

## Thermolysis of a Fluorinated Indolylfulgide Features a Novel 1,5-Indolyl Shift

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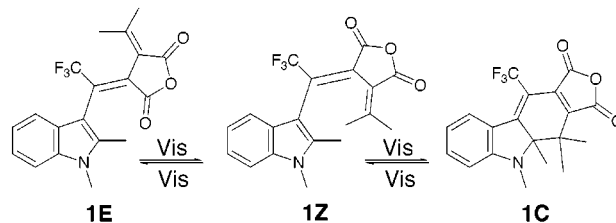
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Rewriteable optical memory devices present a powerful alternative to magnetic data storage.<sup>1,2</sup> One common approach to optical memory is to encode data in a binary system comprised of two distinct colored states of a photoactive organic material. Data are written and erased by wavelength-specific illumination, resulting in conversion between the two states, i.e., photochromism. Two promising classes of photoactive organic compounds are fulgides and diarylethenes.<sup>3,4</sup> In particular, fluorinated indolylfulgides meet many of the requirements for optical memory media including high resistance to photochemical degradation and efficient quantum yields for interconversion of **1Z** and **1C** (Scheme 1).<sup>5</sup> An additional requirement that is essential but poorly understood is thermal stability.

The importance of thermal stability should not be underestimated as present day commercial data storage materials such as magneto-optical drives, rewriteable CDs, and archival tapes are expected to maintain viability to at least 50 °C for prolonged times. Historically, fulgides featuring no hydrogen substituents on the newly formed ring in **1C** have been considered "thermally stable".<sup>2</sup> However, these *C*-form fulgides still decompose over hours to days at 80 °C in polymer films.<sup>6</sup> Even less has been reported about the stability of the *E*- and *Z*-forms.<sup>6b</sup> With few exceptions, the decomposition products or pathways of "thermally stable" fulgides are unknown.<sup>7,8</sup> For the most promising fluorinated indolylfulgides, we have found the *Z*-form to be the limiting factor in thermal stability as it decomposes more rapidly than the previously studied *C*-form.<sup>5</sup> Consequently, rational design of a more heat resistant fluorinated indolylfulgide is dependent upon elucidation of the thermal degradation mechanism for **1Z**.

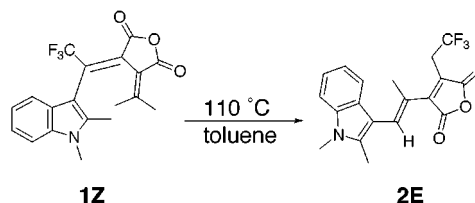
Exploration of the thermal stability of fluorinated indolylfulgide **1** began with isolation and characterization

### Scheme 1. Photochemical Reactions<sup>a</sup>

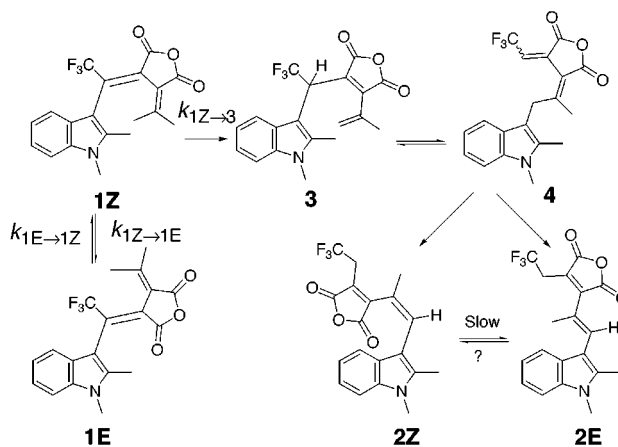


<sup>a</sup> *E* and *Z* nomenclature reflects standard IUPAC rules. For virtually all other fulgides, the *E* and *Z* labels are reversed.

### Scheme 2



### Scheme 3



of the major degradation product. Thermolysis of **1Z**<sup>9</sup> in refluxing toluene for 24 h affords **2E** in 75% yield (Scheme 2). On the basis of the crystal structure of **2E**, a mechanism for the thermal degradation of **1Z** is proposed (Scheme 3). Conversion of **1Z** to **2** involves an initial 1,5-hydrogen shift to form intermediate **3**, followed by a formal 1,5-indolyl migration and a final 1,5-hydrogen shift.

To test this mechanism, thermolysis of **1Z** was followed by UV–vis and <sup>1</sup>H NMR spectroscopies. A solution of **1Z** and 5-methoxy-2-methylindole (internal standard) was prepared in toluene-*d*<sub>8</sub>. The solution was divided into 0.80 mL portions, each of which were transferred to an ampule. Ampules were then sealed under vacuum and submersed in a constant-temperature bath at 80 °C.<sup>5,6</sup> At prescribed times an ampule was removed and its contents analyzed (Figures 1 and 2). Proton NMR resonances attributable to nearly each component of the proposed mechanism were observed and used for quantification. No <sup>1</sup>H NMR resonances assignable to **4** were observed, suggesting **4** is a short-lived intermediate. To

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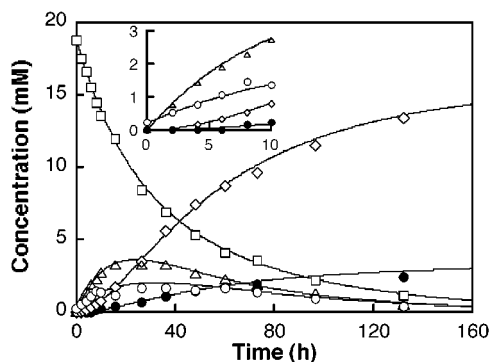
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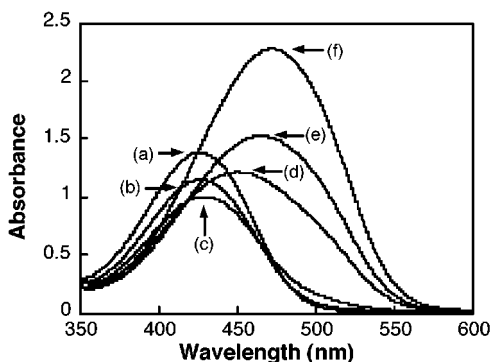
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**Figure 1.** Changing concentrations with time during thermolysis of **1Z** at 80 °C: **1Z** (squares), **1E** (open circles), **2Z** (filled circles), **2E** (diamonds), **3** (triangles). Rate constants were obtained by fitting the NMR data to the proposed kinetic scheme using numerical analysis, Euler's method ( $\Delta t = 1$  min):  $k_{1 \rightarrow 3} = 3.9 \times 10^{-4} \text{ min}^{-1}$ ,  $k_{1Z \rightarrow 1E} = 1.5 \times 10^{-4} \text{ min}^{-1}$ ,  $k_{1E \rightarrow 1Z} = 6 \times 10^{-4} \text{ min}^{-1}$ . Rate constants for conversion of **3** to **2E** and **2Z** were  $8.7 \times 10^{-4}$  and  $1.7 \times 10^{-4} \text{ min}^{-1}$  respectively.



**Figure 2.** Change of UV-vis spectra in toluene with time during the thermolysis of **1Z**: (a) 0, (b) 4, (c) 10, (d) 36, (e) 60, (f) 96 h.

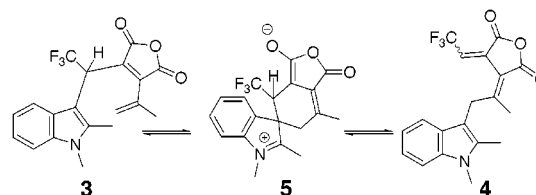
confirm the NMR assignments, compounds **1E**, **2Z**, and **3** were independently isolated and characterized. Control experiments demonstrated that oxygen, 5-methoxy-2-methylindole, or the initial concentration of **1Z** had no effect upon the reaction rate constants within experimental error. Thermolyses of **1E**, **2E**, and **3**; of the nonfluorinated analogue of **1**;<sup>10</sup> and of **1Z** in the presence of 0.05 equiv of *p*-TsOH were followed by <sup>1</sup>H NMR in a similar manner.

The NMR data obtained from the thermolysis reactions supports the proposed mechanism (Figure 1). A rapid initial conversion of **1Z** to **3** and a lag in the production of **2** was observed, suggesting that **1Z** is directly converted to **3** which is then converted to **2**. Furthermore, thermolysis of compound **3** showed no reversion to **1** and proved to rearrange to products **2E** and **2Z** with the same rate constants found in the initial study. Thermolysis of **1E** showed that the bulk, if not all, of **1E** decomposed via **1Z**. Thermolysis of **2Z** displayed slow thermal isomerization to **2E**: 5% in 24 h.

The UV-vis data is characterized by the lack of an isosbestic point and a red shift in the absorption maxima with time (Figure 2). As **1Z** and **1E** have similar spectra ( $\lambda_{\text{max}} = 427$  and 440 nm,  $\epsilon = 5300$  and  $5900 \text{ mol}^{-1} \text{ L}^{-1} \text{ cm}^{-1}$  in toluene, respectively), the absence of an isosbestic point

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#### Scheme 4



strongly suggests the presence of an intermediate. The shift in absorbance maxima coincides with generation of **2E** ( $\lambda_{\text{max}} = 476$  nm,  $\epsilon = 13\,000 \text{ mol}^{-1} \text{ L}^{-1} \text{ cm}^{-1}$  in toluene) and **2Z**. The red shift in  $\lambda_{\text{max}}$  for **2E** relative to **1Z** is due to increased conjugation between the indole and anhydride rings. Steric constraints inhibit coplanarity and limit conjugation of *E*- and *Z*-form indolyfulgides.<sup>11</sup>

The overall thermal stability of **1Z** is limited by a [1,5]-sigmatropic hydrogen shift that generates intermediate **3**. In contrast, a similar 1,5-hydrogen shift is not observed when the nonfluorinated analogue of **1Z** is heated to 80 °C for 48 h. The difference in stability is most likely due to destabilization of the olefin by the trifluoromethyl group. The trifluoromethyl substituent is known to destabilize ethylene by 6 kcal/mol relative to a methyl substituent.<sup>12</sup>

The formal 1,5-migration of the indolyl moiety presents an intriguing mechanistic challenge. Two possible scenarios are a concerted sigmatropic rearrangement or a stepwise process involving a Michael-type addition<sup>13</sup> followed by a retro-Michael reaction (Scheme 4). Since sigmatropic 1,5-aryl shifts have not been observed previously in acyclic systems,<sup>14</sup> the most likely explanation is the stepwise mechanism. However, addition of *p*-TsOH to the thermolysis reaction had little to no effect on any of the measured reaction rates with the exception of the **1Z** to **1E** isomerization. The addition of *p*-TsOH would be expected to catalyze the stepwise mechanism.<sup>15</sup> Therefore, if **4** is indeed involved it must be a relatively high energy intermediate, for it is not detected spectroscopically, and the rate-determining step in the conversion of **3** to **2** is the final 1,5-hydrogen shift.

In light of the mechanistic results, it is apparent that initial hydrogen migration from the isopropylidene group must be eliminated if a more thermally stable fluorinated fulgide is desired. Modification at this position should enhance the thermal stability of indolyfulgides while still maintaining the many propitious optical characteristics attributed to fluorination.

#### Experimental Section

**General Methods.** NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR samples were internally referenced to TMS (0.00 ppm). Purification of the thermolysis components was performed via flash chromatography with 230–400 mesh silica gel [10:1 hexanes/1,4-dioxane]. E&R Microanalytical Laboratory Inc. (Parsippany, NJ) performed all elemental analyses and the mass spectrum was

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obtained by the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign. Synthesis of **1Z** was accomplished in accordance with previous reports.<sup>9</sup>

**(Z)-CF<sub>3</sub>-indolyfulgide (1Z):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.37–7.11 (m, 4H), 3.71 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H), 0.97 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 161.8, 160.8, 159.7, 138.0, 136.9, 132.8 (q, *J*<sub>CCF</sub> = 36 Hz), 127.9, 124.6, 122.4, 122.0 (q, *J*<sub>CCF</sub> = 278 Hz), 121.3, 119.5, 119.4, 109.6, 106.9, 31.0, 26.7, 23.2, 12.2. Anal. Calcd for C<sub>19</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>3</sub>: C, 62.81; H, 4.44; F, 15.69; N, 3.86. Found: C, 62.58; H, 4.06; F, 15.52; N, 3.77.

**(E)-CF<sub>3</sub>-indolyfulgide (1E):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.46–7.10 (m, 4H), 3.75 (s, 3H), 2.49 (s, 3H), 2.37 (s, 3H), 2.28 (q, *J* = 2.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 162.2, 161.6, 160.3, 141.0, 137.0, 132.4 (q, *J*<sub>CCF</sub> = 35 Hz), 127.1, 126.7, 122.4, 123.1 (q, *J*<sub>CCF</sub> = 277 Hz), 121.9, 120.9, 119.6, 109.3, 103.8, 30.1, 26.6, 23.0, 11.5. Anal. Calcd for C<sub>19</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>3</sub>: C, 62.81; H, 4.44; F, 15.69; N, 3.86. Found: C, 62.75; H 4.54; F, 15.88; N, 3.77.

**Major degradation product (2E):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.84 (s, 1H), 7.44 (d, *J* = 6.9 Hz, 1 H), 7.34–7.11 (m, 3H), 3.75 (s, 3H), 3.61 (q, *J* = 9.8 Hz, 2H), 2.44 (s, 3H), 2.19 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 165.3, 164.1, 147.2, 138.7, 137.1, 136.6, 126.1, 124.8, 124.6 (q, *J*<sub>CCF</sub> = 278 Hz), 123.1, 121.8, 120.5, 119.9, 109.4, 109.3, 29.9, 29.8 (q, *J*<sub>CCF</sub> = 32 Hz), 18.3, 11.7. Anal. Calcd for C<sub>19</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>3</sub>: C, 62.81; H, 4.44; F, 15.69; N, 3.86. Found: C, 63.09; H, 4.49; F, 15.76; N, 3.83.

**Minor degradation product (2Z):** <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 7.10–6.97 (m, 3H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.61 (s, 1H), 2.64 (s, 3H), 2.22 (q, *J* = 10.2 Hz, 2H), 2.03 (s, 3H), 1.61 (s, 3H).

**Intermediate (3):** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.30–7.11 (m, 3H), 5.61 (s, 1H), 5.29 (s, 1H), 5.14 (q, *J* = 10.2 Hz, 1H), 3.69 (s, 3H), 2.46 (s, 3H), 2.40 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 163.2, 163.0, 146.9, 136.7, 136.6, 136.5, 133.5, 125.8, 125.1 (q, *J*<sub>CCF</sub> = 278 Hz), 123.5, 121.7, 120.2, 118.7, 109.1, 101.1, 40.2 (q, *J*<sub>CCF</sub> = 33 Hz), 29.9, 21.5, 10.9; HRMS (FAB) calcd for C<sub>19</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>3</sub> [M + H]<sup>+</sup> 364.1161, found 364.1161.

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**Supporting Information Available:** Crystallographic analysis of **2E**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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