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Thermal stability and photochromic properties of a fluorinated indolylfulgimide in a protic and aprotic solvent

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ABSTRACT

The photochromic properties and thermal stability of a newly synthesized fluorinated *N*-ethoxycarbonylmethyl indolylfulgimide substituted on the imide nitrogen were examined in a protic and aprotic environment. The absorption spectra and extinction coefficients of the *Z*- and *C*-forms of the fluorinated indolylfulgimide (open and closed, respectively) were measured in a binary 70/30 ethanol/water system and in toluene. The results demonstrated a favorable bathochromic shift of the absorption maxima for both the open and closed forms of the fulgimide when the solvent was changed from aprotic toluene to protic aqueous ethanol. In addition, the photochemical stability of the new fulgimide was found to be high (0.056 and 0.020% degradation each time the fulgimide is cycled between the open and closed form in 70/30 ethanol/water and in toluene, respectively). The thermal stability of both forms of the fulgimide in 70/30 ethanol/water at 50 °C, toluene at 80 °C, and polymer film (PMMA) at 80 °C was measured using UV–vis and/or ^{1}H NMR spectroscopy. Both forms of indolylfulgimide display high hydrolytic stability in 70/30 ethanol/water at 50 °C, with the *Z*- and *C*-forms degrading 1.3 and 1.2%/day respectively, based on ^{1}H NMR data. At 80 °C in toluene the less stable *Z*-form lost about 20%/day.

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1. Introduction

Photochromic organic compounds, such as fulgides and fulgimides, have the potential to be used as optical switches or as media in optical memory [1]. Fulgides and fulgimides are characterized by a light-induced transformation between an open and closed form, which are converted back and forth by light of different wavelengths (Scheme 1) [2,3]. The reactions correspond to an electrocyclic ring closing and an electrocyclic ring opening, respectively.

Fulgides, especially fluorinated indolylfulgides, possess many favorable properties including readily distinguishable absorption spectra for each form, thermal and photochemical stability, large quantum yields, and large molar absorption coefficients [4]. Fluorinated indolylfulgides were first synthesized by Yokoyama and Takahashi, who demonstrated that the closed form is thermally stable, and that the open and closed forms can be cycled back and forth repeatedly before degrading significantly [4]. Several subsequent studies have dealt with improving the photochemical properties of indolylfulgides by changing their molecular structure [5–13]. The most photochemically stable fulgide undergoes 10,000 photochemical cycles before degrading by 13% [12].

One drawback of fulgides is that their structure contains a succinic anhydride ring, which is very reactive towards protic solvents such as ethanol, methanol, and water, thus limiting their applications [14]. To overcome the chemical reactivity of the succinic anhydride ring, fulgides are converted into fulgimides [15–17], which contain a more stable succinimide ring (Scheme 1). Fulgimides improve the solvolytic stability of the closed form by over three orders of magnitude in 70/30 ethanol/water relative to fulgides at 25 °C, although the closed form is still less solvolytically stable than the open form [18]. The exothermicity of methanolysis of a typical fulgide was calculated to be less for the open form than for the closed form and presumably a similar argument applies to fulgimides [14].

Although there have been reports of fulgimides in protic solvents previously, the properties of fulgimides in protic solvents have not been studied extensively [14,18–21]. One of the few reports of the use of a fulgimide derivative in protic solvents involved the covalent modification of the lectin concanavalin A [20]. The fulgimide derivative in this case was randomly attached to a number of lysine groups on the protein, and the binding constant of a mannoside to concanavalin A was modified by up to a factor of two when the fulgimide was converted from the closed form to the open form. This report demonstrated that the open form of the fulgimide is

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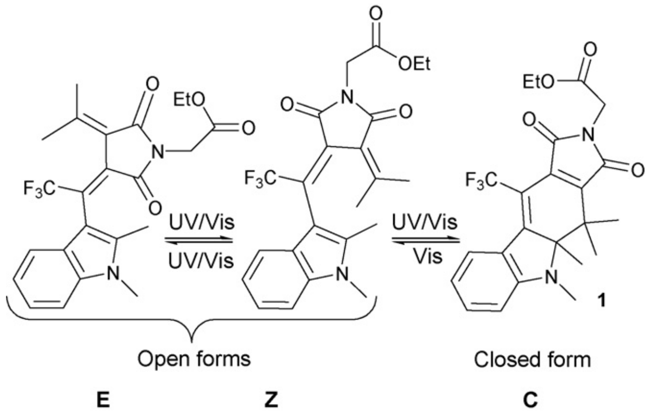
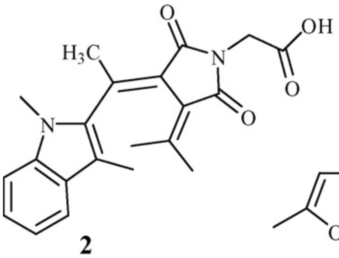


Scheme 1. Photochemical reactions of indolylfulgimide **1**. In fulgides the *N*-CH_2COOEt group in the succinimide ring is replaced by an oxygen atom forming a succinic anhydride ring.

reasonably stable in aqueous solution for 48 h at 25 °C, and that the fulgimide can cycle from the open form to the closed form at least twice. A recent report demonstrated that a fulgimide substituted at the 2-position of the heteroaromatic ring, **2**, does not switch back and forth in aqueous solution but will switch back and forth in less polar environments such as cellular membranes [21]. The rationale provided for the lack of activity in water, however, does not apply to fulgimides substituted at the 3-position of the heteroaromatic ring, similar to those used in the concanavalin A study.



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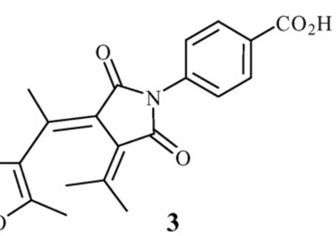

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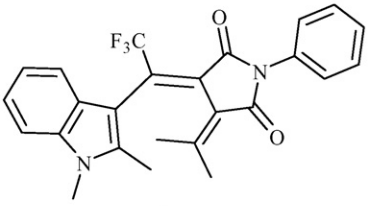

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The properties of an *N*-phenyl furanylfulgimide **3** substituted at the 3-position of the heteroaromatic ring in 50/50 ethanol/water have been examined in more detail [14]. Compound **3** demonstrated good thermal stability at room temperature where the closed form lost about 12% of its absorbance at λ_{max} after 10 days. In pure toluene at 50 °C the corresponding value was 17%. The photochemical stability or the percent degradation when cycled between the open and closed forms was 1.5% per cycle. The result in 50/50 ethanol/water was similar to that found in toluene [14]. Recently, we reported that a series of eight *N*-phenyl fluorinated indolylfulgimides lost between 0 and 45% of their absorbance at λ_{max} after being in 70/30 ethanol/water at room temperature for 14 days [18]. The series differed in terms of the substituents on the *N*-phenyl ring. The most stable compound was the parent *N*-phenyl fluorinated indolylfulgimide **4** for which the closed form lost 5% of its absorbance at λ_{max}. In all cases the closed form was the least stable of the two forms. In addition, a general trend was observed; the more electron withdrawing the substituents on the phenyl ring the greater the loss in absorbance at λ_{max} for the closed form. Therefore, replacement of the *N*-phenyl group with a more electron donating group such as an *N*-alkyl group would be expected to lead to a smaller loss in absorbance at λ_{max} and a concomitant greater hydrolytic stability.

Herein, we describe the synthesis and characterization of a new fluorinated indolylfulgimide **1** derived from glycine ethyl ester. Fluorinated fulgimide **1** was expected to be more water-soluble than the *N*-phenyl fulgimide **4** because of the more hydrophilic ethoxycarbonylmethyl group. In addition, the replacement of the phenyl group with an ethoxycarbonylmethyl group should improve stability towards hydrolysis of the succinimide ring. Hydrolysis of *N*-phenylfulgimides is enhanced by electron withdrawing substituents on the phenyl ring indicating that a more electron donating group, such as an ethoxycarbonylmethyl group, should improve hydrolytic stability. We compare the photochemical properties of **1**, including UV–vis absorbance spectra, extinction coefficient, and fatigue resistance in 70/30 ethanol/water with those observed in toluene. Also, we investigate the thermal stability of **1** in 70/30 ethanol/water, toluene, and PMMA.

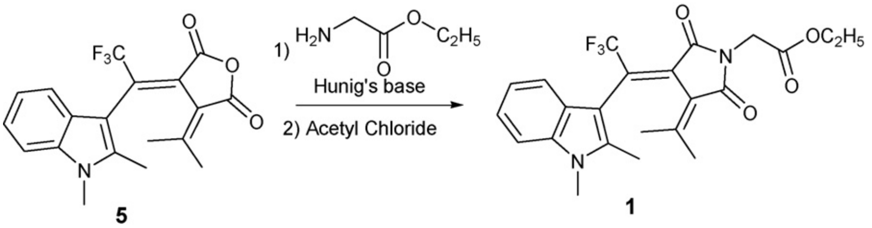
2. Experimental details

2.1. General procedures and materials

All commercially available materials were used without further purification. NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer (400 and 100 MHz for ^1H and ^{13}C, respectively). ^1H and ^{13}C NMR samples were internally referenced to TMS (0.00 ppm) or solvent (7.26 and 77.00 ppm respectively, for $CDCl_3$). 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. Fulgimide **4** was synthesized as described previously [18].

2.1.1. Synthesis

Synthesis of (*Z*)-ethyl 2-(3-(1-(1,2-dimethyl-1H-indol-3-yl)-2,2,2-trifluoroethylidene)-2,5-dioxo-4-(propan-2-ylidene)pyrrolidin-1-yl)acetate (**1**). *N*,*N*-Diisopropylethylamine (1.30 g, 10.1 mmol) was added slowly with stirring to a mixture of the HCl salt of glycine ethyl ester (0.37, 2.6 mmol), trifluoromethylindolylfulgide (**5**, 0.46 g, 1.3 mmol), and 30 mL of acetonitrile at 0 °C, (Scheme 2). After stirring overnight the solvent was removed in vacuo. The residue was added to 0.5 M HCl (30 mL) and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the residue by silica gel chromatography (60:40:2 hexane/EtOAc/AcOH) provided 0.46 g of the crude amide acid ester. The amide acid ester was added to 8 mL of acetyl chloride (8.8 g, 112 mmol) and the reaction mixture was refluxed under argon for 24 h. Then the solvent was removed in vacuo. The residue was added to 30 mL of H_2O and extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification was performed via silica gel chromatography (10:1 toluene/EtOAc) followed by recrystallization from methanol to provide 22 mg (4%) of the ethyl ester indolylfulgimide. *Z*-form: ^1H NMR ($CDCl_3$) δ, 7.32–7.26 (m, 2H), 7.21 (td, *J* = 7.0, 1.2 Hz, 1H), 7.13 (td, *J* = 7.5, 1.3 Hz, 1H), 4.42 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 2.23 (s, 3H), 2.13 (s, 3H), 1.60 (s, 1H), 1.29 (t, *J* = 7.1 Hz, 1H), 0.96 (s, 3H). ^{13}C NMR ($CDCl_3$) δ, 166.3, 165.9, 163.6, 153.9, 136.5, 136.1, 131.8 (q, *J* = 35 Hz), 128.7, 124.8, 121.8, 121.7 (q, *J* = 277 Hz), 121.3, 120.3, 119.0,



Scheme 2. Synthesis of fulgimide **1**.

108.5, 106.9, 61.2, 38.4, 29.3, 26.0, 21.7, 13.4, 11.2. Anal. Calcd for $C_{23}H_{23}F_3N_2O_4$: *C*, 61.60, *H*, 5.17; *N*, 6.25. Found: *C*, 61.33; *H*, 5.34; *N*, 6.19. λ_{max}(toluene) = 400 nm, ε_{max} = 5800 mol^{-1} L cm^{-1}. *C*-form: ^{1}H NMR (CDCl$_3$) δ, 7.73 (d, *J* = 8.1 Hz, 1H), 7.35 (td, *J* = 7.8, 1.1 Hz, 1H), 6.78 (td, *J* = 7.7, 0.7 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 4.27–4.17 (m, 2H), 4.26 (s, 2H), 2.92 (s, 3H), 1.79 (s, 3H), 1.35 (s, 3H), 1.28 (s, 3H), 1.25 (t, 3H). λ_{max}(toluene) = 549 nm, ε_{max} = 6600 mol^{-1} L cm^{-1}.

2.2. Preparation of thin films

An initial solution was prepared by adding 2–4 mg of fulgimide 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.

2.3. Spectral determination

Concentrated, air-saturated stock solutions of the *Z*-form of fulgimide **1** in toluene were prepared. 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*-form was obtained by irradiating *Z*-form solutions with 405 nm light 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 (>510 nm) and the concentration of fulgimide 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. A similar methodology was used to determine these values in 70/30 ethanol/water. The *C*-form fulgimide used in 70/30 ethanol/water, however, was still prepared in toluene and purified chromatographically on silica gel using toluene. The scan rate was 600 nm/min, the integration time was 0.1 s, and slit bandwidth was 2 nm. Each extinction coefficient was determined three times and the error from the *Z*-form was propagated to the error for the *C*-form.

2.4. Photostationary state (PSS) measurements

PSS was measured using ^{1}H NMR spectroscopy. An NMR tube containing the *Z*-form of fulgimide **1** in 70/30 ethanol-d_6/D_2O or in toluene-d_8 was illuminated with light that had passed through a hot mirror and a 405 nm bandpass filter until PSS was reached. A ^{1}H NMR spectrum was then acquired and integrated.

2.5. Photochemical stability

Air-saturated solutions of the *Z*-form of fulgimide **1** were prepared in toluene with an initial absorbance of approximately 0.6 at the absorption maxima. Samples were irradiated to the PSS with light supplied from an Oriel 1000 W Hg(Xe) lamp utilizing a water filter followed by a hot mirror followed by a 405 nm narrow bandpass filter. After measuring the UV–vis spectrum of the photostationary state, PSS$_{405\,nm}$, a pure *Z*-form solution was irradiated to 90% of the PSS and the reaction was timed. The 90% PSS mixture was then decolorized with >515 nm light using a separate filter and again the reaction was timed. Absorbance at the *C*-form λ_{max} was <0.01 upon decolorization. Once the duration of irradiation was established for both the 90% PSS coloration and <1% *C*-form decolorization 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$_{405\,nm}$ and their UV–vis spectra scanned. The photochemical fatigue was then determined by comparison with the initial PSS$_{405\,nm}$ absorption spectrum. The procedure was then repeated in 70/30 ethanol/water for **1** and **4** and in PMMA for **1**. The cycling times for **1** were approximately 50 s (*Z*–*C*) and 20 s (*C*–*Z*) in toluene, 90 s (*Z*–*C*) and 35 s (*C*–*Z*) in 70/30 ethanol/water, and 35 s (*Z*–*C*) and 20 s (*C*–*Z*) in PMMA. The photochemical stability was measured three times in toluene, ethanol/water, and PMMA.

2.6. Thermal stability

2.6.1. Polymer-based study

Thin films containing the *Z*-form of the fulgimide **1** were wrapped in aluminum foil and placed in an oven maintained at 80 °C. The films were removed at predetermined 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 (405 nm bandpass filter) until the PSS 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 predetermined intervals and their UV–vis spectra measured. The experiment was repeated three times.

2.6.2. Solution-based study

The thermal stability of the *Z*- and *C*-forms of fulgimide **1** in 70/30 ethanol/water and in toluene was measured using UV–vis and ^{1}H NMR spectroscopy. The *Z*-form solutions of fulgimide **1** were prepared in 70/30 ethanol/water and toluene, or their deuterated analogs and then transferred into several ampoules or NMR tubes, respectively. Ampoules and NMR tubes were sealed and submersed in water baths maintained at 50 °C (ethanol/water) or at 80 °C (toluene). At predetermined times ampoules and NMR tubes were removed and their contents analyzed by UV–vis and ^{1}H NMR spectroscopy, respectively. To determine the stability of

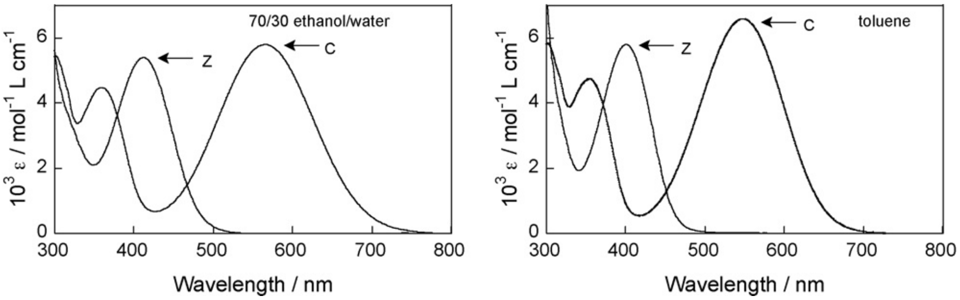


Fig. 1. UV–vis absorption spectra of fulgimide **1** in 70/30 ethanol/water and toluene.

the *C*-form in these solvents, fresh *Z*-form solutions were illuminated with blue light (405 nm bandpass filter) until the PSS was achieved. The thermal stability was then measured as described for the *Z*-form. A similar experiment was also performed with the *Z*-form of **4** in 70/30 ethanol/water. For ^{1}H NMR spectroscopy the residual solvent peak was used as an internal standard and signals corresponding to the individual species were integrated relative to the internal standard. A similar decomposition pathway to that reported for fluorinated indolylfulgides was assumed: Reversible *Z*- to *E*-isomerization followed by an irreversible 1,5-hydrogen shift to form an intermediate, which subsequently rearranged irreversibly to a mixture of two products [8,12]. Rate constants were determined by fitting the integrated peak areas from the ^{1}H NMR spectra acquired at various times to the kinetic scheme using least squares and Euler's method ($\Delta t = 1$ min) [8,12]. The reported rate constants are the average of three independent experiments with the corresponding errors.

3. Results and discussion

3.1. UV–vis absorption spectra

The UV–vis absorbance spectra of the open and closed forms of **1** acquired in 70/30 ethanol/water and in toluene are shown in Fig. 1. The ratio of 70/30 ethanol/water was selected to ensure adequate solubility of both forms and to allow comparison with previous results [18]. Both the open and closed forms showed bathochromic shifts as the solvent polarity increased. The absorbance maxima of the *Z*- and *C*-forms (also called the open and closed forms, respectively) increased by 12 and 17 nm. A slight drop in the extinction coefficients of the *Z*- and *C*-forms was observed in going from toluene to 70/30 ethanol/water (Table 1).

Interestingly, for the 2-indolylfulgimide, **2**, switching from toluene to methanol caused a bathochromic shift in the absorbance maxima of the closed form of 15 nm but not for the open form [21]. In the case of the *p*-substituted benzoic acid furylfulgimide derivative, **3**, the absorbance maxima of the closed form also exhibited a bathochromic shift of 22 nm in going from toluene to 50/50 ethanol/water [14]. A bathochromic shift of the closed form with increasing solvent polarity appears to be general and of similar magnitude for these fulgimides. Such a shift, however, is less general for the open form.

3.2. Thermal stability

The thermal stability of fulgimides in a variety of environments is important as it allows for their wider application. Switches that do not stay "on" or do not stay "off" as a result of slow thermal interconversion or decomposition are of less utility than those that stay "on" or "off." The thermal stability of both forms of **1** was determined in 70/30 ethanol/water, in toluene, and in thin films of poly(methyl methacrylate) (PMMA). The standard temperature for thermal stability is 80 °C for PMMA and toluene but due to the lower boiling point of ethanol, studies in ethanol/water were per-

Table 1
Extinction coefficients at λ_{max} for fulgimide **1** in 70/30 ethanol/water and in toluene

Medium	λ_{max}/nm (ε_{max}/mol^{-1} L cm^{-1})[a]		PSS$_{405\,nm}$
	Z-form	*C*-form	*C*:*Z*:*E*
70/30 Ethanol/water	412($5.4 \pm 0.2 \times 10^3$)	566 ($5.8 \pm 0.2 \times 10^3$)	76 : 19 : 5
Toluene	400($5.8 \pm 0.2 \times 10^3$)	549 ($6.6 \pm 0.2 \times 10^3$)	91 : 7 : 2

[a] Error is the standard deviation for three measurements.

Table 2
Thermal decomposition for fulgimide **1** in 70/30 ethanol/water, toluene, and PMMA

Medium	UV–vis[a]				^{1}H NMR[a]			
	Z-form		*C*-form		*Z*-form		*C*-form	
	A/*A*$_0$	%/day	*A*/*A*$_0$	%/day	[**1**]/[**1**]$_0$	%/day	[**1**]/[**1**]$_0$	%/day
Ethanol/water 70/30 (50 °C)[b]	0.78 ± 0.05	1.1	0.90 ± 0.01	0.5	0.74 ± 0.03	1.3	0.74 ± 0.03	1.2
Toluene (80 °C)[c]	0.57 ± 0.02	2.6	0.96 ± 0.01	0.2	0.03 ± 0.01	[d]	0.93 ± 0.02	0.5
PMMA (80 °C)[e]	0.62 ± 0.02	3.8	[f]	[f]	–	–	–	–

[a] Error is the standard deviation for three measurements.

[b] Absorbance at λ_{max} relative to initial absorbance after 500 h.

[c] Absorbance at λ_{max} relative to initial absorbance after 400 h.

[d] *Z*-form almost completely decomposed after 400 h, it decomposed 20% during the first day.

[e] Absorbance at λ_{max} relative to initial absorbance after 240 h.

[f] No decomposition observed after 240 h.

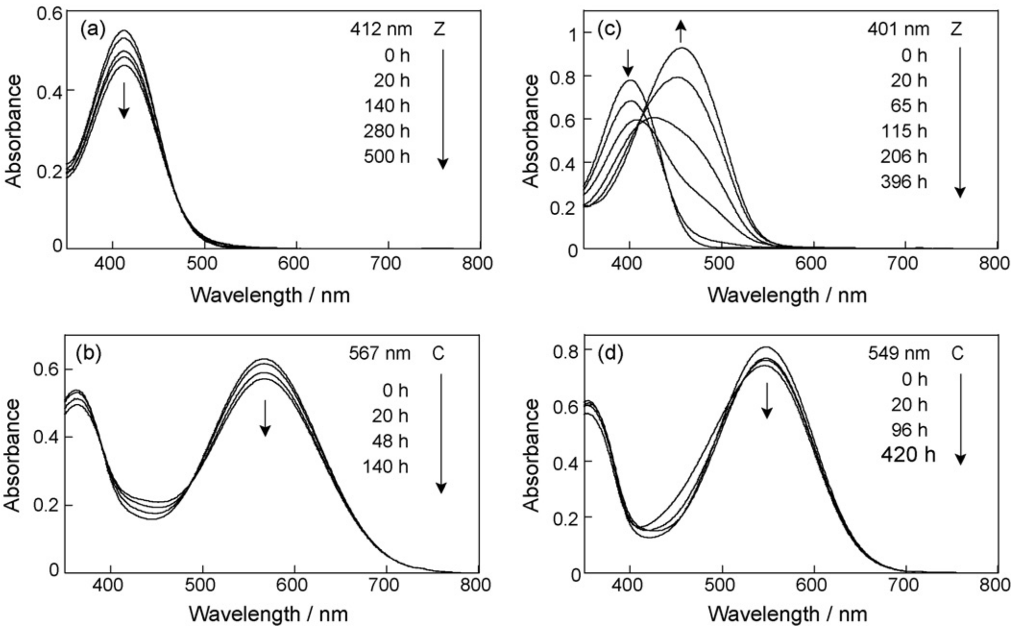


Fig. 2. Thermal decomposition of *Z*- and *C*-forms of fulgimide **1** in 70/30 ethanol/water at 50 °C (a and b) and in toluene at 80 °C (c and d). Arrows indicate the change in absorbance with time. After 140 h (b) spectra did not change.

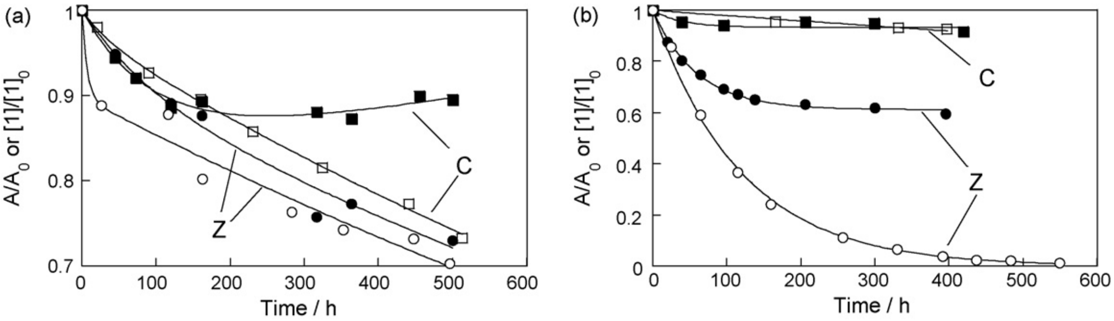
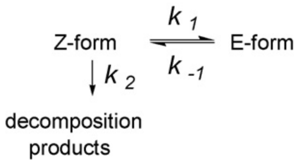


Fig. 3. Thermal decomposition of *Z*- (circles) and *C*-forms (squares) of fulgimide **1** as a function of time as measured by UV–vis spectroscopy (closed symbols) and NMR spectroscopy (open symbols) in 70/30 ethanol/water (a) at 50 °C and in toluene at 80 °C (b).

formed at 50 °C [14]. The thermal stability in solution was followed by both ^{1}H NMR spectroscopy and by UV–vis spectroscopy.

In 70/30 ethanol/water at 50 °C, both forms showed minimal loss in absorbance at the absorbance maxima after 21 days, 22 ± 5% for the *Z*-form and 10 ± 1% for the *C*-form (Fig. 2(a and b), Table 2). For comparison the *Z*-form of *N*-phenyl fulgimide, **4**, loses 52% of its absorbance after 21 days at 50 °C. Hydrolytic opening of the fulgimide ring would lead to a loss in absorbance at the absorbance maxima. Since the *C*-forms of fulgimides and fulgides were previously demonstrated to be hydrolytically less stable than the *Z*-forms at room temperature, we wanted to confirm the results with **1** [18]. The stability of both forms of fulgimide **1** was also followed by ^{1}H NMR spectroscopy in sealed tubes at 50 °C containing 70/30 ethanol-d_6/D_2O (Fig. 3, Table 2). After 21 days the *Z*- and *C*-forms had degraded by 26 ± 3%. The degradation rate constant for the *C*-form was obtained by fitting the curve to a first order decay, $0.8 \pm 0.1 \times 10^{-5}$ min^{-1}. In the case of the *Z*-form, the degradation rate constant was obtained by fitting the data after the first 120 h to a first order decay ($k_2 = 0.5 \pm 0.1 \times 10^{-5}$ min^{-1}). During the first 120 h the *Z*- and *E*-forms rapidly equilibrate ($k_1/k_{-1} = 0.12 \pm 0.02$). Degradation could be taking place from either the *E*- or *Z*-form since they are kinetically one species due to the rapid equilibration; however, for comparison, vide infra, we assume degradation takes place from the major *Z*-form (Scheme 3). The degradation rate of the *C*-form as determined by NMR is higher compared with UV–vis because presumably some of the decomposition products absorb at the absorbance maxima. Interestingly, both the *C*- and *Z*-forms have similar stabilities in 70/30 ethanol/water and are surprisingly robust.

In toluene at 80 °C, the *Z*-form and *C*-form decomposed 43 ± 2% and 4 ± 1% respectively, after 17 days according to absorbance measurements (Fig. 2(c and d), Table 2). According to ^{1}H NMR spectroscopy the *Z*-form decomposed 97 ± 1% and the *C*-form decomposed 7 ± 2% after 17 days at 80 °C in deuterated toluene (Fig. 3, Table 2). For fluorinated indolylfulgides the *Z*-form is normally the least stable of the two forms in toluene. The thermal decomposition pathway for fluorinated indolylfulgides in



Scheme 3. Kinetic scheme for thermal degradation.

toluene has been elucidated and involves either a reversible *Z*- to *E*-form isomerization or the conversion of the *Z*-form to an intermediate via a 1,5-hydrogen shift [8,12]. The intermediate subsequently rearranges to form a mixture of two isomers. Assuming a similar decomposition pathway for fulgimide **1**, the rate constant for the corresponding *Z*- to *E*-form isomerization would be $k_1 = 1.2 \pm 0.7 \times 10^{-5}\,\text{min}^{-1}$ in the forward direction and $k_{-1} = 5 \pm 5 \times 10^{-5}\,\text{min}^{-1}$ in the reverse direction (Scheme 3). These values are an order of magnitude less than those obtained for the corresponding fulgide, although the equilibrium constant is similar ($k_1/k_{-1} = 0.2 \pm 0.3$). The rate constant for the 1,5-hydrogen shift would be $k_2 = 14.3 \pm 0.6 \times 10^{-5}\,\text{min}^{-1}$, while for the corresponding fulgide the rate constant was $39 \times 10^{-5}\,\text{min}^{-1}$ [12]. Ultimately, the stability of the *Z*-form is less than the *C*-form in toluene at 80 °C.

In PMMA at 80 °C, the *Z*-form of fulgimide **1** decomposed 38 ± 2% after 10 days according to absorbance measurements (Fig. 4, Table 2). The *C*-form showed no decomposition after 10 days in PMMA at 80 °C (Table 2). Given the similarity in the changes of the absorbance spectra in toluene and PMMA for the *Z*-form at 80 °C, the decomposition pathways and rates are expected to be similar. In both toluene and PMMA at 80 °C the absorbance maxima at 401 or 405 nm respectively, decreases with time and a new absorbance maximum at approximately 450 nm appears, suggesting the same decomposition product. The rate of decomposition in PMMA appears to be somewhat slower than that in toluene as after 240 h the absorbance at 450 nm is not greater than the original absorbance at 405 nm as is the case in toluene. In addition, in PMMA an isosbestic point is observed, which suggests a two-state process and thus the intermediate observed in toluene is probably shorter lived in PMMA. Again, the stability of the *Z*-form is less than that of the *C*-form at 80 °C.

3.3. *Photochemical stability*

The photochemical stability of fulgides is important for their application as optical switches. Switches that can be turned “on” and “off” repeatedly are of more utility than those that can only be turned “on” and “off” once or twice. In toluene, fulgides can be switched back and forth over 10,000 times before degrading by 20% [12], although for most fulgides the number is less. The eight fluorinated indolylfulgimides previously tested cycled back and forth between 700 and 3000 times in toluene before degrading by 20% [18].

In solely protic solvents such as methanol, ethanol/water, or water, the number of times a fulgimide can cycle back and forth has been examined only in a limited number of cases [14,21]. Compound **1** degraded by 15% after 10 cycles in 50/50 ethanol/water and indolylfulgimides substituted at the 2-position of the indole ring were examined in methanol and water but their cyclicity was not determined due to the low closed to open form quantum yields of 0.003 or less [14,21]. Several reports demonstrating the application of fulgimides in aqueous biological systems have demonstrated that the fulgimides can be cycled back and forth once or twice [20]. The fluorinated indolylfulgimide **1** cycled back and forth 360 ± 20 times before degrading 20% in 70/30 ethanol/water while the fulgimide **4** cycled 170 times. In toluene and PMMA the corresponding numbers for **1** were 1000 ± 100 and 1700 ± 400 respectively (Fig. 5).

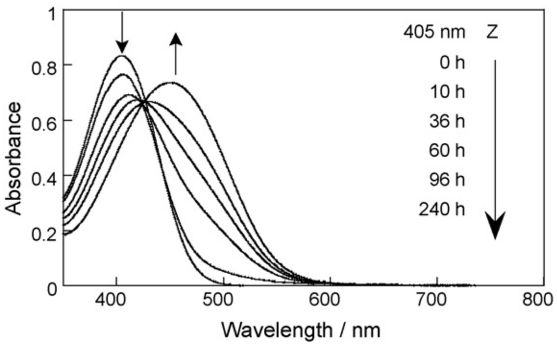


Fig. 4. Thermal decomposition of *Z*-form of fulgimide **1** in PMMA at 80 °C. Arrows indicate the change in absorbance with time.

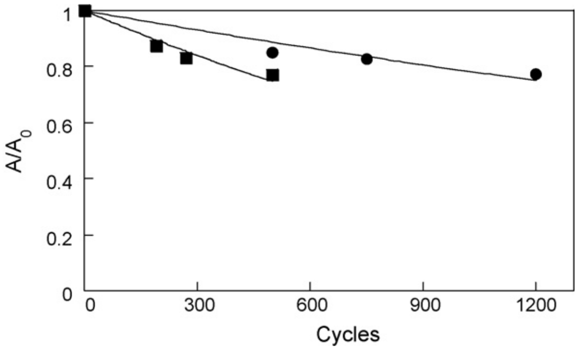


Fig. 5. Photochemical decomposition of fulgimide **1** in 70/30 ethanol/water (squares) and in toluene (circles). Decrease in absorbance with repeated coloration and decoloration cycles.

4. Conclusion

In summary, we synthesized a new fluorinated indolylfulgimide, **1** and determined its UV–vis absorbance spectra, extinction coefficient, and fatigue resistance in 70/30 ethanol/water and toluene. Furthermore, we studied the thermal stability of both the open and closed forms of **1** in 70/30 ethanol/water, toluene, and PMMA. According to UV–vis and ^{1}H NMR data, the *Z*- and *C*-forms of **1** are stable in 70/30 ethanol/water at 50 °C for 21 days degrading 22 and 10% (UV–vis) or 26 and 26% (NMR) respectively, while the *Z*-form of **4** degraded 52% (UV–vis). In toluene and PMMA the closed form is the most stable of the two forms. The fatigue resistance of compound **1** appears to be somewhat solvent dependent. Fulgimide **1** can be exposed to 360 photochemical cycles (coloration/decoloration) in 70/30 ethanol/water and to 1000 cycles in toluene before degrading by 20%. In comparison the *N*-phenyl indolylfulgimide **4** underwent 170 cycles in 70/30 ethanol/water. Ultimately, fulgimide **1** is a stable and efficient photochromic compound in protic and aprotic solvents.

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References

[1] Y. Yokoyama, Chem. Rev. 100 (2000) 1717.
[2] M.-G. Fan, L. Yu, W. Zhao, in: J.C. Crano, R.J. Guglielmetti (Eds.), Organic Photochromic and Thermochromic Compounds, vol. 1, Plenum Press, New York, 1999, pp. 140–206.
[3] H. Bouas-Laurent, H. Durr, Pure Appl. Chem. 73 (2001) 639.
[4] Y. Yokoyama, K. Takahashi, Chem. Lett. (1996) 1037.
[5] Y. Yokoyama, S. Uchida, Y. Yokoyama, Y. Sugawara, Y. Kurita, J. Am. Chem. Soc. 118 (1996) 3100.
[6] S. Uchida, Y. Yokoyama, J. Kiji, T. Okano, H. Kitamura, Bull. Chem. Soc. Jpn. 68 (1995) 2961.
[7] M.A. Wolak, N.B. Gillespie, C.J. Thomas, R.R. Birge, W.J. Lees, J. Photochem. Photobiol. A 144 (2001) 83.
[8] M.A. Wolak, J.M. Sullivan, C.J. Thomas, R.C. Finn, R.R. Birge, W.J. Lees, J. Org. Chem. 66 (2001) 4739.

[9] M.A. Wolak, N.B. Gillespie, C.J. Thomas, R.R. Birge, W.J. Lees, J. Photochem. Photobiol. A 147 (2002) 39.
[10] Y. Liang, A.S. Dvornikov, P.M. Rentzepis, J. Photochem. Photobiol. A 146 (2001) 83.
[11] Y. Liang, A.S. Dvornikov, P.M. Rentzepis, J. Photochem. Photobiol. A 125 (1999) 79.
[12] N.I. Islamova, X. Chen, S.P. Garcia, G. Guez, Y. Silva, W.J. Lees, J. Photochem. Photobiol. A 195 (2008) 228.
[13] M.A. Wolak, N.R. Gillespie, R.R. Birge, W.J. Lees, Chem. Comm. 8 (2003) 992.
[14] R. Matsushima, H. Sakaguchi, J. Photochem. Photobiol. A 108 (1997) 239.
[15] H.G. Heller, R.M. Megit, J. Chem. Soc. Perkin Trans. 1 (1974) 923.
[16] R.J. Hart, H.G. Heller, K. Salisbury, J. Chem. Soc. Chem. Comm. (1968) 1627.
[17] H.G. Heller, K. Koh, C. Elliot, J. Whittall, Mol. Cryst. Liq. Cryst. 246 (1994) 79.
[18] M.A. Wolak, C.J. Thomas, N.B. Gillespie, R.R. Birge, W.J. Lees, J. Org. Chem. 68 (2003) 319.
[19] I. Willner, S. Rubin, Angew. Chem. Int. Ed. Engl. 35 (1996) 367.
[20] I. Willner, S. Rubin, J. Wonner, F. Effenberger, P. Bauerle, J. Am. Chem. Soc. 114 (1992) 3150.
[21] M.W. Berns, T. Krasieva, C.-H. Sun, A. Dvornikov, P.M. Rentzepis, J. Photochem. Photobiol. B 75 (2004) 51.