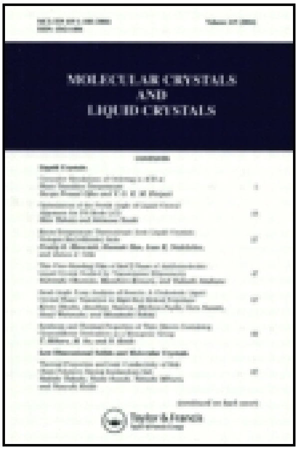


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromism and Kinetics of Heliochromic Benzothienylfulgides

Yasushi Yokoyama [a], Hiroshi Nakata [a], Koichi Sugama [a] & Yayoi Yokoyama [b]

[a] Department of Materials Chemistry, Yokohama National University, 79-5, Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan

[b] Department of Home Economics, Tokyo Kasei Gakuin University, 2600, Aihara-cho, Machida, Tokyo, 194-0292, Japan

Version of record first published: 24 Sep 2006

To cite this article: Yasushi Yokoyama, Hiroshi Nakata, Koichi Sugama & Yayoi Yokoyama (2000): Photochromism and Kinetics of Heliochromic Benzothienylfulgides, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 344:1, 253-258

To link to this article: http://dx.doi.org/10.1080/10587250008023845

Mol. Cryst. Liq. Cryst., 2000, Vol. 344, pp. 253-258
Reprints available directly from the publisher
Photocopying permitted by license only

Photochromism and Kinetics of Heliochromic Benzothienylfulgides

YASUSHI YOKOYAMA[a], HIROSHI NAKATA[a], KOICHI SUGAMA[a]
and YAYOI YOKOYAMA[b]

[a]*Department of Materials Chemistry, Yokohama National University, 79–5, Tokiwadai, Hodogaya-ku, Yokohama 240–8501, Japan and* [b]*Department of Home Economics, Tokyo Kasei Gakuin University, 2600, Aihara-cho, Machida, Tokyo 194–0292, Japan*

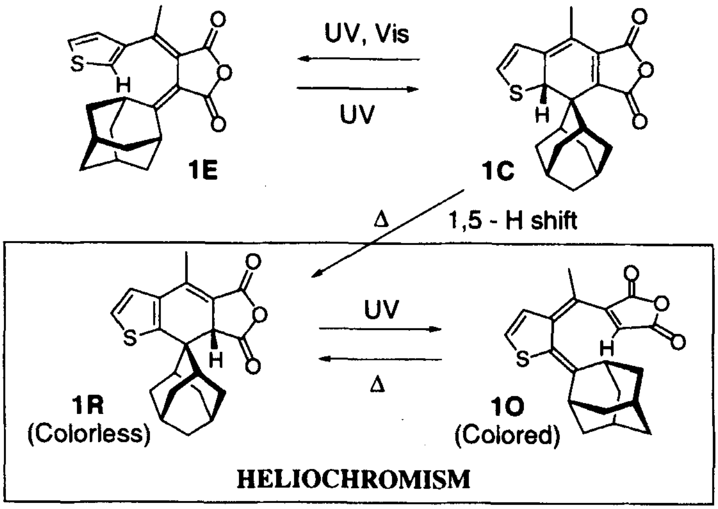
Four heliochromic benzothienylfulgides were synthesized and their spectral properties, photochromism, and the decoloration kinetics were examined. Photocyclization of E-form occurred on the benzothiophene ring but not on the phenyl ring for **4** and **5.** Introduction of an isopropyl group (**3**) or a phenyl group (**4, 5**) on the benzothienylmethylidene group retarded the decoloration rate of O-forms. Introduction of a phenyl group (**4, 5**) also resulted in 40-nm red-shift of absorption and three-fold increase in molar absorption coefficients of O-forms in the visible region.

Keywords: photochromism; heliochromism; fulgide; 1,5-sigmatropy; benzothiophene; adamantylidene

INTRODUCTION

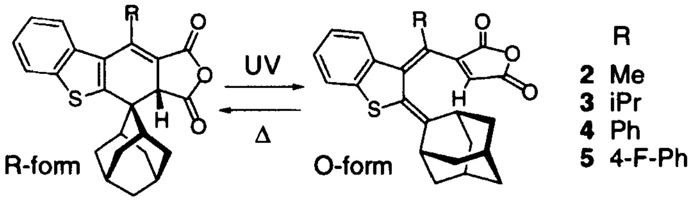
Heliochromic Fulgides

Fulgides are known to be thermally irreversible photochromic compounds since 1981 when Heller *et al.* synthesized a fulgide with 2,5-dimethyl-3-furyl group.[1] However, during the course of improvement of photochromic properties of fulgides, Heller *et al.* discovered a unique behavior of adamantylidene-substituted fulgides such as **1**, with a hydrogen atom on the UV-induced bond-forming aromatic carbon atom of E-form.[2,3]



Irradiation of UV-light to a solution of E-form generates the usual ring-closed and colored C-form. However, the hydrogen atom on the bond-forming carbon atom on the aromatic ring rearranges in a manner of thermal 1,5-sigmatropic shift to give the colorless R-form (rearranged form). The cyclohexadiene ring of the R-form opens to give the colored O-form (open form) by the UV-light which has been passing through the solution from the beginning of photoreaction. When irradiation of UV-light is stopped, the color gradually or rapidly disappears because the O-form returns to the colorless R-form thermally. Heller named this phenomenon as "Heliochromism" after the Greek word "Helio (sun)" because most of these compounds exhibit color under the sunlight and their colors fade in the dark.[2,3]

Despite their unique behaviors, these compounds scarcely appeared in the journals because of their applications to ophthalmic lenses have been preferred.[4] We here report the fundamental photochromic and thermal data of benzothiophene-containing heliochromic fulgides (heliofulgides) **2** - **5**.



RESULTS AND DISCUSSION

Synthesis of Heliofulgides

Synthesis of the R-forms of heliofulgides **2** - **5** were commenced by the synthesis of the corresponding E-forms by Stobbe condensation of the 3-acylbenzothiophenes and diethyl adamantylidenesuccinate. The E-forms of fulgides were dissolved in ethyl acetate and irradiated by 366-nm light from high pressure Hg lamp at room temperature for a few hours. The irradiation was stopped and the solution was kept in the dark for over night. Silica gel column chromatography gave fulgides **2R** (27%), **3R** (21%), **4R** (18%), and **5R** (20%) from the corresponding E-forms.

Photocoloration and Thermal Decoloration of Heliofulgides

Irradiation of 366-nm light to toluene solution of the R-form of a heliofulgide caused coloration. When the change in the absorption was no more observed, the irradiation was stopped, and the fading of color with time was monitored at the designated temperature. Typical examples of the spectral change of **3** and **4** are shown in Figs. 1 and 2.

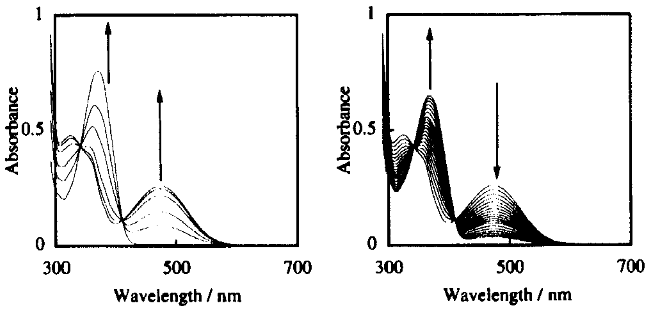


FIGURE 1. Change of absorption spectra of **3** in toluene.
(a) 366-nm irradiation to **3R** (1.0 x 10^{-4} mol dm^{-3}) in a period of 5 min.
(b) Thermal decoloration of **3O** from PSS at 24.0 ℃ in a period of 20 h.

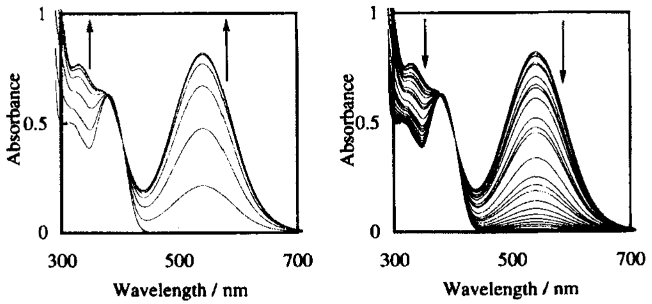


FIGURE 2. Change of absorption spectra of **4** in toluene.
(a) 366-nm irradiation to **4R** (1.0 x 10^{-4} mol dm^{-3}) in a period of 12 min.
(b) Thermal decoloration of **4O** from PSS at 24.4 ℃ in a period of 18 h.

In each case, only one R-form was produced upon UV irradiation.

As **4E** (or **4Z**) and **5E** (or **5Z**) have two aromatic rings that can cyclize upon UV irradiation, we examined which aromatic ring, benzothienyl or phenyl, would participate in the photocyclization. We thus synthesized **4E/Z**-d_5 starting from benzothiophene and benzoyl chloride-d_5 by way of Friedel - Crafts reaction. If the photocyclization of **4E/Z**-d_5 occurs on the phenyl ring, the corresponding R-form should have D on the juncture of the acid anhydride ring and the cyclohexadiene ring as the result of 1,5-sigmatropy. However, the R-form obtained from **4E/Z**-d_5 has H as the migrated atom. We therefore concluded that the photocyclization of **4E/Z** occurs on the benzothiophene ring exclusively.

The kinetic data of thermal decoloration of O-forms are listed in Table 1. Replacement of the methyl group with a larger group resulted in the significant retardation of thermal decoloration.

TABLE 1. Arrhenius activation energy (E_a) and frequency factor (A)[a]

	2O to **2R**	**3O** to **3R**	**4O** to **4R**	**5O** to **5R**
E_a / kJ mol^{-1}	78.4	89.1	94.5	91.9
A / sec^{-1}	9.72×10^{10}	1.07×10^{11}	3.22×10^{12}	1.61×10^{12}

a) In toluene.

Absorption Spectral Properties of R-form of Heliofulgides

The absorption spectral data of R-form and O-form of heliofulgides are shown in Table 2. Relatively large differences were observed for O-forms. Increase in the bulkiness of the alkyl substituent R from methyl to isopropyl resulted in 25-nm blue shift of λ_{max}. The large isopropyl group must have disturbed the planarity of the conjugating system. Introduction of a phenyl group resulted in a red shift of more than 40 nm. It was attributed to the extended conjugation.

In order to estimate the molar absorption coefficients of O-forms, the ratio of **3O/3R** and **4O/4R** at photostationary state was examined by HPLC, since **3O** and **4O** return to their R-forms rather slowly. As the result, **3O/3R** was about 87/13 and **4O/4R** was about 91/9 when no more spectral change was observed upon UV irradiation to the R-form in toluene. The molar absorption coefficients of **3O** and **4O** based on these ratios and the absorption spectra at their photostationary states were 3000 and 8500 $mol^{-1}dm^3cm^{-1}$, respectively. This result shows that the replacement of the alkyl group with a phenyl group gives rises to the 40-nm red-shift as well as the three-fold enlargement of the molar absorption coefficient of the O-form.

TABLE 2. Absorption spectral data of heliochromic fulgides in toluene[a)]

	2	**3**	**4**	**5**
R-form	367 (6500)	371 (7500)	382 (5880)	375 (7520)
O-form	501 (------)	476 (3000)	543 (8500)	544 (------)

a) Absorption maximum wavelength / nm. Values in parentheses are molar absorption coefficients / mol^{-1} dm^3 cm^{-1}.

Acknowledgments
This work was supported by Grant-in-Aid for Scientific Research on Priority Area (A) "Molecular Synchronization for Design of New Materials System" from The Ministry of Education, Science, Sports and Culture of Japan, Grant-in-Aid for Scientific Research (C) from Japan Society for the Promotion of Science, and Nissan Science Foundation.

References

[1] P. J. Darcy, H. G. Heller, P. J. Strydom, and J. Whittall, *J. Chem. Soc.*, **1981,** 202.

[2] J. Whittall, Chapter 9, "4+2 Systems: Fulgides," in *Photochromism: Molecules and Systems,* H. Dürr and H. Bouas-Laurent eds., Elsevier, Amsterdam, 1990, pp. 467 – 492.

[3] H. G. Heller, Chapter 31, "Photochromism for the Future," in *Electronic Materials, from Silicon to Organics,* L. S. Miller, J. B. Mullin eds., Plenum Publishing, New York, 1991, pp. 471 – 483.

[4] H. G. Heller, S. N. Oliver, J. Whittall, W. Johncock, P. J. Darcy, and C. Trundle, *E. P. A.* 0–140540, 1984.