Photochromic Fulgides: Transformation of the Non-photochromic (*Z*)-Isomer of a Fulgide into a Highly Photochromic (*E*)-Isomer *via* Structural Modification Involving Enhanced Conjugation

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The non-photochromic fulgide (**1-Z**) has been successfully converted into the highly photochromic (**3-Z**) analogue. A dicyanomethylene group was introduced at the 5-position of **1-Z** in order to enhance the latter's conjugation properties that would facilitate the photochemical **Z**→***E*** isomerization process. The irradiation of the product **3-Z** with a UV light at λ_{max} 350 nm formed a bluish green solution which absorbed at λ_{max} 620 nm, corresponding to the ring-closed product **4**. The latter was also formed from the reference dicyanomethylene product **3-*E*** synthesized from **1-*E***. The irradiation of **4** at λ_{max} 532 nm produced the reversion to the original pale yellow color of **3-*E***.

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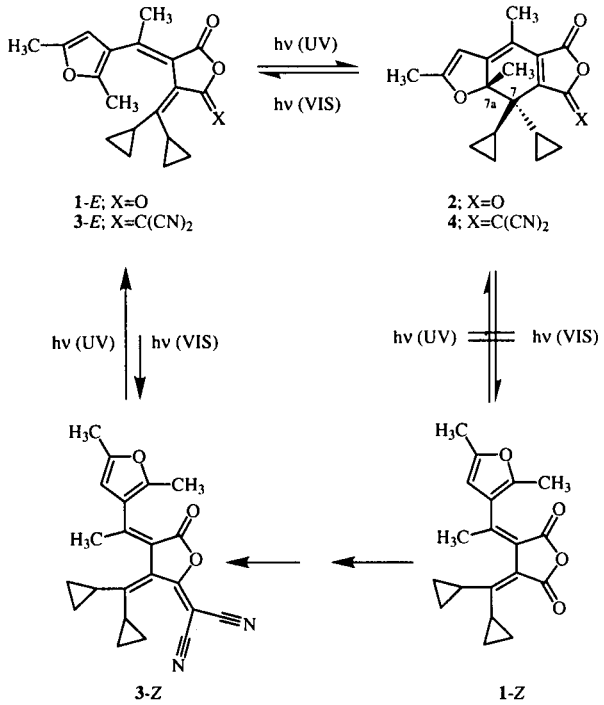
Introduction.

Fulgides are a class of organic compounds that undergo photochemically reversible color and structural changes, called photochromism [1,2]. This property has a number of practically beneficial applications including optical data storage, waveguides, holograms, photochromic lenses, integrated optics, sunlight attenuation, and sensor protection. We have recently reported [3] the synthesis of a mixture of two isomeric fulgides, **1-*E*** and **1-Z** (Scheme 1), but later discovered that while the mixture as a whole exhibits photochromism, it is only the **1-*E*** isomer in the mixture that is responsible for the observed photochromism. Thus, upon irradiation with a UV light, the nearly colorless **1-*E*** undergoes conrotatory electrocyclic ring-closure to form the colored cyclized product **2** which absorbs in the visible region. The colored product **2** reverts back to colorless **1-*E*** upon irradiation with a visible light. The **1-Z** isomer, on the other hand, is unable to cyclize under the same conditions, apparently because of its structural constraints for cyclization. We reasoned that the introduction of additional conjugation in the molecule would facilitate photochemical isomerization of the *Z* isomer into the required *E* form for cyclization with UV irradiation. We report herein the transformation of the totally non-photochromic **1-Z** into the highly photochromic **3-Z.** Compound **3-Z** apparently undergoes facile photochemical isomerization into the corresponding **3-*E*** which, in turn, undergoes reversible electrocyclic ring-closure to form **4**.

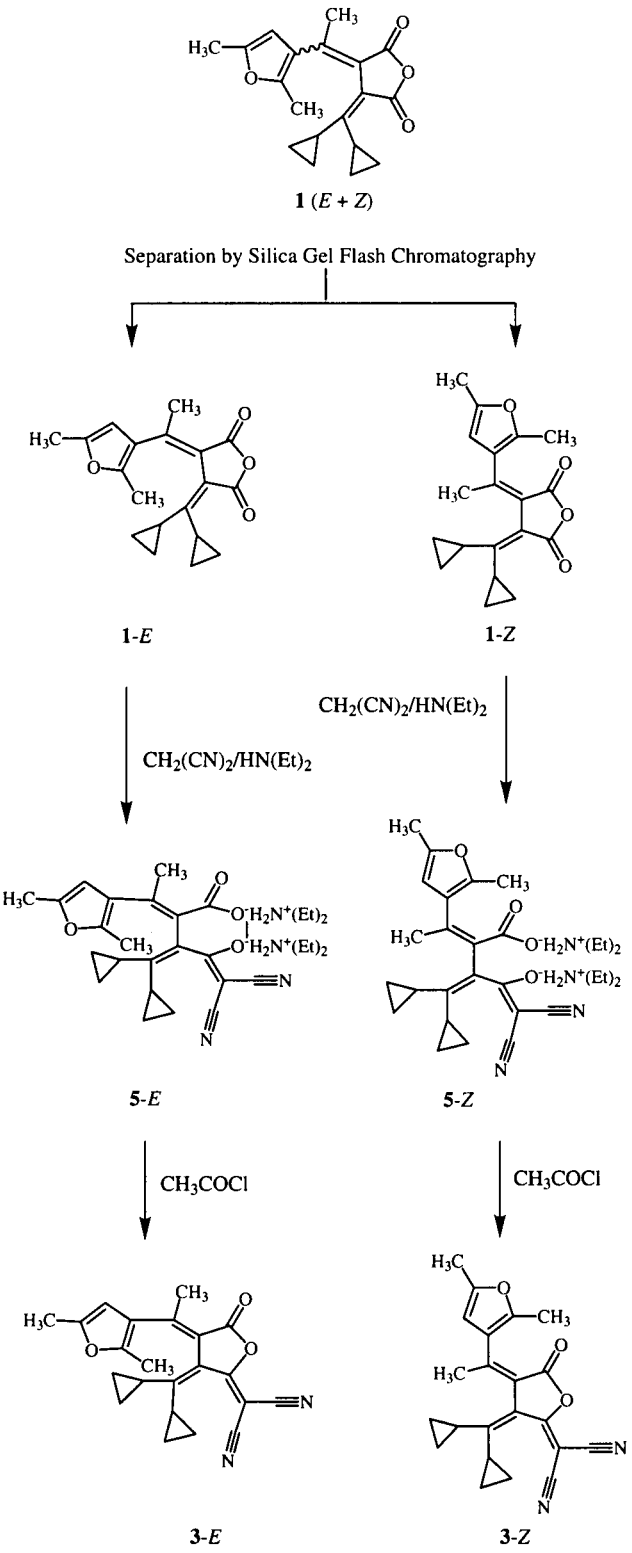
Scheme 1



Results and Discussion.

Compound **1** was obtained as a mixture of *E* and *Z* isomers (**1-*E*** + **1-Z**) as reported previously [3]. The mixture was separated on a silica gel column, using a mixture of ethyl acetate and petroleum ether (40-60 °C) (1:3), which afforded 55% *E* and 42% *Z* isomer. The two isomers could be easily distinguished by ^{1}H nmr. While the two furan methyl groups of the **1-*E*** isomer showed two distinct absorptions at δ 2.22 and 2.60 ppm, consistent with the relatively shielded environment of one methyl group relative to the other, both the furan methyl groups of

Scheme 2



the **1-Z** isomer, on the other hand, had nearly identical chemical shifts, δ 2.25 and 2.27 ppm, consistent with their nearly identical, relatively unshielded environments. Furthermore, the cyclopropyl proton absorptions of **1-Z** were, in general, relatively shifted downfield as compared to those of **1-E**, as anticipated, because of the relatively less steric crowding of the cyclopropyl groups in **1-Z**.

The isomers **1-E** and **1-Z** were separately reacted with a molar equivalent of malononitrile in the presence of two equivalents of diethylamine to yield the corresponding dicyanomethylidene derivatives as the bis-diethylammonium salts **5-E** and **5-Z**, respectively (Scheme 2). One of the carbonyl groups of the anhydride ring in **1-E** or **1-Z**, located at juxtaposition to the ethylidene moiety, is resonance-conjugated to the furan oxygen atom, and hence is relatively deactivated as compared with the other carbonyl. This results in a preferential nucleophilic attack of the malononitrile anion at the latter carbonyl. Since no external water was added, the observed ring opening of the anhydride ring to form the bis-oxyanionic salts must be due to the water molecule generated *in situ* upon reaction of malononitrile with the mentioned carbonyl group. The final ring-closure of **5-E** and **5-Z** to obtain **3-E** and **3-Z** was accomplished by reaction of each with acetyl chloride. Both **3-E** and **3-Z** were fully characterized by spectroscopic and microanalytical data. The cyclopropyl methylene protons in the ^{1}H nmr spectra of both **3-E** and **3-Z** were shifted considerably downfield as compared with those in **1-E** and **1-Z**, respectively due to the strong electron-withdrawing mesomeric effects of the neighboring dicyanomethylene functionalities. The two methyl groups attached to the furan ring of **3-E**, like those in **1-E**, showed two distinct methyl absorptions as singlets at δ 2.22 and 2.42, whereas the two furan methyl groups of **3-Z**, akin to **1-Z**, appeared as two overlapping singlets at δ 2.28.

Finally, The irradiation of a 10^{-4} *M* solution of **3-Z** with a uv light at λ_{max} 350 nm formed a bluish green solution which absorbed at λ_{max} 620 nm, corresponding to the ring-closed product **4** (see Scheme 1). The latter was also formed from **3-E** under the same conditions. The irradiation of the bluish green solution of **4** at λ_{max} 532 nm produced reversion to the original pale yellow color of **3-E**.

EXPERIMENTAL

The nmr spectra were recorded at 300 MHz. The data are reported in the following format: chemical shift (all relative to tetramethylsilane), multiplicity (s = singlet, d = doublet, dt = double triplet, dd = double doublet, t = triplet, q=quartet, m=multiplet, b=broad, coupling constants, integration and assignment). Elemental microanalyses were performed by Atlantic Microlab, Inc., Norcross, Georgia or the Research Institute of Elemento Organic Chemistry, Nankai University, P. R. China. Evaporations were done under reduced pressure on a rotary evaporator. Thin layer chromatography was performed on Merck Kieselgel 60 F_{254} (0.2 mm thickness). Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Dry solvents were prepared as follows: tetrahydrofuran was distilled over sodium and was stored over 3Å molecular sieves; acetonitrile was distilled from calcium hydride, followed by distillation from phosphorus pentoxide and stored over

3Å molecular sieves; methanol was distilled from calcium hydride and was stored over molecular sieves (type 3Å); methylene dichloride was distilled from calcium hydride and were stored over molecular sieves (type 3Å). All starting materials were purchased from Aldrich Chemical Co. All solvents were reagent grade and were purchased from VWR Scientific with the exception of ethyl acetate, which was purchased from Aldrich Chemical Co. All yields reported are for dry compounds that require no further purification for use in other reactions.

Separation of the Mixture of (*E*)- and (*Z*)-4-Dicyclopropylmethylene-3-[1-(2,5-dimethylfuryl)ethylidene]tetrahydrofuran-2,5-dione (**1-*E*** and **1-*Z***).

A mixture of (*E*)- and (*Z*)-4-dicyclopropylmethylene-3-[1-(2,5-dimethylfuryl)ethylidene]tetrahydrofuran-2,5-dione (**1-*E*** + **1-*Z***) [3] (1.7 g, 5.45 mmoles) was separated by flash chromatography on a silica gel column, using ethyl acetate: petroleum ether (bp 60-80 °C) (1:3) to yield 0.94 g (55.3%) of **1-*E*** and 0.72 g (42.3%) of **1-*Z***.

(*E*)-4-Dicyclopropylmethylene-3-[1-(2,5-dimethylfuryl)-ethylidene]tetrahydrofuran-2,5-dione (**1-*E***).

Pale red solid, mp 122-125 °C; ^{1}H nmr (deuteriochloroform): δ 0.26 (m, 1H, cyclopropyl H's), 0.39 (q, 2H, cyclopropyl H's), 0.58 (q, 2H, cyclopropyl H's), 0.90-1.04 (m, 4H, cyclopropyl H's), 2.07 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 5.90 (s, 1H, furan H).

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.25; H, 6.53.

(*Z*)-4-Dicyclopropylmethylene-3-[1-(2,5-dimethylfuryl)-ethylidene]tetrahydrofuran-2,5-dione (**1-*Z***).

Yellow solid, mp 144-148 °C; ^{1}H nmr (deuteriochloroform): δ 0.56 (br s, 2H, cyclopropyl H's), 0.85 (br s, 2H, cyclopropyl H's), 1.07-1.23 (m, 4H, cyclopropyl H's), 1.31 (m, 1H, cyclopropyl H), 2.16 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 3.18 (m, 1H, cyclopropyl H), 5.99 (s, 1H, furan H).

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.15; H, 6.34.

(*E*)-5-Dicyanomethylene-4-dicyclopropylmethylene-3-[1-(2,5-dimethylfuryl)ethylidene]tetrahydrofuran-2-one (**3-*E***).

A mixture of the above (*E*)-4-dicyclopropylmethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]tetrahydrofuran-2,5-dione (**1-*E***) (0.3 g, 1 mmole) and malononitrile (0.07 g, 1 mmole) was dissolved in tetrahydrofuran (5 ml), and stirred at room temperature for 5 minutes. Diethylamine (0.14 g, 2 mmoles) was added to the solution dropwise, and the mixture was stirred at room temperature for an hour, when a solid precipitate separated out of the solution. The white solid was filtered, washed with tetrahydrofuran (2 x 2 ml), and dried to collect **5-*E*** as a white solid, yield 0.4 g (76.3%), mp 138-139 °C (dec); ^{1}H nmr (deuteriochloroform): δ 0.18-1.16 (m, 10H, cyclopropyl H's), 1.30 (t, 12H, ethyl CH_3's), 2.16 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.97 (q, 8H, ethyl CH_2's), 6.16 (s, 1H, furan H), 7.52 (br s, 4H, NH_2's).

The above salt **5-*E*** (0.1 g, 0.19 mmole) was dissolved in dichloroethane (2 ml), and cooled to 0-5 °C. Acetyl chloride (2 ml) was added dropwise at 0-5 °C, and the resultant mixture was stirred at 5 °C for 1 hour. The solvent and excess acetyl chloride were removed under reduced pressure using a rotary evaporator at <30 °C. Methanol (3 ml) was added to the residue, and the mixture was stirred at room temperature for 5 minutes. The solid was filtered *in vacuo*, washed with methanol (1 ml), and dried to yield **3-*E*** as a yellow-green solid, yield 40 mg (58.5%), mp 143-145 °C; ^{1}H nmr (deuteriochloroform): δ 0.40 (m, 2H, cyclopropyl H's), 0.63 (br s, 2H, cyclopropyl H's), 1.03 (m, 4 H, cyclopropyl H's), 1.18 (m, 1H, cyclopropyl H), 2.11 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 3.0 (m, 1H, cyclopropyl H), 5.80 (s, 1H, furan H).

Anal. Calcd. for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.26; H, 5.58; N, 7.66.

(*Z*)-5-Dicyanomethylene-4-dicyclopropylmethylene-3-[1-(2,5-dimethylfuryl)ethylidene]tetrahydrofuran-2-one (**3-*Z***).

A mixture of the above (*Z*)-4-dicyclopropylmethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]tetrahydrofuran-2,5-dione (**1-*Z***) (0.3 g, 1 mmole) and malononitrile (0.07 g, 1 mmole) was dissolved in tetrahydrofuran (5 ml), and stirred at room temperature for 5 minutes. Diethylamine (0.14 g, 2 mmoles) was added to the solution dropwise, and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure. Petroleum ether (bp 60-80 °C) (5 ml) was added to the residue, and the mixture was stirred at room temperature for 10 minutes, when a solid separated out of the solution. The solid was filtered, washed with tetrahydrofuran (2 ml), and dried to yield **5-*Z*** as an off-white solid, yield 0.34 g (64.9%), mp 160-161 °C; ^{1}H nmr (deuteriochloroform): δ 0.20-1.70 (m, 10H, cyclopropyl H's), 1.19 (t, 12H, ethyl CH_3's), 2.08 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 3.09 (q, 8H, ethyl CH_2's), 5.90 (s, 1H, furan H), 7.52 (br s, 4H, NH_2's).

The above salt **5-*Z*** (0.1 g, 0.19 mmole) was dissolved in dichloroethane (2 ml), and cooled to 0-5 °C. Acetyl chloride (2 ml) was added dropwise at 0-5 °C, and the resultant mixture was stirred at 5 °C for 1 hour. The solvent and excess acetyl chloride were removed under reduced pressure using a rotary evaporator at <30 °C. Methanol (2 ml) was added to the residue, and the mixture was stirred at room temperature for 10 minutes. The solid was filtered *in vacuo*, washed with methanol (1 ml), and dried to yield **3-*Z*** as a yellow-green solid, yield 45 mg (65.5%), mp 164-165 °C (dec); ^{1}H nmr (deuteriochloroform): δ 0.67 (m, 2H, cyclopropyl H's), 1.17 (m, 6H, cyclopropyl H's), 1.83 (m, 2H, cyclopropyl H's), 2.23 (s, 3H, CH_3), 2.28 (s, 6H, 2 CH_3), 5.98 (s, 1H, furan H).

Anal. Calcd. for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.06; H, 5.45; N, 7.58.

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