room temperature.

UV and ^{1}H NMR spectra were measured with a spectrophotometer (Hitachi U-3200) and 60-MHz spectrometer (JEOL JNM-PMX60 NMR).

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