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Improving the stability of photochromic fluorinated indolylfulgides

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Abstract

Fluorinated indolylfulgides are a class of photochromic organic compounds. It is possible to consider potential applications of these compounds in optical devices such as switches and memory. Two novel fulgides, a deuterated trifluoromethyl indolylfulgide and a trifluoromethyl dicyclopropyl indolylfulgide, were designed based on prior mechanistic studies to have greater thermal stability and potentially greater photochemical stability. The absorption spectra, thermal stabilities in both toluene and polymer films, and photochemical fatigue resistances of both fulgides were measured. The cyclizable *Z*-form of the dicyclopropyl fulgide displayed a significant red shift of the absorption maximum compared to any other fulgide. Deuteration led to greater thermal stability of the fluorinated fulgide. Moreover, the *Z*-form of the dicyclopropyl fulgide showed excellent durability in PMMA at 80 °C. The solution-based study of the dicyclopropyl fulgide demonstrated only *E*–*Z*-isomerization after prolonged treatment (380 h) at 80 °C in toluene. In addition, the trifluoromethyl dicyclopropyl indolylfulgide is the most photochemically stable yet reported; it underwent 10,000 photochemical cycles, coloration followed by bleaching, before degrading by 13%.

Keywords: Photochromism; Fluorinated indolylfulgide; Thermal stability; Photochemical stability

1. Introduction

It is possible to consider potential applications of indolyl-substituted fulgides in optical devices such as switches and memory [1–13]. The photochromism of fulgides is characterized by a reversible transformation between the open cyclizable form and the closed form (*C*). The transformation can be induced by wavelength-specific illumination (Scheme 1) [2,14].

Several properties are required for fulgides to be useful, such as readily distinguishable absorption spectra for each form, thermal and photochemical stability, large quantum yields, and large molar absorption coefficients [1,15]. In particular, fluorinated indolylfulgides, which were first synthesized by Yokoyama and Takahashi [16], meet many of these requirements. The advantages of fluorination include longer wavelength absorption maximum for the cyclizable (*Z*) isomer, enhanced photochemical stability in both toluene and polymer films, high coloration quantum yields in solution, and improved thermal resistance of the *C*-form upon treatment at 80 °C in poly(methylmethacrylate) (PMMA) polymer films [16]. However, the *Z*-form of the fluorinated substituted indolylfulgides showed decomposition in both solution [17] and PMMA upon prolonged exposure to elevated temperatutes [18]. The proposed thermolysis mechanism is illustrated in Scheme 2 [17]. The thermal stability of fluorinated fulgides is controlled by the irreversible conversion of **1Z** to intermediate **4** via a 1,5-hydrogen shift from the isopropylidene group.

Interestingly, the photochemical degradation of the fulgide may also depend upon a 1,5-hydrogen migration from the isopropylidene group. Yokoyama's proposed photochemical degradation mechanism of non-fluorinated fulgides is shown in Scheme 3 [16]. The first step involves a 1,5-hydrogen migration, which ultimately leads to a non-conjugated product and concomitant loss of photochromic properties.

Such a mechanism is impossible for fluorinated fulgides as the CH_3-group is replaced by a CF_3-group which has no hydrogens. However, a parallel mechanism may be operating using the isopropylidene and the second carbonyl group. Therefore, modifications of the isopropylidene group that diminish the rate of the 1,5-hydrogen shifts may lead to greater thermal stability

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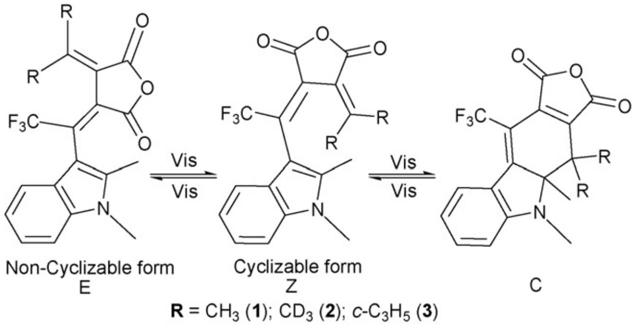
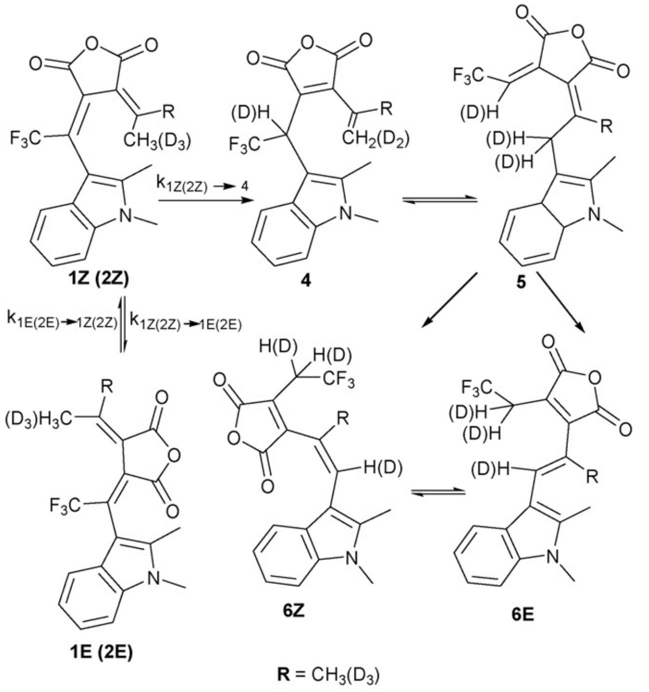
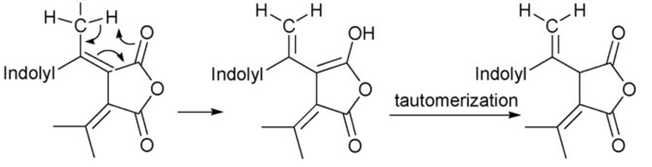


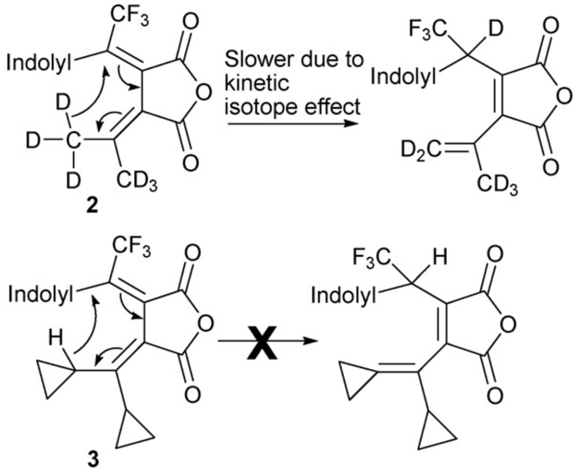
Scheme 1. Photochemical reactions of fluorinated indolylfulgides **1**–**3**.



Scheme 2. Proposed thermolysis mechanism of fluorinated indolylfulgides **1** and **2**.



Scheme 3. Potential photochemical degradation pathway for non-fluorinated indolylfulgide.



Scheme 4. Thermal degradation pathway for fulgides **2** and **3**.

and potentially improved photochemical stability. Initial studies dealt with substituting the isopropylidene with an adamantylidene group. However, the time to cycle between the *Z*- and *C*-forms was too long to measure the photochemical stability [19]. Herein, we report the photochemical, thermal and optical properties of two newly synthesized fulgides—deuterated trifluoromethyl indolylfulgide and trifluoromethyl dicyclopropyl indolylfulgide (Scheme 1), which are expected to be more thermally stable. Because in the case of deuterated trifluoromethyl indolylfulgide (**2**) the rate determining step for thermal decomposition, a 1,5-hydrogen shift, will be slowed by a large kinetic isotope effect, and in the case of trifluoromethyl dicyclopropyl indolylfulgide (**3**) the 1,5-hydrogen shift will introduce an unfavorable exocyclic double bond into the cyclopropyl ring (Scheme 4). Previously dicyclopropyl group has been incorporated into furyl-, pyrryl-, and thienylfulgides and derivatives [15,20–24].

2. Experimental details

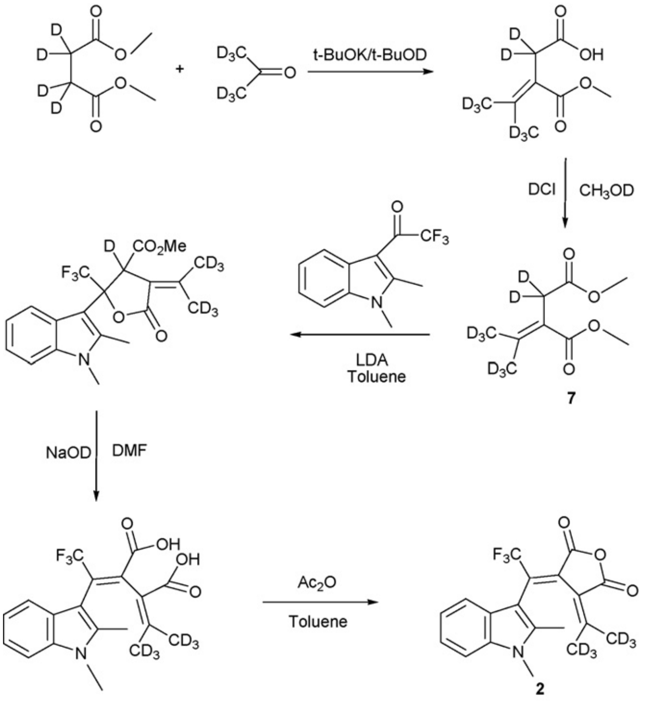
2.1. General procedures and materials

All commercially available materials were used without further purification with the exception of *tert*-butanol which was distilled from CaH_2. NMR spectra were recorded on a Brüker 400 MHz NMR spectrometer. ^{1}H and ^{13}C NMR samples were internally referenced to TMS (0.00 ppm) or solvent (7.26 and 77.00 ppm, respectively for chloroform). UV–vis spectra were recorded with a Cary 300 Spectrophotometer. Flash chromatography was performed with 230–400 mesh silica gel. Galbraith performed all elemental analysis. Fulgide **1** was synthesized as described previously [25].

2.1.1. Synthesis

*2.1.1.1. Dimethyl octadeuteroisopropylidenesuccinate (**7**).* To potassium *tert*-butoxide (3.4 g, 30.1 mmol) in 50 mL monodeuterated *tert*-butanol was added a mixture of 5 mL monodeuterated *tert*-butanol, dimethyl 2,2,3,3-tetradeuterosuccinate (5.0 g, 33.3 mmol) and perdeuterated acetone (1.7 g, 26.6 mmol) under argon gas. The mixture was refluxed for 4 h. The monodeuterated *tert*-butanol was evaporated and diethyl ether (25 mL) was added, immediately followed by the addition of 2 M NaOD (50 mL) in D_2O. The aqueous solution was extracted with 3 × 50 mL diethyl ether. The aqueous solution was then acidified with deuterated sulfuric acid (8.5 mL D_2SO_4 in 40 mL D_2O) and further extracted with 4 × 75 mL CH_2Cl_2. The combined organic layers were dried with magnesium sulfate ($MgSO_4$), filtered, and concentrated *in vacuo* to yield the octadeuterated half-acid, half-ester. A Fischer esterification followed via addition of 50 mL of acidified monodeuterated methanol to the half-acid, half-ester. The reaction mixture was stirred for 6 days under argon and then concentrated *in vacuo*. The resulting liquid was added to 50 mL of a deuterated ice water slurry, which was extracted with 4 × 20 mL diethyl ether. The organic layers were combined and extracted with 3 × 20 mL deuterated sodium carbonate solution. The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to provide 1.95 g of product (38% yield).

*2.1.1.2. Hexadeuterated indolylfulgide (**2**).* Dimethyl octadeuteroisopropylidenesuccinate (0.95 g, 4.89 mmol) was added to a mixture of toluene (100 mL) and 1,2-dimethyl-3-trifluoroacetylindole (0.66 g, 2.71 mmol). The mixture was evaporated *in vacuo* to approximately 50 mL. LDA (2.45 mL of a 2 M solution, 4.90 mol) was added slowly at room temperature under argon gas. After 16 h, the mixture was acidified with aqueous acid (1.5 mL H_2SO_4 in 29 mL D_2O) and then extracted with diethyl ether (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting liquid was purified by silica gel column (1:1 CH_2Cl_2/hexanes) and then recrystallized in ethanol to provide 0.370 g of the hexadeuterated indole lactone as a *cis*/*trans* mixture. To the indole lactone (0.388 g) dissolved in DMF (40 mL) at 0 °C was added 1.5 mL of sodium deuteroxide (30% in D_2O). The solution was stirred and allowed to warm to room temperature overnight. Solvent was removed *in vacuo* and partitioned between H_2O (20 mL) and EtOAc (50 mL). The aqueous layer was then separated, acidified with 5% H_2SO_4 and, extracted with EtOAc (4 × 25 mL). The combine layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to provide a solid. The solid was then triturated with $CHCl_3$ to provide 0.328 g of crude diacid. The diacid was suspended in a mixture of toluene (7 mL) and acetic anhydride (4 mL). The solid immediately dissolved and the solution turned dark orange. After stirring overnight, the solvent was removed *in vacuo*. Crystallization was accomplished using isopropanol/dichloromethane to provide 0.163 g of deuterated fulgide (17% yield from 1,2-dimethylindole). The ^1H NMR spectrum matched that of the proteo-compound with the exception that the resonances at 2.16 and 0.97 ppm were greatly diminished. The two methyl groups were approximately 85% deuterated. The synthetic route is illustrated in Scheme 5.



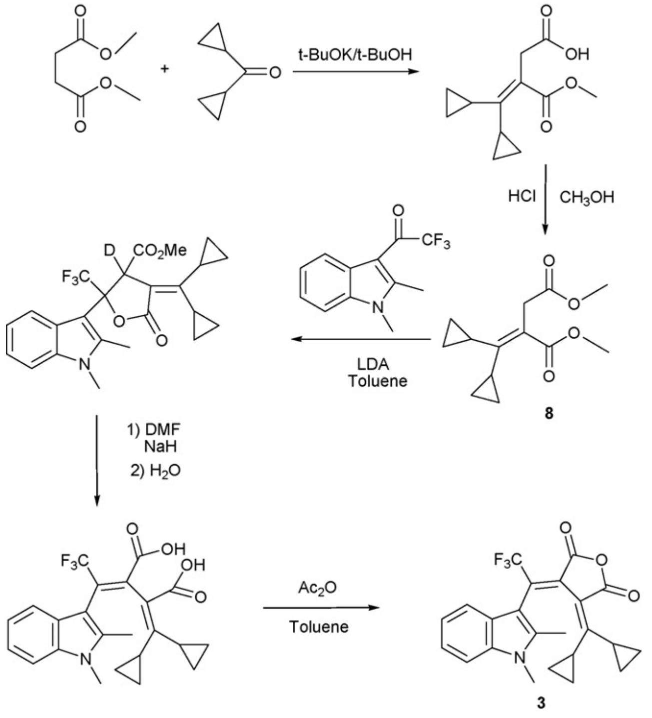
Scheme 5. Synthesis of fulgide **2**.

*2.1.1.3. Dimethyl dicyclopropylmethylenesuccinate (**8**)[26].* To a refluxing mixture of potassium *tert*-butoxide (5.02 g, 44.7 mmol) in freshly distilled *tert*-butanol (50 mL) was added a solution of dicyclopropylketone (95%, 4.84 g, 43.9 mmol) and dimethyl succinate (6.49 g, 44.5 mmol) in freshly distilled *tert*-butanol (10 mL) over 30 min. After 3 h at reflux the reaction mixture was concentrated *in vacuo* and partitioned between 70 mL 2N NaOH and 150 mL diethyl ether. The aqueous layer was then separated and acidified with 6N HCl to pH 1. The acidic solution was then extracted with CH_2Cl_2 (3 × 250 mL). The combined organics were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to provide 6.67 g of crude product. The crude product was then dissolved in 500 mL of methanol. The solution was acidified with HCl gas and stirred for 75 min, before being concentrated *in vacuo*, and partitioned between sat. $NaHCO_3$ (250 mL) and diethyl ether (250 mL). The aqueous layer was then extracted with diethyl ether (2 × 250 mL). The combined organics were back extracted with water (250 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resulting liquid was purified by silica gel chromatography (gradient from 3:1 CH_2Cl_2/hexanes to neat CH_2Cl_2) to provide 3.54 g of crude product. An analytical sample was prepared by further purifying a small portion of the crude product using silica gel chromatography (10:1 hexanes/EtOAc). ^1H NMR ($CDCl_3$) δ 3.76 (s, 3H), 3.68 (s, 3H), 3.59 (s, 2H), 1.75 (tt, $J = 8.6$, 5.9 Hz, 1H), 1.37 (tt, $J = 8.4$, 5.8 Hz, 1H), 0.81–0.76 (m, 2H), 0.75–0.70 (m, 2H), 0.68–0.64 (m, 2H), 0.52–0.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 171.7, 169.6, 152.6, 125.7, 51.8, 51.5, 35.9, 15.1, 14.2, 6.4, 6.3. Anal. calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.91; H, 7.81.

*2.1.1.4. Dicyclopropylindolylfulgide (**3**) [26].* A mixture of crude dimethyl dicyclopropylmethylenesuccinate (3.42 g, 14.4 mmol), 1,2-dimethyl-3-trifluoroacetylindole (1.78 g, 7.4 mmol) and toluene (300 mL) was partially concentrated *in vacuo* to 200 mL. To the stirred solution under argon at room temperature was added LDA (7.3 mL of a 2 M solution, 14.6 mmol) over 5 min. After 30 min the reaction was quenched with 5% H_2SO_4 (100 mL). The aqueous layer was extracted with diethyl ether (3 × 150 mL) and the combined organics were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by silica gel chromatography (gradient from 1:1 CH_2Cl_2/hexanes to neat CH_2Cl_2) followed by recrystallization (ethanol) to provide 1.61 g of the indole lactone as a *cis*/*trans* mixture. To the indole lactone (1.02 g, 2.3 mmol) in DMF (100 mL) at 0 °C was added NaH (60% in oil, 0.248 g, 6.2 mmol). After 15 min, the mixture was warmed to room temperature and stirred for 90 min. Water (0.30 mL, 17 mmol) was then added. After an additional 14 h, the mixture was concentrated *in vacuo* and partitioned between 0.1N NaOH (150 mL) and ethyl acetate (150 mL). The aqueous layer was then separated, acidified with 5% H_2SO_4, and extracted with ethyl acetate (3 × 150 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to provide a solid. The solid was then triturated with $CHCl_3$ to provide 0.888 g of crude diacid. The solid was then suspended in a mixture of toluene (60 mL) and acetic anhydride (40 mL) at 35 °C for 45 min. The resulting solution was concentrated *in vacuo* and the residue recrystallized from a mixture of CH_2Cl_2/isopropanol. The recrystallization was performed several times on the same material. Each time the (*Z*) to (*E*) ratio increased suggesting isomerization was occurring during recrystallization. On the third recrystallization 0.482 g of (*Z*)-product was obtained (yield = 25% from 1,2-dimethyl-3-trifluoroacetylindole). (*Z*)-form: ^1H NMR ($CDCl_3$) δ 7.27–7.24 (m, 1H), 7.20–7.16 (m, 2H), 7.12–7.08 (m, 1H), 3.68 (s, 3H), 2.57 (br s, 1H), 2.28 (s, 3H), 0.84–0.81 (m, 2H), 0.46–0.36 (m, 4H), 0.30–0.24 (m, 2H), −0.15 to −0.18 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 172.1, 161.7, 160.0, 137.4, 137.0, 132.3 (q, J = 35 Hz), 127.9, 124.5, 122.2, 122.1 (q, J = 276 Hz), 120.9, 120.4, 120.2, 109.3, 107.5, 30.0, 16.7, 16.6, 12.7, 10.6, 10.1, 9.8; anal. calcd for $C_{23}H_{20}F_3NO_3$: C, 66.50; H, 4.85; N, 3.37. Found: C, 66.46; H, 4.82; N, 3.46. (*E*)-form was obtained if the initial recrystallization was performed using cold $CDCl_3$. (*E*)-form: ^1H NMR ($CDCl_3$) δ 7.40 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 8.2 Hz, 1H), 7.20 (td, J = 7.6, 1.0 Hz, 1H), 7.11 (td, J = 7.5, 1.0 Hz, 1H), 3.74 (s, 3H), 3.07–3.04 (m, 1H), 2.37 (s, 3H), 1.67–1.63 (m, 1H), 1.27–1.09 (m, 6H), 0.79 (br s, 2H); anal. calcd for $C_{23}H_{20}F_3NO_3$: C, 66.50; H, 4.85; N, 3.37. Found: C, 66.45; H, 4.55; N, 3.52. (*C*)-form: ^1H NMR ($CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 1H), 7.42 (td, J = 7.8, 1.1 Hz, 1H), 6.83 (td, J = 7.7, 0.7 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 3.09 (s, 3H), 1.47 (s, 3H), 1.34–1.20 (m, 2H), 1.03–0.93 (m, 1H), 0.90–0.79 (m, 1H), 0.78–0.68 (m, 2H), 0.42–0.34 (m, 1H), 0.30–0.22 (m, 1H), 0.07 to −0.02 (m, 1H), −0.08 to −0.15 (m, 1H). The synthetic route is illustrated in Scheme 6.

2.2. Preparation of thin films

An initial solution was prepared by adding 2–4 mg of fulgide to a solution of 10% poly(methylmethacrylate) (PMMA—low molecular weight, average M_w *ca.* 120,000) in CH_2Cl_2 (5 mL). The polymer solution (1.5 mL) was then deposited via pipet onto circular 1 in. × 1/16 in. BK-7 glass slides (escoproducts) and allowed to spread over the surface of the slide. The sample was allowed to dry overnight inside a glass Petri dish at room temperature. The resulting films were utilized in the thermal stability studies.



Scheme 6. Synthesis of fulgide **3**.

2.3. Spectra determination

Concentrated, air-saturated stock solutions of the *Z*-form or *E*-form of the fulgides in toluene were prepared in duplicate or triplicate. From each stock solution, 5 samples ranging in concentration from 0.20 to 0.05 mM were then prepared by dilution with toluene. Absorption coefficients and λ_{max} were determined.

The *C*-forms were obtained by irradiating *Z*-form solutions with 419 nm light in a Rayonet reactor followed by purification via flash column chromatography (silica gel, toluene). Stock solutions containing freshly purified *C*-form in toluene were diluted to 4 or 5 different concentrations and their UV–vis spectra obtained. Each *C*-form solution was then quantitatively converted to *Z*-form with yellow light and the concentration of fulgide present was ascertained using the predetermined *Z*-form extinction coefficients. Absorption coefficients and λ_{max} for the *C*-forms were then determined from the initial spectra.

2.4. PSS measurements

The photostationary state (PSS) was measured using NMR spectroscopy. An NMR tube containing *Z*-form fulgide in toluene-d_8 was illuminated with 436 nm light until photostationary state was reached. A spectrum was then acquired and integrated.

2.5. Photochemical stability

Air-saturated solutions of the *Z*-form were prepared in toluene with an initial absorbance of 0.6 at the absorption maxima. Samples were irradiated to the photostationary state with light supplied from an Oriel 1000 W Hg(Xe) lamp utilizing a water filter followed by a hot mirror followed by a 435 nm narrow bandpass filter. After measuring the UV–vis spectrum of the photostationary state, $PSS_{435\,nm}$, a pure *Z*-form solution was irradiated to 90% of the PSS and the reaction was timed. The 90% PSS mixture was then bleached with >560 nm light using a separate filter and again the reaction was timed. Absorbance at the *C*-form λ_{max} was <0.01 upon bleaching.

Once the duration of irradiation was established for both the 90% PSS coloration and < 1% *C*-form bleaching reactions, the system was automated through the use of a filter switch. All solutions were capped and stirred. Control experiments were performed to correct for evaporation. After a designated number of irradiation cycles, the samples were fully converted to $PSS_{435\,nm}$ and their UV–vis spectra scanned. The photochemical fatigue was then determined by comparison with the initial $PSS_{435\,nm}$ absorption spectrum. The cycling times were approximately 35 s (*Z*–*C*) and 25 s (*C*–*Z*) for fulgides **1** and **2** and 55 s (*Z*–*C*) and 10 s (*C*–*Z*) for fulgide **3**.

2.6. *Thermal stability—thin films*

2.6.1. *Polymer-based study*

Thin films containing the *Z*-form of the fulgides were wrapped in aluminum foil and placed in an oven maintained at 80 °C. The films were removed at prescribed intervals and their UV–vis spectra measured.

To determine the stability of the *C*-form, the thin films, containing the *Z*-form, were illuminated with blue light (435 nm bandpass filter) until the photostationary state had been obtained. The thin films were then wrapped in aluminum foil and placed in an oven maintained at 80 °C. The films were removed at prescribed intervals and their UV–vis spectra measured.

2.6.2. *Solution-based study*

A solution of the *Z*-forms of deuterated trifluoromethyl indolylfulgide and 5-methoxy-2-methylindole (internal standard) was prepared in toluene-d_8. The solution was transferred to an NMR tube. The tube was then sealed and submersed in a water bath maintained at 80 °C. At prescribed times the tube was removed and its contents analyzed by ^{1}H NMR-spectroscopy. A control experiment in which approximately a 1:1 mixture of **1** and **2** was degraded was also performed. The results were consistent with the reported rate constants.

3. Results and discussion

3.1. *UV–vis absorption spectra*

The UV–vis absorption spectra of the *Z*-, *E*-, and *C*-isomers of trifluoromethyl dicyclopropyl indolylfulgide (**3**) measured in toluene are shown in Fig. 1. The wavelength of maximum absorbance and the corresponding extinction coefficients of fulgides **1**–**3** in toluene are presented in Table 1. The replacement of the methyl groups by cyclopropyl groups results in a bathochromic shift of the absorption maximum as reported previously by Heller et al. for a furyl fulgide [15]. The absorption maxima of fulgides **1**–**3** are in the visible region, which allows for the use of inexpensive light sources.

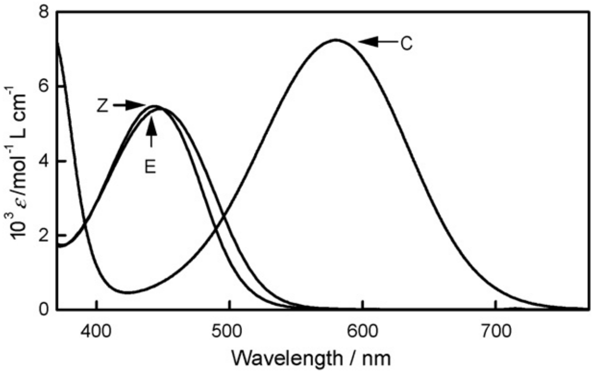


Fig. 1. UV–vis absorption spectra of fulgide **3** in toluene.

Table 1
Extinction coefficients at λ_{max} for fulgides **1**–**3** in toluene

Fulgide	λ_{max}, nm (ε_{max}, mol^{-1} L cm^{-1})			$PSS_{436\,nm}$
	Z-form	*E*-form	*C*-form	*C*:*Z*:*E*
1	427 (5800)	441 (5600)	571 (7000)	95:3:2
2	427 (5900)	–	571 (7000)	94:3:2
3	444 (5500)	449 (5400)	580 (7200)	87:13:<4

3.2. *Thermal stability*

Several studies have dealt with the ability of fulgides to resist thermal stress [6,12,13,18,19,27]. In the present study, the thermal stability of fulgides **2** and **3** was measured in both toluene and PMMA. In toluene thermal stability was determined using NMR spectroscopy. The thermolysis pathway is illustrated in Scheme 2 [17]. As mentioned above the conversion of **1*Z*** to product **6** involves an initial 1,5-hydrogen shift from the isopropylidene group to form intermediate **4**, followed by a 1,5-indolyl migration and a final 1,5-hydrogen shift. Fig. 2 demonstrates the changing concentrations with time during thermolysis of deuterated fulgide **2** at 80 °C. Rate constants were obtained by fitting the NMR data using least-squares (Table 2).

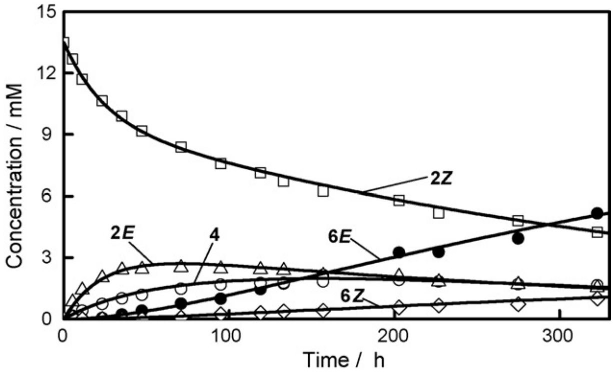


Fig. 2. Concentration profiles for thermolysis of **2*Z*** at 80 °C in toluene.

Table 2
Rate constants (min^{-1}) obtained by fitting the NMR data using Euler's method

Rate constants (min^{-1})	Fulgide **1**[a]	Fulgide **2**	Ratio of rate constants
$k_{1Z(2Z)\to 4}$	3.9×10^{-4}	5.8×10^{-5}	6.7
$k_{1Z(2Z)\to 1E(2E)}$	1.5×10^{-4}	1.7×10^{-4}	0.9
$k_{1E(2E)\to 1Z(2Z)}$	6×10^{-4}	5.2×10^{-4}	1.2
$k_{4\to 6E}$	8.7×10^{-4}	1.9×10^{-4}	4.6
$k_{4\to 6Z}$	1.7×10^{-4}	3.9×10^{-5}	4.3

[a] From Ref. [17].

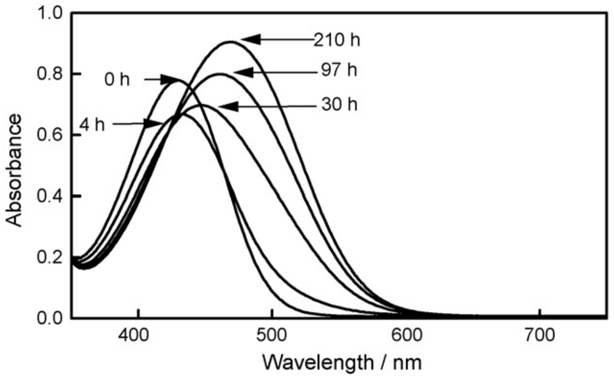


Fig. 3. UV–vis absorption spectra of **1Z** in PMMA with continuing treatment at 80 °C.

The results showed that deuteration improves the thermal stability of **2** by a factor of 7 relative to **1**, ($k_{1Z(2Z)\to 4}$) because in the case of **2** the rate of determining step for thermal decomposition, a 1,5-hydrogen shift, has a large kinetic isotope effect. Fulgide **2** degrades at about 4%/day. The *Z*-form of **3** displays only *Z*- to *E*-form thermal isomerization after 380 h at 80 °C in toluene. No other signals were observed. In this case a 1,5-hydrogen shift is unfavorable as it introduces an exocyclic double bond into the already strained cyclopropyl ring. These results support the proposed thermolysis mechanism.

In PMMA, the enhanced thermal stability of the *Z*-forms of **2** and **3** was also observed. Figs. 3 and 4 illustrate UV–vis absorption spectra of **1Z** and **2Z** fulgides, respectively, in PMMA with continuing treatment at 80 °C. At 80 °C the absorbance spectrum of the *Z*-form of **1** reached a low point after only 4 h but the *Z*-form of the deuterated analog **2** took 97 h before reaching a similar low point. Fulgide **3***Z* exhibited significantly improved thermal stability, it lost only 13% of its absorbance after 530 h (3 weeks) at 80 °C (0.6%/day) (Fig. 5). The *C*-forms of **1** and **2** reverted back to the corresponding *Z*-forms at a rate of 0.3%/day over 23 days and 0.7%/day over 11 days, respectively at 80 °C. Fulgide **3*C*** reverted back to **3Z** with a half-life of approximately 1 h at 80 °C. For **1** and **2** the *Z*-forms limit thermal stability, but for **3** it is the *C*-form.

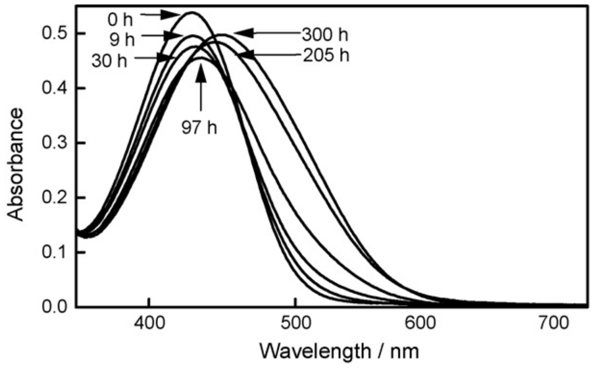


Fig. 4. UV–vis absorption spectra of **2Z** in PMMA with continuing treatment at 80 °C.

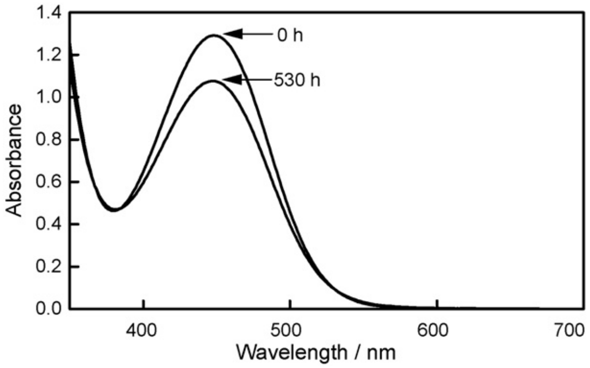


Fig. 5. UV–vis absorption spectra of **3Z** in PMMA with continuing treatment at 80 °C.

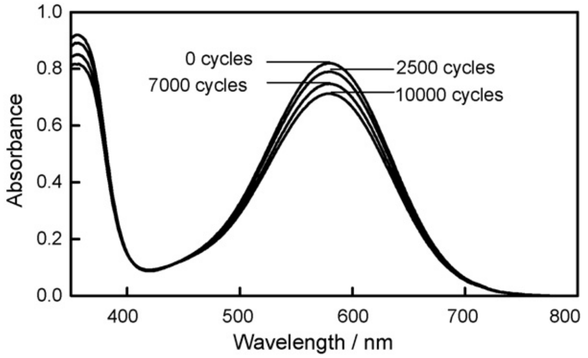


Fig. 6. PSS absorbance of fulgide **3** in toluene after the indicated number of cycles.

3.3. Photochemical stability

Photochemical stability was measured in toluene and fulgide **3** was shown to be the most stable fulgide yet. Fulgide **3** can withstand 10,000 photochemical cycles (coloration followed by bleaching) before degrading by 13% (Fig. 6, Table 3). Fulgide **1** and its deuterated analog **2** demonstrate similar behavior. They degrade at a rate of 0.008% per photochemical cycle indicating

Table 3
Photochemical fatigue resistance of fulgides **1**–**3**

Fulgide	Photochemical decomposition		
	Number of cycles	A/A_0	%/Cycle
1	4,000	0.679	0.008
2	3,000	0.766	0.008
3	10,000	0.871	0.0013

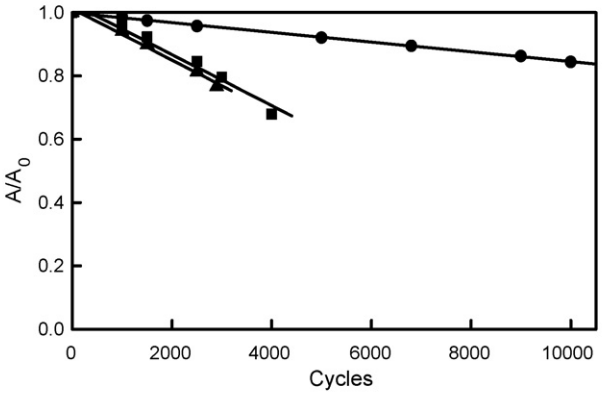


Fig. 7. Photochemical decomposition of **1**–**3** in toluene: decreasing absorbance with repeated coloration and bleaching cycles: squares (**1**), triangles (**2**), circles (**3**).

that deuteration does not affect photochemical stability significantly (Fig. 7, Table 3).

Kaneko et al. [6] have reported that the non-fluorinated indolylfulgide analog of fulgide **1** (CF_3-group replaced with CH_3) in PMMA and toluene degrades at a rate of aproximately 0.1% per photochemical cycle [18]. The fluorinated indolylfulgides are more fatigue resistant, supporting the assumption that the decomposition process involves a hydrogen migration via a 1,5-sigmatropic rearrangement in the case of the non-fluorinated indolylfulgide (Scheme 3) [16]. However, the mechanism of photochemical decomposition of fluorinated indolylfulgides remains unclear. Our results demonstrate that replacing the methyl groups, fulgide **1**, with the more bulky dicyclopropyl groups, fulgide **3**, decreases photochemical fatigue by a factor of 6 (Table 3). Thus, the degradation pathway might involve a 1,5-hydrogen shift from the isopropylidene group to the second carbonyl group. Therefore, modifications of the isopropylidene group that diminish the rate of the 1,5-hydrogen shift could lead to improved photochemical stability.

4. Conclusion

In summary, we have synthesized two novel photochromic fluorinated indolylfulgides with many advantageous properties. The new fulgides differ from the standard fluorinated fulgide **1** in that the isopropylidene group was altered. Deuterated indolylfulgide **2** has similar properties as its non-deuterated analog **1** but the *Z*-form exhibits much better thermal stability as predicted from mechanistic considerations and kinetic isotope effects (Scheme 2). Deuteration should be a general strategy to enhance the thermal stability by a factor of 7 for all fulgides that degrade via a similar mechanism. Dicyclopropyl fulgide **3** exhibits a significant red shift in the absorbance maximum of the *Z*-form making it one of the highest values yet reported for a fulgide. The photochemical stability of **3** is by far the best yet reported for a fulgide (0.0013%/cycle) and is similar to the best diarylethenes (0.0007%/cycle) [28,29], another important class of photochromic organic compounds. The *Z*-form of fulgide **3** also exhibits excellent thermal stability in toluene and PMMA, as can be justified based on mechanistic considerations. As demonstrated here, the rational design of fulgides is a powerful tool, which can improve the properties of fulgides.

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