

Cyclic Fulgenates. Enlargement of Quantum Yield of Coloring Reaction of Photochromic Fulgenates

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Four cyclic indolylfulgenates, derivatives of fulgenates with 1,4-butane-, 1,5-pentane-, and 1,10-decanediols and 1,2-bis(hydroxymethyl)benzene, were synthesized and their photochromic properties were compared with those of dimethyl indolylfulgenate. The most notable feature of cyclic fulgenates with relatively short alkyl chains is that the coloring quantum yield of UV-light irradiation is much larger than that of the acyclic fulgenate and that of the cyclic fulgenate with a long alkyl chain.

Fulgides such as **1** have been known as the representative thermally irreversible photochromic compounds.¹ Recently we have reported that the diester² (fulgenates) as well as the lactone³ (fulgenolides) derivatives of fulgides are also photochromic. Although the fulgenates such as **2** have invaluable merits that they can carry two functional groups (*e. g.* interactive groups to other chemical species) on the diester moiety and they are durable toward hydrolysis, the formidable demerit is that the conversion to the colored form at photostationary state of UV-light irradiation (UV-pss) is only 12% at the highest. In this communication, we report that we have overcome this defect by bridging the ester moiety with a short carbon chain.

The synthetic pathway is shown in Scheme 1. Reaction of diols with the indolylfulgide **1E** in pyridine in the presence of 4-dimethylaminopyridine afforded the half esters **3** in 60–80% yield. Cyclization of **3** with 2-chloro-1-methylpyridinium iodide and triethylamine in refluxing acetonitrile (for **3a**, **3b**, and **3d**, Mukaiyama lactonization)⁴ or diethyl azodicarboxylate and triphenylphosphine in tetrahydrofuran at room temperature (for **3c**, Mitsunobu reaction)⁵ gave the desired cyclic fulgenate as a mixture of *E*- and *Z*-forms (5–14% from **1E**). Cyclization of the half esters of 1,3-propanediol and 1,2-ethanediol were unsuccessful. Separation of the *E*- and *Z*-isomers by silica-gel flash column chromatography followed by recrystallization gave cyclic indolylfulgenates **4a–d**.

Photoreactions of **4a–d**, involving *E*-, *Z*-, and *C*-forms, were carried out as reported previously.⁶ Changes of absorption spectra of **4b** upon irradiation of 313-nm light to the *Z*-form in hexane (coloring) and upon irradiation of 446-nm light to the solution of UV-pss (bleaching) were shown in Figures 1 and 2, respectively. The quantum yields of photoreactions and absorption spectroscopic data of cyclic fulgenates **4a–d**, together with those of the acyclic indolylfulgenate **2** and the indolylfulgide **1**, are summarized in Table 1.

The most remarkable effect of bridging of the two ester moieties with the tetra- or pentamethylene chains is that the

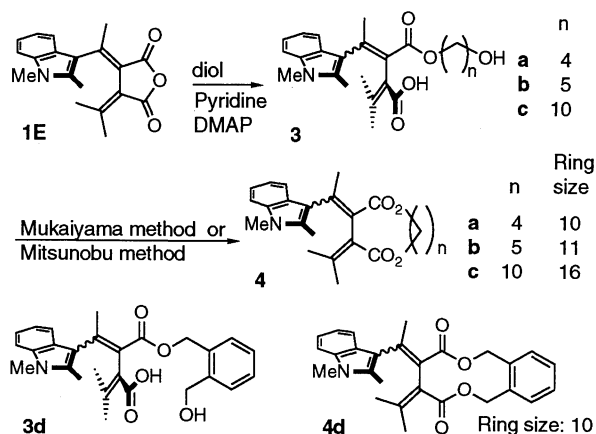
coloring quantum yield of UV-light irradiation became larger than that of non-bridged **2**. The short alkyl bridges worked to make the two bond-forming carbon atoms close enough for effective photochemical ring closure.⁷ As the result, the ratio of *C*-form at UV-pss increased from 10% for **2** to 39–44% for **4a**, **b**, and **d**. To the contrary, the bleaching quantum yields of visible-light irradiation to the *C*-forms of **4a–d** are practically the same as that of the non-bridged fulgenate **2**.

The ten-carbon bridging of **4c** did not improve the photochromic properties of **2** in any respects. The long alkyl chain did not work to keep the bond-forming carbon atoms of the hexatriene moiety close.

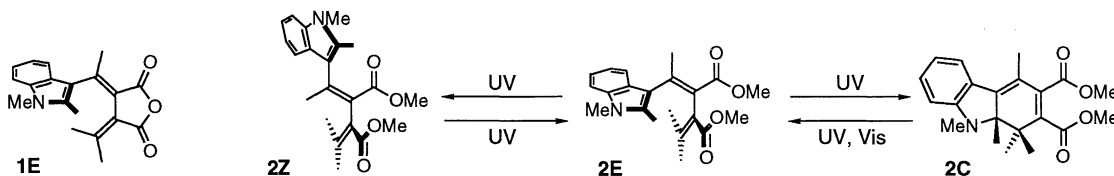
Before we had started this project, we also intended to lengthen the absorption maximum of the colored form by making the succinate moiety of the colored form planar by a short alkyl chain. The absorption maximum wavelengths of *C*-forms of **4a** and **4b**, however, are longer than that of **2** only by 5–10 nm.

AM1 molecular orbital calculations⁸ proved that even in the most stable conformation of *C*-form of **4a**, the two carbonyl groups were slanting out of the molecular plane and they were not conjugating with the double bond in between effectively. To attain better planarity, **4d** was synthesized, in that two *sp*³ carbon atoms of **4a** were replaced with *sp*² carbon atoms. As expected, although a little, the absorption maximum wavelength of its *C*-form lengthened.

In summary, bridging of the ester groups of fulgenates by a short alkyl chain (i) greatly increased the coloring quantum yield



Scheme 1.



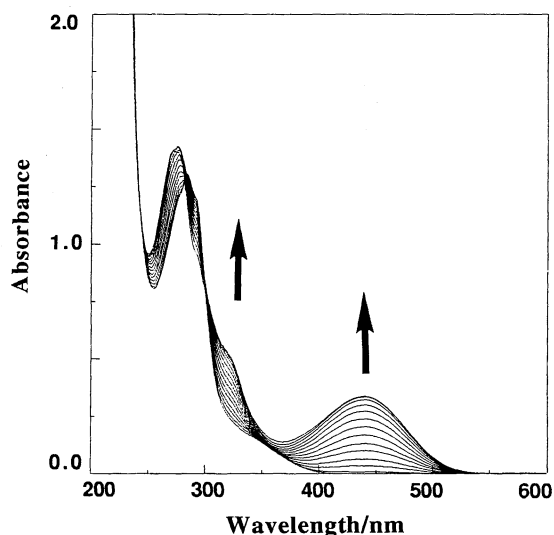


Figure 1. Absorption spectral change of **4b** (starting from **4bZ**, $1.32 \times 10^{-4} \text{ mol dm}^{-3}$) in hexane upon irradiation of 313-nm light (2.15 mW cm^{-2}). Irradiation time/min: 0, 0.5, 1.5, 2.5, 4.1, 5.5, 7.5, 10, 13, 17, 22, 30, 40, 60

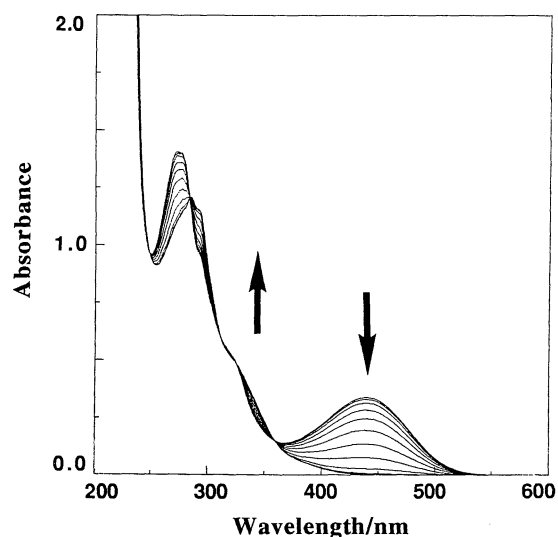


Figure 2. Absorption spectral change of **4b** (starting from **4bE/4bZ/4bC** = **48/13/39**, $1.32 \times 10^{-4} \text{ mol dm}^{-3}$) in hexane upon irradiation of 446-nm light (0.058 mW cm^{-2}). Irradiation time/min: 0, 0.5, 1.5, 3.5, 6, 10, 16, 25, 40, 60, 90

Table 1.^a Absorption spectroscopic properties and quantum yields of photoreactions of fulgenates **4a–4d** and **2** and fulgide **1**

	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/(\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1})$)			<i>E:Z:C</i> at UV-pss	UV irradiation ^b				Vis irradiation ^c
	<i>E</i>	<i>Z</i>	<i>C</i>		Φ_{EC}	Φ_{CE}	Φ_{EZ}	Φ_{ZE}	
4a	331 (5900)	347 (4000)	447 (6900)	38:18:44	0.37	0.32	0.020	0.073	0.25
4b	287 (9800)	284 (10100)	442 (6700)	48:13:39	0.32	0.37	0.0078	0.056	0.35
4c	292 (10800)	285 (8500)	432 (7000)	40:55: 5	0.026	0.39	0.046	0.098	0.33
4d	334 (4300)	346 (2400)	454 (5200)	43:17:40	0.41	0.40	0.015	0.064	0.40
2	293 (11500)	285 (9300)	437 (7100)	39:51:10	0.065	0.40	0.054	0.10	0.27
1^d	385 (8150)	397 (14300) ^e	584 (6810)	35: 9:56 ^f	0.045	0.16	0.040	0.072	0.051

^a In hexane. ^b **4a–4d** and **2**: 313 nm, **1**: 405 nm. ^c **4a–4d** and **2**: 446 nm, **1**: 608 nm. ^d In toluene. ^e Obtained by subtraction of the spectrum of the *E*-form from the spectrum of an *E/Z* mixture. ^f Determined by ¹H NMR at UV-pss in toluene-d₈.

of UV irradiation, (ii) and therefore greatly increased the relative ratio of the colored form at UV-pss, and (iii) lengthened the absorption maximum of the colored form slightly.

References and Notes

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