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Photochromism of a Furylfulgide, 2-[1-(2,5-Dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic Anhydride in Solvents and Polymer Films

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The quantum yields of the photochromic reaction between (*E*)- and (*Z*)-2-[1-(2,5-dimethyl-3-furyl)-ethylidene]-3-isopropylidenesuccinic anhydride and the cyclized valence isomer were determined in various solvents and polymers. In both media the ring-opening quantum yield (Φ_{CE}) depended on the dielectric constant of the media. In some polymer films, Φ_{CE} were larger, and the cyclization quantum yield (Φ_{EC}) and olefinic isomerization quantum yields (Φ_{EZ} and Φ_{ZE}) were smaller than those in the corresponding solvents.

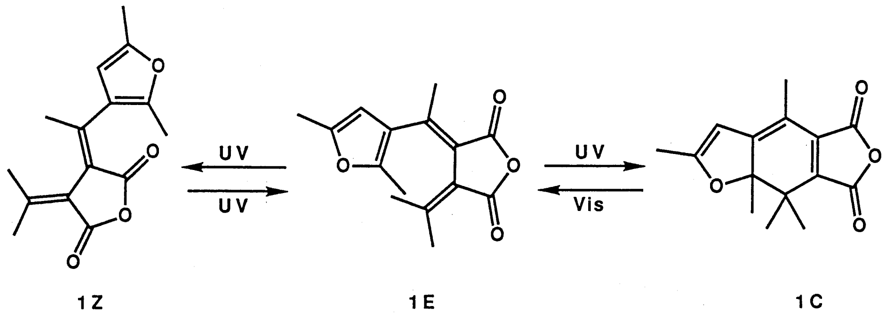
Fulgides, which were discovered by Stobbe[1] and developed by Heller and co-workers,[2] are the most promising candidates for applications to erasable and rewritable organic photomemory. By now, Heller,[2] Kaneko,[3] and we[4] have independently clarified that the photochromic properties of fulgides, such as the absorption maximum of the colored form or quantum yields of the reactions, are controllable by modifying the molecule, itself. While there are many unsolved problems, such as to lengthen the absorption maximum of the colored form to the diode laser wavelength and to append further thermal stability and resistivity toward photochemical fatigue, the ultimate photomemory media will certainly be provided as a plastic disc containing photochromic compounds. It is therefore very important to study environmental effects on the photochemical reaction of fulgides. Although there are some precedents concerning media effect on the photochromism of fulgides,[5–8] nobody considered the undesirable *E-Z* isomerization. We here report on the effect of the reaction media on the entire photochemical behavior of a representative fulgide, 2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (**1**) in order to find a clue to what kind of chemical and physical environmental properties would enhance the desired photochromic characters and prevent the undesirable ones.

Results and Discussion

Photochromism of 1 in Solvents. Table 1 shows the photochemical properties of the fulgides **1E**, **1Z**, and **1C** in various solvents, along with the physical properties of the solvents. While the absorption maximum (λ_{max}) of **1E** and **1Z** varied around 9 and 11 nm, respectively, without any relation to the electronic feature of the solvents, that of **1C** changed significantly. The shortest is 484 nm in carbon tetrachloride, and the longest is 510 nm in chloroform and in 1,2-dichloroethane. Yoshioka and Irie studied the molecular structure of **1** by X-ray diffraction analysis[9] and MO theories.[10] Both **1E** and **1Z** have a twisted structure, and the succinic anhydride moiety and furan ring are not coplanar to each other. MNDO calculations of **1C** gave a planar structure having a delocalized π-molecular orbital over the molecule; this is the reason why **1C** possesses an absorption maximum in the visible light region. The results are in good agreement with the description that planar molecules are polarized much more by polar solvents than less planar ones.[8] However, no suitable characteristic index of solvents for explaining the difference in the absorption maxima was found.

The values of the molar absorption coefficient at λ_{max} (ε_{max}) of **1Z** are about four thirds those of **1E** in most solvents, except in acetonitrile. The values of λ_{max} of **1E** are always about 10 nm shorter than those of **1Z**. This fact means that the degree of π-conjugation in **1E** is poorer than that in **1Z**.

The quantum yield of the cyclization (Φ_{EC}) ranges from 0.17 to 0.26, mostly around 0.20. There is a



Formula 1. Photochromic furylfulgide **1**.

Table 1. Φ, λ_{max}, and ε_{max} of **1** in Solvents with Their Physical Properties[a]

	λirr/nm	CCl_4	C_6H_6	C_6H_5Me	$CHCl_3$	AcOEt	$(ClCH_2)_2$	CH_3CN
Φ_{EC}	366	0.26	0.22	0.18	0.19	0.20	0.20	0.17
Φ_{EZ}	366	0.13	0.21	0.13	0.13	0.18	0.17	0.32
Φ_{ZE}	366	0.14	0.18	0.11	0.11	0.21	0.14	0.36
Φ_{CE}	502	0.067	0.067	0.048[b]	0.035[b]	0.039	0.037	0.027
λ_{max}(**1E**)/nm		338	344	343	347	340	345	342
ε_{max}(**1E**)/M^{-1} cm^{-1}[c]		6600	6300	6700	6800	6200	6400	7800
λ_{max}(**1Z**)/nm		352	353	353	358	349	352	347
ε_{max}(**1Z**)/M^{-1} cm^{-1}[c]		8800	9200	8400	8900	8500	8300	7800
λ_{max}(**1C**)/nm		484	495	494	510	492	510	504
ε_{max}(**1C**)/M^{-1} cm^{-1}[c]		8700	8700	9200	9700	8500	9100	10800
Dielectric Constant[d]		2.24	2.28[e]	2.38[e]	4.81	6.02[e]	10.36[e]	37.5
η/mPa		1.04[f]	0.65	0.59	0.60[f]	0.43[e]	0.89[f]	0.38[f]
D_N/kcal mol^{-1}[g,h]		0.0	0.1	—[i]	—[i]	17.1	0.0	14.1
$E_T(30)$/kcal mol^{-1}[g,h]		32.5	34.5	33.9	39.1	38.1	41.9	46.0

a) Photoreaction was carried out at ambient temperature. b) Values for 492 nm light irradiation. c) 1 M=1 mol dm^{-3}. d) Taken from Ref. 11. Values at 20 °C unless otherwise noted. e) Values at 25 °C. f) Values at 15 °C. g) Taken from Ref. 12. h) 1 cal=4.184 J. i) Not found in literature.

tendency that Φ_{EC} decreases only slightly as the solvent polarity increases. This result is understandable since photocyclization does not require any thermal activation energy.[13] On the other hand, the quantum yields of *E*-*Z* and *Z*-*E* isomerization (Φ_{EZ} and Φ_{ZE}) depend on the kind of solvents used. Except in benzene, they show a tendency to increase with a decrease in the solvent viscosity, as in the case of some stilbenes, presumably because olefinic isomerization requires a large reaction volume.[14] The quantum yield of the decoloration (Φ_{CE}) decreases with an increase in the dielectric constant of the solvent.

Photochromism of 1 in Polymer Films. Table 2 shows the photochemical properties of fulgides **1E**, **1Z**, and **1C** in a number of polymer films, along with the physical properties of the polymers. In polar polymers, such as cellulose acetate (CA) or nitrocellulose (NC), **1E**, **1Z**, and **1C** have a relatively longer absorption maximum than that in less polar matrices. In NC, the absorption maximum of **1C** shifts to 528 nm. This phenomenon can not be attributed to the existence of a nitrate moiety, since the absorption maximum of **1C** in isopentyl nitrate is 498 nm.

Unlike in solvents, the factor affecting values of Φ_{EC} in polymer films is not clear. The quantum yields of olefinic isomerization, Φ_{EZ} and Φ_{ZE}, do not seem to depend on the kind of the polymer films, and the largest values for both were recorded in PMMA. On the other hand, the quantum yield of decoloration, Φ_{CE}, is highly dependent on the polymer used. Similar to the result in solution, Φ_{CE} decreases as the dielectric constant of the polymer increases.

The quantum yields of fulgide **1** in polymer films have been reported previously: Smets et al. reported 0.158 for Φ_{EC} in PS,[7] which is larger than ours. The present value of 0.059 for Φ_{CE} in PMMA is comparable with the value of 0.051 (at 25 °C) observed by Saito et al.[18]

Table 2. Φ, λ_{max}, and ε_{max} of **1** in Polymers with Their Physical Properties[a]

	λirr/nm	PS	PMMA	PMA	CA	NC
Φ_{EC}	366	0.12	0.094	0.14	0.12	0.095
Φ_{EZ}	366	0.066	0.091	0.078	0.069	0.064
Φ_{ZE}	366	0.074	0.13	0.083	0.085	0.055
Φ_{CE}	502	0.10	0.059	0.049	0.028[b]	0.017[b]
λ_{max}(**1E**)/nm		346	343	344	349	352
ε_{max}(**1E**)/M^{-1} cm^{-1}[c]		6400	7900	6900	5600	7400
λ_{max}(**1Z**)/nm		356	350	352	354	361
ε_{max}(**1Z**)/M^{-1} cm^{-1}[c]		8000	6000	6800	6300	7900
λ_{max}(**1C**)/nm		502	500	502	508	528
ε_{max}(**1C**)/M^{-1} cm^{-1}[c]		9200	10200	8900	6600	9100
T_g/°C[d]		100	105	10	30—46[e]	53(66)
Dielectric Constant[d]		2.5—3.1	3.3—3.9	5—6[f]	3.5—7.5	7.0—7.5

a) Photoreaction was carried out at ambient temperature. b) Values for 492 nm light irradiation. c) 1 M=1 mol dm^{-3}. d) Taken from Ref. 15 unless otherwise noted. e) Taken from Ref. 16. f) Taken from Ref. 17.

Recently, Horie et al. reported the kinetics of the reaction from **1C** to **1E** in PMMA film.[6] They clarified that the reaction proceeded only in the "mobile site" where the fulgide molecule was able to isomerize, and the fraction of "mobile site" in the film varied according to the temperature; *i,e.*, only 13 % of **1C** isomerized to **1E** at 4K, whereas complete isomerization occurred at 298K. The reaction rate for a mobile site at 4K was shown to be almost the same as that at 298K. All through our experiments at room temperature no existence of an "immobile site" was observed; *i.e.*, the reaction could be described by first-order equations for the starting fulgides.

Comparison of the Quantum Yields in Polymer Films with Those in Solvents. A comparison of the photochemical properties of **1** in polymer films and in solvents is very interesting. First, Φ_{EC} in polymer is substantially smaller than that in the corresponding solvent. In PS, Φ_{EC} is 0.12 while the value in benzene is 0.22 and in toluene 0.18. In PMMA and PMA, Φ_{EC} is 0.094 and 0.14, respectively, while in ethyl acetate it is 0.20. Second, the decoloration quantum yield Φ_{CE} in a polymer film is larger than that in the corresponding solvent. These two observations could be explained by the unified concept described below. As a consequence of a severe compression from the environment, when a rigid **1C** is placed in a polymer matrix, the potential energy of the ground state of **1C** becomes higher than that in solution (Fig. 1). This compression effect of the polymer may have a stronger effect on **1C** than on relatively flexible **1E**. Therefore, the transition state ($TS^{\neq}$) of the thermal reaction between **1C** and **1E** on the reaction coordinate comes closer to **1C**; *i.e.*, the structure of the transition state of the thermal reaction becomes more similar to **1C**. Both the photochemically excited **1C** (**1C***) and the photoactivated common intermediate of both **1C**-to-**1E** and **1E**-to-**1C** photoconversion (**D***) can also be destabilized by a steric repulsion in the polymer matrix; the structure of **D*** in polymer might therefore be very close to that in solution. These considerations suggest that in polymer, **D***, generated either from **1C*** or **1E***, undergoes a non-radiative deactivation to give a ground state intermediate which would give **1E** with greater possibility than in solution. Details about the potential energy curves evidenced by photophysical experiments will be reported elsewhere.[13]

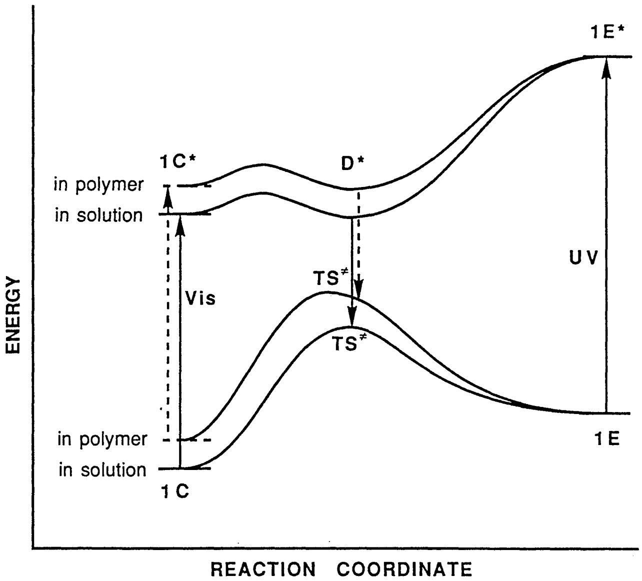
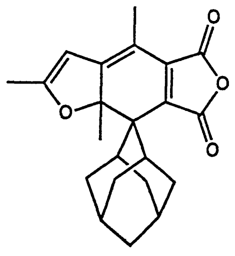


Fig. 1. Qualitative diagram of the potential energy curves of fulgide **1**.

Since Heller's adamantylidene-substituted furylfulgide **2C**,[2] which has a strong strain inside the molecule itself, recorded 0.38 for Φ_{CE},[19] the result obtained here revealed that the steric interaction from outside of the molecule also increased the quantum yield of decoloration. In cellulose polymers, however, Φ_{CE} are smaller than the values obtained in most of solvents.



2C

Formula 2. Heller's adamantylidenefulgide **2c**.

Third, the quantum yields of olefinic isomerization, Φ_{EZ} and Φ_{ZE}, also showed a remarkable difference. In polymer films, they are nearly half to one third of those in the corresponding solvents, as illustrated by comparing the value in PS with those in benzene or toluene, and comparing the values in PMMA or PMA with that in ethyl acetate. Because olefinic isomerization (i.e., turning over the 1-(dimethylfuryl)-ethylidene moiety) requires a large reaction volume, it should be strongly interfered by a rigid polymer matrix. A similar effect is observed when the bulkiness of the alkyl group on the furylalkylidene moiety of the fulgide is increased.[4] It should be noted that the glass transition temperature seems to have had nothing to do with the quantum yields of both directions of the olefinic isomerization in our experiments at room temperature.

In conclusion, the quantum yields of coloration and *E*-*Z* and *Z*-*E* olefinic isomerization were suppressed in polymer matrices, compared to those in solution. However, that of decoloration, which decreased with an increase in the dielectric constant of the polymer, was enlarged. Less polar polymers, like PS, are advantageous from the standpoint of attaining high photochromic quantum yields.

Experimental

UV-Vis spectra were recorded on a Hitachi UV-200-20 Spectrometer. The UV light source was 250 W high-pressure mercury lamp (Nihon Denchi), from which 366 nm light was isolated by filters (aqueous solution of $CuSO_4$, Toshiba UV-D35 and UV-35 glass filters). The visible-light wavelengths used were 502 and 492 nm. The former was taken from an Ar-ion laser (Lexel Co., Model 95-4), the beam size of which was increased by a convex lens. The latter was isolated from a 500 W Xenon lamp (Ushio Electric) through a 10 cm water filter and Toshiba glass filters (IRA-25-S, Y-46, and KL-50). The light intensity was determined with a trioxalatoferrate(III) chemical actinometer.

Fulgide **1** was synthesized from diethyl isopropylidenesuccinate and 3-acetyl-2,5-dimethylfuran according to a method from the literature,[20] and **1E** and **1Z** were separated by flash column chromatography[21] (hexane–ethyl acetate), followed by recrystallization from hexane–ether. Solvents of spectrograde (Dojin Chem. Co.) were used for photoreaction and measurements of electronic spectra. Solutions of **1E** and **1Z** with 1.0×10^{-4} mol dm^{-3} concentration were used for the photoreaction in solvents. Photoreaction of **1C** was performed on a photostationary state solution resulting from 366 nm light irradiation on **1E** in the solvent. Polymer films with the fulgide were prepared by casting a solution of a mixture of the fulgide and the polymer into a flat Petri dish, followed by complete evaporation of the solvent. The thickness of the film, about 0.1 mm, was accurately measured by a micrometer. Specification of the polymers used were as follows: polystyrene; Wako Pure Chemical Industries, Ltd., average molecular weight 170,000—190,000: poly(methyl methacrylate); Wako Pure Chemical Industries, Ltd., average molecular weight 100,000—150,000: poly(methyl acrylate); Aldrich Chemical Co., M_W 30,700, M_N 10,600: cellulose acetate; Kanto Chemical Co., 55% acetylated, average molecular weight 35,000: nitrocellulose; Asahi Chemical Industries Co., LIG 1/2, 65% nitrated, M_W 74,000, M_N 26,000 (calculated from standard polystyrene calibration).

Photoreaction was monitored by UV-Vis spectroscopy, and the spectrum was analyzed to give the component concentration as a function of the time of light irradiation. Using the photochemical rate equations, the functions were analyzed by numerical integration to give the quantum yields.

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