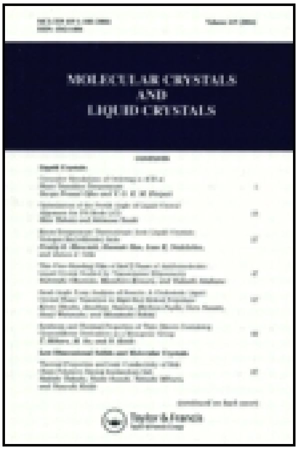

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Photochromism of Fulgenates Possessing Crown-Ether Moiety

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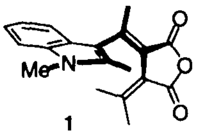
Three indolylfulgenates possessing diesters of 14-crown-4 (**2**), 17-crown-5 (**3**), and 20-crown-6 (**4**) groups were synthesized and their photochromic behaviors in the presence or absence of alkali metal cations (Li^+, Na^+, K^+) were investigated. Notable features are: (1) The association constant of Na^+ was the largest for **3**, and that for K^+ was the largest for **4.** (2) The association of E- and Z-forms are stronger than C-form. (3) In the cases of Na^+-**3** and K^+-**4**, no photocoloration occurred. (4) As for the photochromism of **2,** no effects of alkali metal species were observed. These phenomena were elucidated by molecular mechanics calculations.

Keywords: photochromism; fulgide; fulgenate; crown-ether; alkali metal cation; association constant

INTRODUCTION

Photochromism and Crown-Ethers

Shinkai's pioneering work of crown-ether-possessing azobenzenes early in 1980s [1] opened photochromism-controlled supramolecular chemistry [2]. The most notable advantage of this method is that one can switch uptake and release of cationic species only by applying light irradiation from outside. Photochromic compounds used for such researches are spiropyrans [3,4], dihydroazulenes [5], fulgides[6,7], and diarylethenes [8]. When we started the research in this field, no reports were found in the literature that are dealing with thermally irreversible photochromic crown-ether-possessing compounds. We here report the thermally irreversible photochromic fulgide derivatives possessing a crown ether moiety. They are a series of fulgenates derived from an indolylfulgide **1** with three different sizes of crown ether rings (**2**, **3**, **4**).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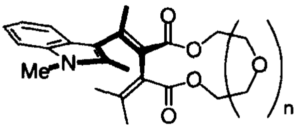
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3 n = 3
4 n = 4

Photochromism of Fulgenates

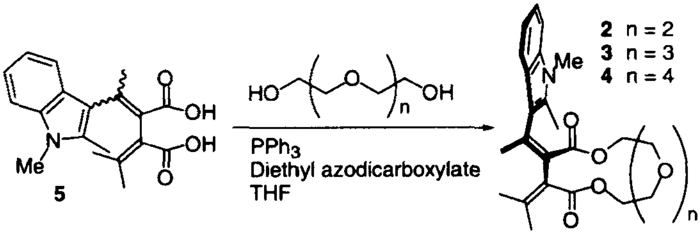
In 1994 we have shown that the diester derivatives of fulgides, the anhydride moiety of fulgides are replaced by diesters, are photochromic. The absorption maximum wavelengths of them were shorter than the parent fulgide **1**. A fault was that the conversion ratio to their colored C-forms were about 10% [9]. Later, this was overcome by bridging the alkyl groups of the esters (*i.e.* cyclic diesters using diols) [10].

As the extension, we have aimed to synthesize fulgenates **2** - **4** using tri-, tetra-, and pentaethyleneglycols, to see how the alkali metal cations affect the photochromic properties, and to see the difference of association constants to alkali metal cations between the colorless and colored forms.

RESULTS AND DISCUSSION

Synthesis of Crowned Fulgenates

Synthesis of crowned fulgenates **2** - **4** were conducted as shown below, using indolylfulgenic acid **5** and the corresponding oligoethyleneglycol by double Mitsunobu esterification reaction. Yields were 46, 43, and 48%, respectively, as the Z-form of the fulgenates.



5

2 n = 2
3 n = 3
4 n = 4

Photoreaction of Crowned Fulgenates

Photochromic reaction of crowned fulgenates **2** - **4** were examined in acetonitrile, starting from their Z-forms. The solution of fulgenates were irradiated by 313 nm light from high pressure mercury lamp. The concentration of components (E, Z, and C-forms) were determined by HPLC and the absorption spectra were recorded occasionally. After the components reached the photostationary state, 437 nm light from xenon lamp was irradiated. The change in concentration was analyzed to give the quantum yields of photoreactions, which are shown in Table 1.

The amount of the colored C-form produced was affected by the ring size. As for the fulgenate **2**, which corresponds to 14-crown-4, gave the largest ratio of the C-form (Fig. 1), whereas **3** and **4**, corresponding to 17-crown-5 and 20-crown-6, respectively, gave only a few percent of the fulgenate changed to their C-forms at photostationary state of UV-light irradiation. This is in good agreement to the previous observation about cyclic fulgenates [10].

TABLE 1. Quantum yields of photoreactions of **2**, **3**, and **4**[a)]

			313 nm				437 nm
	M^+	E:Z:C[b)]	Φ_{EC}^{UV}	Φ_{CE}^{UV}	Φ_{EZ}^{UV}	Φ_{ZE}^{UV}	Φ_{CE}^{Vis}
2	none	51:28:21	0.15	0.41	0.023	0.064	0.20
2	Li^+	50:30:21	0.17	0.42	0.047	0.13	0.28
2	Na^+	51:28:21	0.14	0.32	0.032	0.078	0.36
2	K^+	48:31:21	0.12	0.32	0.033	0.073	0.36
3	none	49:45:6	0.016	0.21	0.035	0.068	0.32
3	Li^+	20:78:2	0.0097	0.25	0.055	0.033	0.17
3	Na^+	26:74:0	0.00	0.32	0.067	0.054	0.29
3	K^+	47:50:3	0.014	0.37	0.037	0.065	0.28
4	none	46:50:4	0.0096	0.20	0.035	0.060	0.18
4	Li^+	37:55:8	0.11	0.66	0.033	0.041	0.16
4	Na^+	38:57:5	0.038	0.35	0.036	0.049	0.15
4	K^+	36:64:0	0.00	0.49	0.039	0.041	0.31

a) In acetonitrile. b) At photostationary state of 313-nm light irradiation. E and Z: Geometric isomers of colorless forms. C: Colored form.

The photoreactions were also carried out in the presence of excess amount of alkali metal perchlorates in acetonitrile. Although **2** was affected little by the addition of cations, quantum yields of **3** and **4** changed drastically by the kind of added cations. In particular in the cases of **3** - Na^+ and **4** - K^+, photocoloration reaction did not occur. Change of absorption spectra were shown in Figs. 2 and 3.

Association Constants of Isomers with Alkali Metal Cations

Association constants were determined from the change in absorption spectra upon gradual addition of cations by Nagakura-Baba's method [11,12], and the results were shown in Table 2. It is obvious that (i) The association constants for Na^+ are large for **3E** and **3Z**, and those for K^+ are large for **4E** and **4Z**; (ii) The size of crown cavity for E- and Z-forms are larger than the corresponding C-form; (iii) E- and Z-forms bind more strongly than C-form; (iv) isomers of **2** do not bind to cations effectively.

These findings are strongly correlated to the observation for quantum yields of photochromism described previously. E-forms strongly binding with cations do not cyclize.

TABLE 2. $\log K_a$ of **2**, **3**, and **4** with alkali metal perchlorates in acetonitrile at 20 ± 1 ℃.

M^+	2E	2Z	2C	3E	3Z	3C	4E	4Z	4C
Li^+	1.30 ±0.32	1.14 ±0.23	ND	1.97 ±0.06	1.94 ±0.02	1.58 ±0.05	1.32 ±0.27	2.18 ±0.12	1.79 ±0.07
Na^+	0.87 ±0.07	ND	ND	4.04 ±0.03	2.17 ±0.03	1.18 ±0.07	2.03 ±0.03	2.43 ±0.02	2.28 ±0.09
K^+	ND	ND	ND	2.09 ±0.09	1.84 ±0.10	ND	3.36 ±0.06	2.91 ±0.07	2.28 ±0.06

ND: Not determined due to little change of absorption spectra.

To explain these observations, molecular mechanics calculations were done by CAChe MM2. The three double bonds of the stable conformations of **3E** - Na^+ are lying in *s-trans–s-trans* (most stable) and *s-cis–s-trans* (second most stable). The combination of **4E** - K^+ exhibits similar results. As cyclization occurs from *s-cis–s-cis* of E-form, *s-trans* conformation stops photocyclization.

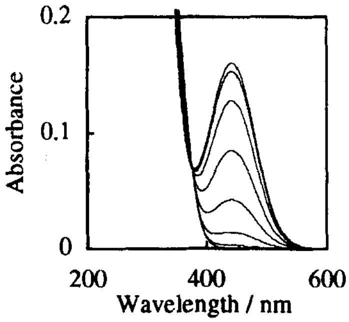


FIGURE 1. Change of absorption by 313-nm light irradiation to **2Z** in CH_3CN.

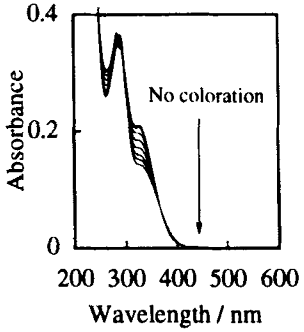


FIGURE 2. Change of absorption by 313-nm light irradiation to **3Z** - Na^+ in CH_3CN.

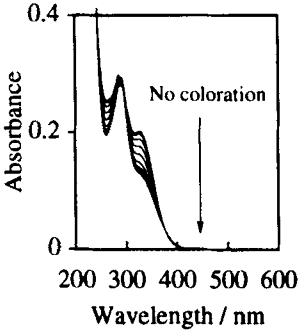


FIGURE 3. Change of absorption by 313-nm light irradiation to **4Z** - K^+ in CH_3CN.

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