Photochromism of Fulgides and Stereoelectronic Factors: Synthesis of (*E*)-4(3)-Adamantylidene-(5)-dicyanomethylene-3(4)-[1-(2,5-dimethylfuryl)ethylidene]tetrahydrofuran-2-one **4** and **4a** and (*E*)-4-Adamantylidene-3-[2,6-dimethyl-3,5-bis(*p*-diethylaminostyryl)benzylidene]tetrahydrofuran-2,5-dione **10**

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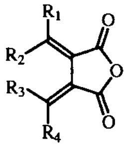
Received July 25, 1995
Revised August 18, 1995

In the search for fulgides with potential semiconductor laser compatibility, 4-adamantylidene-5-dicyanomethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]tetrahydrofuran-2-one (**4**), along with its regioisomer **4a**, have been synthesized from the corresponding fulgide **6** containing a succinic anhydride ring by reaction with malononitrile in the presence of diethylamine. Upon irradiation with a uv light at λ_{max} 350 nm, a mixture of **4** and **4a** revealed a considerably enhanced bathochromic shift to the visible region, λ_{max} 605 nm as compared with the starting fulgide **6** which, upon analogous uv irradiation, absorbed at λ_{max} 515 nm. In the search for semiconductor-laser-compatible fulgides with increased efficiency for the reverse bleaching reaction, another fulgide (*E*)-4-adamantylidene-3-[2,6-dimethyl-3,5-bis(*p*-diethylaminostyryl)-benzylidene]tetrahydrofuran-2,5-dione (**10**) was synthesized in seven steps starting from 2-bromo-*m*-xylene. However, **10** failed to undergo electrocyclic ring-closure upon irradiation with a uv light at λ_{max} 350 nm. The analogous fulgide **8**, which contains an isopropylidene functionality in place of the adamantyl group of **10**, was resynthesized for comparison, and showed two absorption maxima, one at 545 nm and the other at 620 nm. The missing physico-chemical data for **8** have also been provided.

J. Heterocyclic Chem., **32**, 1819 (1995).

Introduction.

Fulgides, represented by the general formula **1**, are derivatives of bis-alkylidenesuccinic anhydride which often exhibit photochromic properties. Photochromic fulgides undergo major color and structural changes upon irradiation with light of certain wavelengths, normally near the uv absorption maxima of fulgides. The products of irradiation revert back to the original structures and colors either thermally or photochemically upon irradiation with light of certain other wavelengths, usually near the absorption maxima of the products in the visible region. This unique characteristic of fulgides can be exploited in a number of important practical applications, including but not limited to, optical data storage, waveguides, holograms, photochromic lenses, integrated optics, sunlight attenuation, and sensor protection. Therefore, fulgides have continued to attract attention [1] both academically and commercially since they were first discovered and named (after 'fulgere' from Latin, meaning glisten and shine) by Stobbe [2] around the turn of the century.



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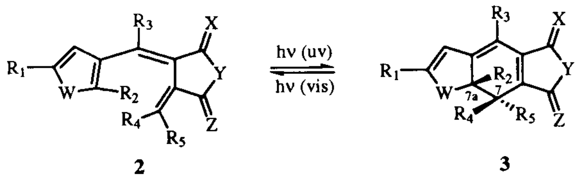
Photochromic compounds must satisfy the following performance criteria for optical recording on a write-read-erase disc: (a) the fatigue or the chemical instability upon repeated cycling should be minimum so as to afford maximum encoding/decoding repeatability, (b) the thermal stability or preservability of a colored or decolored state at room temperature must be excellent, (c) the sensitivity to long wavelength regions must be adequate so as to afford semiconductor laser compatibility, (d) the quantum efficiency for conversion of the colorless form to the colored form upon irradiation with ultraviolet light must be high, and (e) the quantum efficiency for bleaching when optical recording is carried out by visible light must be high.

There are several fulgides known to-date which meet the above criteria (a), (b), and (d), but very few, if any, adequately satisfy the requirements (c) and (e). The latter two criteria are especially important if optical decoding and encoding are to be performed in conjunction with semiconductor lasers. For a sufficiently high decoding (erasure) sensitivity, the colored products must exhibit absorbance in the long wavelength (visible) region. Likewise, since the rate at which information can be recorded is directly proportional to the rate of transformation of the colored form to the colorless (bleaching), a high quantum efficiency for bleaching would be necessary to attain high encoding sensitivity. We present here the results of our investigations directed at enhancement of these latter two properties, (c) and (e), of some photochromic fulgides that are already known to fulfill other requirements delineated in (a), (b), and (d).

Results and Discussion.

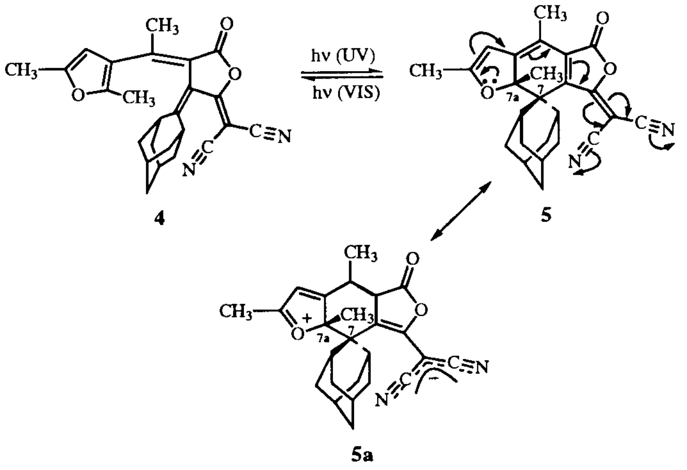
The pioneering work of Heller and coworkers [1b,c] has uncovered a series of photochromic fulgides that are thermally stable, fatigue-resistant, and practically colorless, and undergo near-quantitative conversion to their colored forms upon exposure to uv light [3]. With chronological improvement of photochemical properties, dictated by judicial structural modifications and molecular tailoring, Heller, *et al* [4-5] have come up with a number of near-perfect photochromic fulgides bearing the general structure **2** shown in Scheme 1. These compounds were shown to undergo reversible color change and conversion to the cyclized products **3** upon irradiation with a light of appropriate wavelength. They have further demonstrated that a simple replacement of an isopropylidene group of **2** ($R_4 = R_5 = Me$) with a bulky, rigid adamantylidene (**2**, R_4, R_5 = adamantyl) group markedly increases the quantum efficiency for bleaching (φ_b) by five- to tenfold without adversely affecting the thermal stability, fatigue resistance, or other photochemical properties. This has been attributed to the weakening of the 7-7a sigma bond in **3** because of back strain and steric interactions. As the adamantyl group has the chair conformation and hence is free of any angle or conformational strain, the fulgide **2** (R_4, R_5 = adamantyl) is thermally stable and photochemically fatigue-resistant. Furthermore, the quantum yield for coloring (φ_c) was only slightly reduced upon substitution of the adamantylidene group for the isopropylidene group. Nevertheless, while these adamantylidene fulgides (and fulgimides) adequately satisfy the aforementioned criterion (e), they nevertheless fall short of meeting the requirement (c) for long wavelength absorption that would accord them with semiconductor laser compatibility. These compounds only absorb in the region of λ_{max} 495-520 nm. Therefore, our first objective was to introduce an additional functional group that would cause further bathochromic shift in the uv absorption of the most promising fulgides represented by the general formula **2**. Reported here are the preparation and photochemical properties of 4-adamantylidene-5-dicyanomethylene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]tetrahydrofuran-2-one (**4**) (**2**, W = X = Y = O, Z = $C(CN)_2$, $R_1 = R_2 = R_3 = Me$, R_4, R_5 = adamantyl), along with its isomer **4a** (**2**, W = Y = Z = O, X = $C(CN)_2$, $R_1 = R_2 = R_3 = Me$, R_4, R_5 = adamantyl). The introduction of a dicyanomethylene group at the 5-position of the tetrahydrofuran ring of **4** would provide an extended conjugation in the cyclized product **5** (see Scheme 2). This conjugation would extend from the heteroatom of the 2,5-dimethylfuran ring at the one end to the nitrogen atoms of the nitrile groups at the other end, resulting in a resonance-delocalized species such as **5a**. The resonance stabilization of the colored form is believed to be partly responsible for the good thermal stabilities of fulgides.

Scheme 1



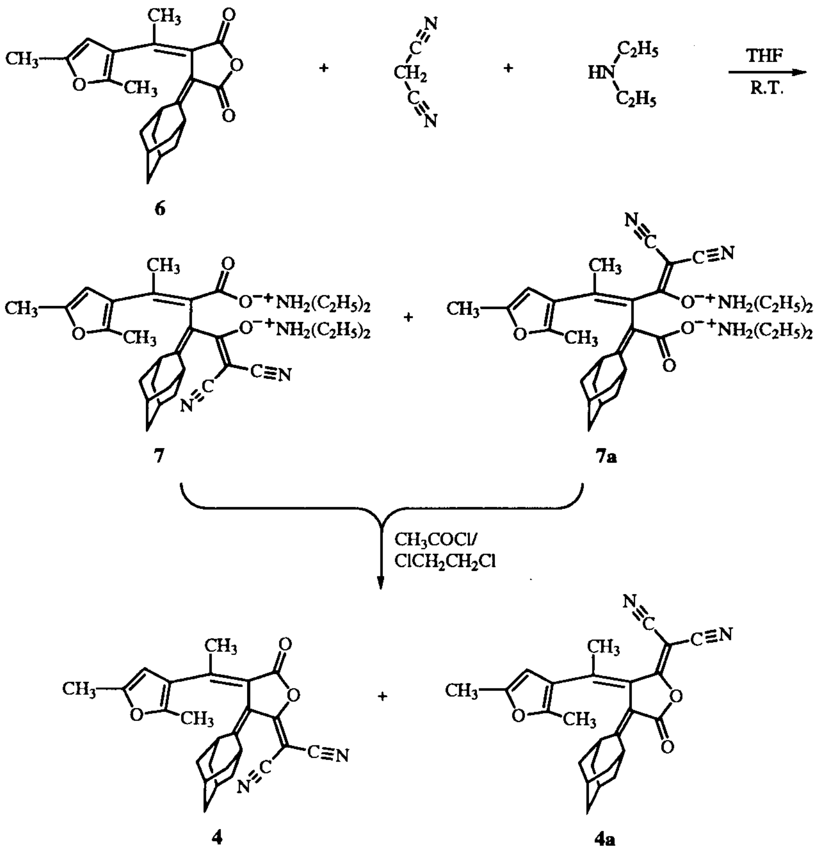
where, R_1, R_2, R_3 R_4, R_5 = alkyl, cycloalkyl, aryl, or aralkyl groups and W, X, Y, Z = O, S, or NR groups

Scheme 2



The fulgide **4** was prepared commencing with (*E*)-4-adamantylidene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]-tetrahydrofuran-2,5-dione (**6**) [5] (Scheme 3). The latter was reacted with malononitrile in the presence of diethylamine to give the bis-diethylammonium salt **7**, along with its isomer **7a**. The mixture of **7** and **7a** was reacted with acetyl chloride to provide a mixture of **4** and **4a**. The 300 MHz ^1H nmr spectrum of the latter mixture clearly indicated the presence of two isomers, one of which showed considerable downfield shift of its two methyl absorptions as compared with those of the other. The relatively downfield absorptions were assigned to the two methyl groups of **4a**, one from the ethylidene functionality and the other

Scheme 3



attached to the 2-position of the 2,5-dimethylfuran ring, as they are both conjugated to the electron-withdrawing nitriles of the dicyanomethylene group through resonance. Likewise, the two adamantylidene methine absorptions, corresponding to the two hydrogens on either side of the adamantylidene double bond, exhibited downfield shifts

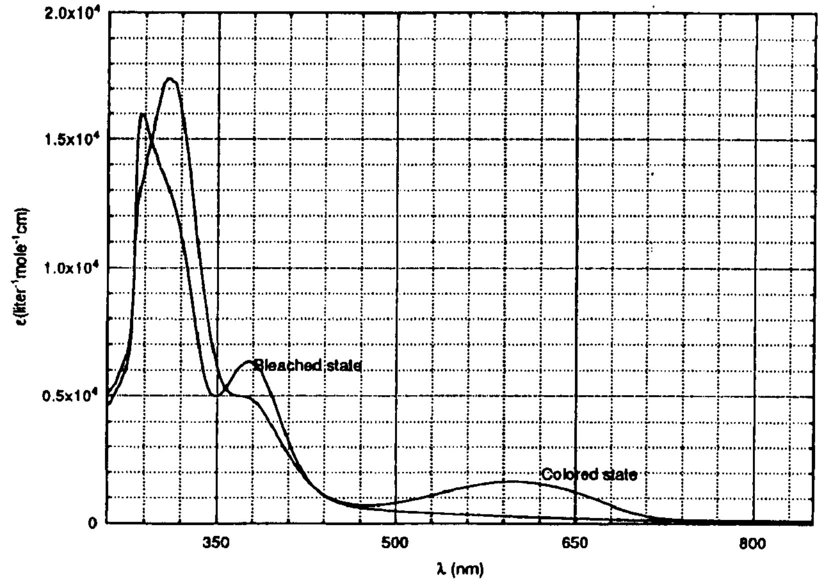


Figure 1. Absorption spectra of the bleached and colored forms of a mixture of fulgides **4** and **4a** in toluene (1.55 x 10^{-4} *M* solution).

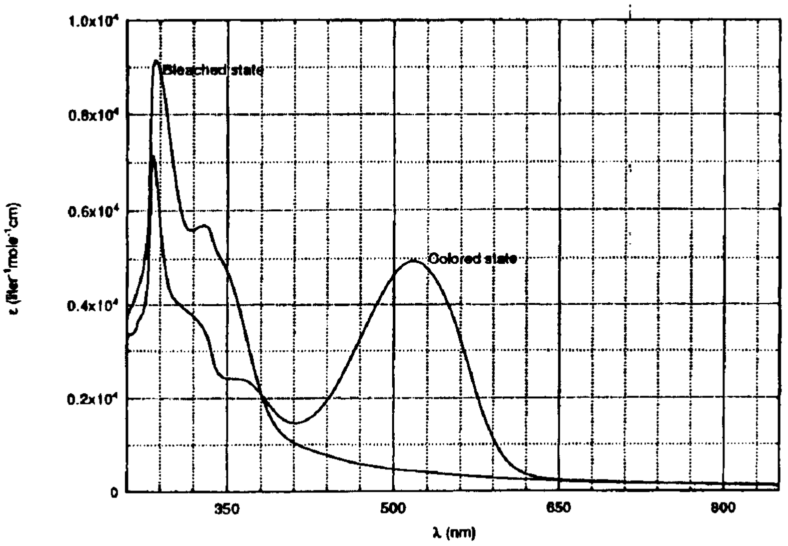


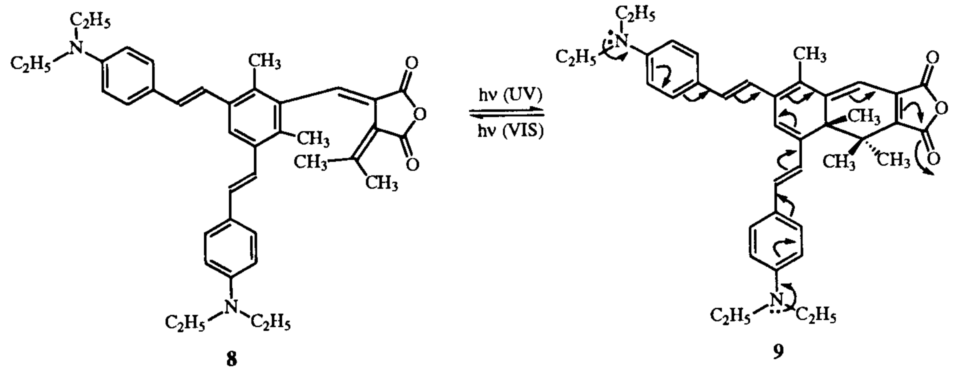
Figure 2. Absorption spectra of the bleached and colored forms of a solution of **6** in toluene (1.24 x 10^{-4} *M*).

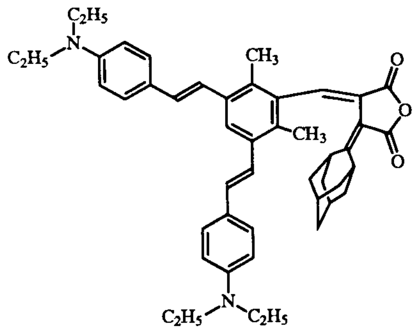
in one isomer as contrasted with those of the other. These relatively downfield methine absorptions were attributed to the isomer **4** because of the possibility of hyperconjugation of these hydrogens with the dicyanomethylene group in **4**, but not **4a**. No further attempts were, however, made to separate the two isomers from the mixture.

Upon irradiation at λ_{max} 350 nm, a 10^{-4} *M* solution of a mixture of **4** and **4a** in toluene revealed a marked bathochromic shift to the visible region with a λ_{max} = 605 nm (see Figure 1). By contrast, irradiation of a similar solution of **6** at 350 nm gave an absorption peak at λ_{max} = 515 nm (see Figure 2). It can be inferred, therefore, that the introduction of a dicyanomethylene group into the succinic anhydride ring of fulgide **6** results in a further bathochromic shift of ≈ 90 nm with respect to their respective colored forms.

Another fulgide that caught our attention in terms of its potential for semiconductor laser compatibility is compound **8** (Scheme 4) which has recently been reported by Tomoda, *et al* [6]. It was observed that the corresponding cyclized colored form **9**, formed upon irradiation of **8** with a uv light at λ_{max} 350 nm, exhibited a significant red shift to the near-infrared region at λ_{max} 633 nm with a high molar extinction coefficient. This has been attributed to the two strong electron-donating *p*-diethylaminostyryl substituents on the aromatic ring, which are completely conjugated to one of the carbonyl groups in the colored form **9** as shown. The major drawback of this fulgide system, however, is the poor quantum yield for the reverse bleaching reaction, which ranged only 2.8-5.2%. Therefore, our second objective was to compensate for this deficiency by replacing the isopropylidene group at the 4-position of the succinic anhydride ring of fulgide **8** with a bulky and rigid adamantylidene functionality. As stated earlier, the introduction of the adamantyl group, as in **10**, is anticipated to result in a high quantum efficiency for the bleaching reaction, which would satisfy the criterion (e) for semiconductor laser compatibility. The steric strain imposed by the bulky adamantyl group in the corresponding photo-cyclized form of **10** weakens the bond connecting the carbon bear-

Scheme 4





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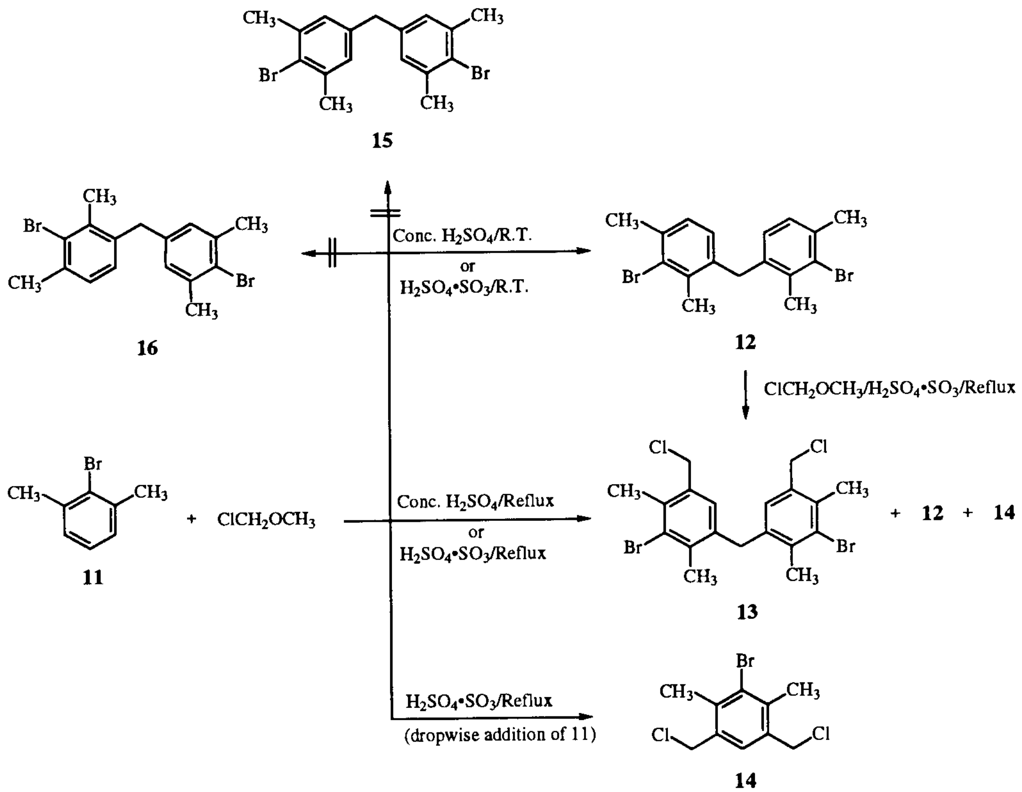
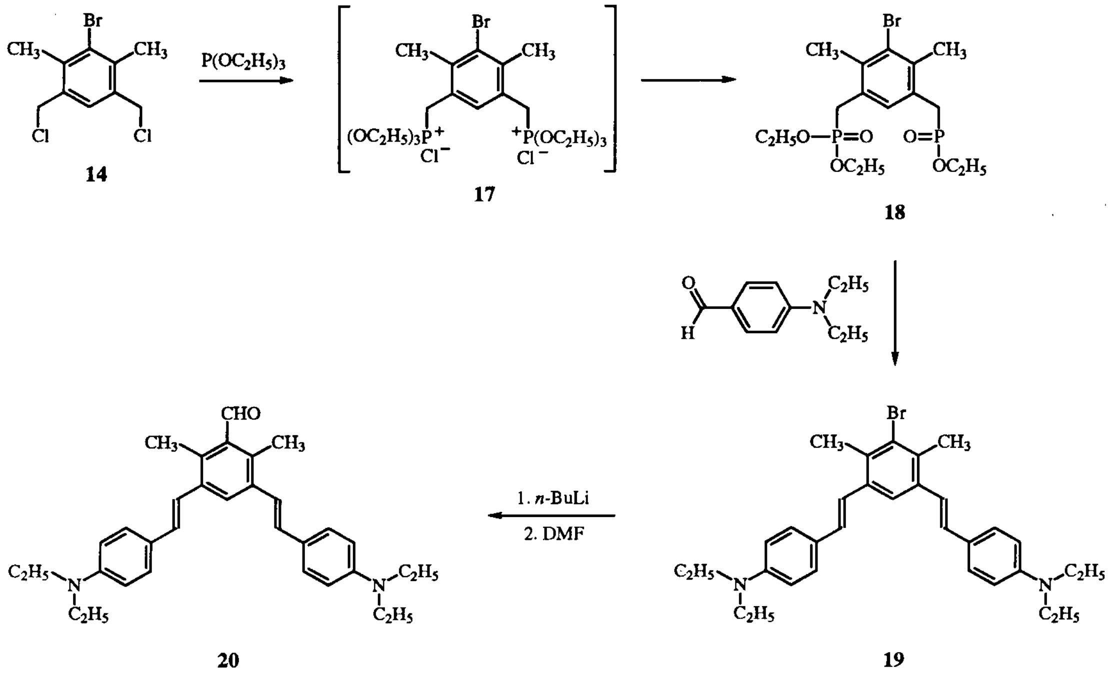
ing the adamantyl group to the carbon attached to the methyl group on the phenyl ring. Furthermore, the adamantyl group, which is virtually free of both angular and conformational strain, would be expected to exhibit a marked thermal stability as well as an ability to undergo a large number of color change cycles without substantial deterioration (*i.e.*, fatigue resistance). With this rationale, we set out to synthesize (*E*)-4-adamantylidene-3-[2,6-dimethyl-3,5-bis(*p*-diethylaminostyryl)benzylidene]tetrahydrofuran-2,5-dione (**10**). In addition, since neither the melting point nor the spectral data for **8** itself have been reported by Tomoda, *et al.* [6], we report here the synthesis and complete characterization of **8** as well.

The synthesis of **8** and **10** commenced with the common starting material, 2-bromo-*m*-xylene (**11**) (Scheme 5). The reaction of **11** with chloromethyl methyl ether in the presence of either concentrated sulfuric acid or fuming sulfuric acid at room temperature, employing the procedure of Tomoda, *et al.* [6], however, in our hands, yielded the dimeric products **12** instead of the desired product, 2-bromo-4,6-bis(chloromethyl)-*m*-xylene (**14**). Upon further heating with an excess of chloromethyl methyl ether at reflux, in the presence of fuming sulfuric acid, **12** was converted into **13**. Compound **13** was also obtained as a mixture with **12** and **14** by reaction of **11** with excess chloromethyl methyl ether under refluxing conditions in the presence of concentrated or fuming sulfuric acid. The ^1H nmr spectrum of **12** revealed two distinct sets of methyl groups, each integrating for 6 protons, and two sets of methine absorptions, each being a doublet integrating for two protons, with a coupling constant J = 7-8 Hz (*ortho* protons). This spectral data is consistent with structure **12**, and ruled out an alternative symmetrical structure **15** which would have exhibited a single absorption for all of the methyl groups, integrating for 12 protons, and a single absorption for the methine groups, integrating for 4 protons. Another possible structure **16** was also ruled out as it would have revealed three different methyl and methine absorptions. The ^1H nmr spectral data analogously enabled the structural assign-

Scheme 5



Scheme 6



ment of **13**. The formation of **12** can be explained by invoking the Friedel-Crafts reaction of **11** on the preformed monochloromethyl product of **11**, whereas **13** would be formed by further chloromethylation of **12**. Finally, the desired **14** was obtained as the sole product by dropwise addition of **11** to the refluxing mixture of chloromethyl methyl ether and fuming sulfuric acid. The ^{1}H nmr spectrum of **14** is consistent with the structure assigned.

Compound **14** was further condensed with triethyl phosphite to obtain the bis-diethyl phosphonate derivative **18** (Scheme 6). The Wittig reaction of **18** with *p*-diethylaminobenzaldehyde provided the bis-diethylaminostyryl derivative **19**. The latter was transformed into the aldehyde **20** by sequential reactions with *n*-butyllithium and dimethylformamide. Compound **20** served as the common starting material for the completion of synthesis of the target fulgides **8** and **10** (Scheme 7). The reaction of **20** with

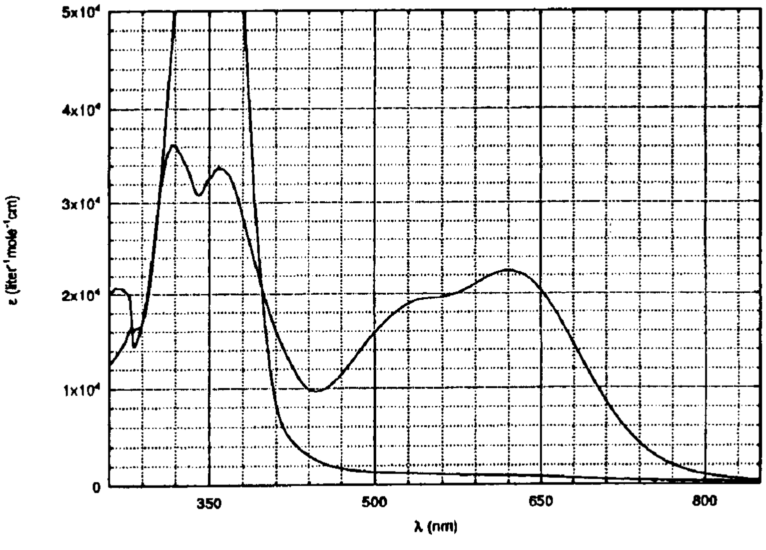
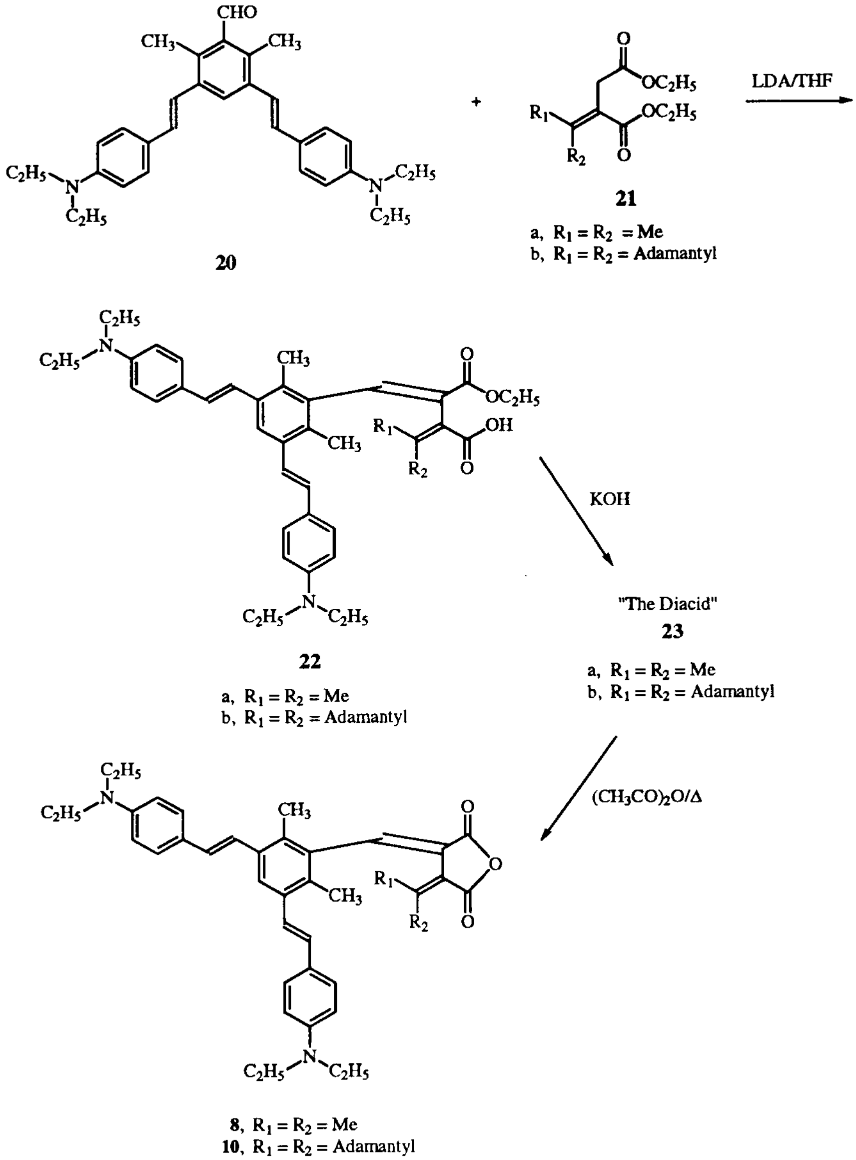


Figure 3. Absorption spectra of the bleached and colored forms of a solution of fulgide **8** in toluene (6 x 10^{-5} *M*).

Scheme 7



diethyl 2-isopropylidenesuccinate (**21a**) or dimethyl 2-adamantylidenesuccinate (**21b**) afforded the corresponding half esters **22a** or **22b**. Hydrolysis of **22a** or **22b** was carried out using alcoholic potassium hydroxide to yield the corresponding diacids **23a** and **23b**. The target anhydrides **8** and **10** were prepared by heating the respective diacids **23a** and **23b** in acetic anhydride at reflux. The structures of **8** and **10** were consistent with their respective ^{1}H nmr and microanalytical data.

Irradiation of a 10^{-5} *M* solution of **8** in toluene with a uv light at λ_{max} 350 nm gave an absorption spectrum with two λ_{max}'s in the visible region, one at 545 nm and the other at 620 nm (see Figure 3). On the other hand, the analogous irradiation of a 10^{-4} *M* solution of **10** in toluene resulted in no change in its absorption spectrum (see Figure 4). Apparently **10** fails to undergo photochemical electrocyclic ring-closure. We believe this is due to steric crowding of the bulky adamantyl group attached at the 4-position of the benzene ring during the photochemically-induced conrotatory electrocyclic ring-closure. The molecular modeling of **10** along with its expected cyclized product confirmed this notion.

Conclusions.

In the search for fulgides with suitable semiconductor laser compatibility, we have modified the promising fulgide **6** by introducing extended conjugation with a dicyanomethylene group at the carbonyl junction of the fulgide's anhydride ring. The resulting fulgide **4**, upon irradiation with a uv light, is transformed into a colored

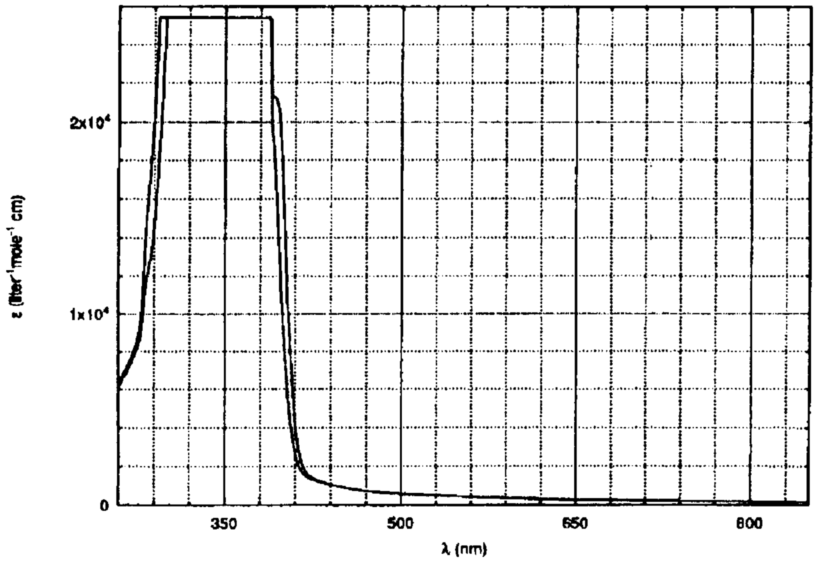


Figure 4. Absorption spectra of a solution of fulgide **10** in toluene (1.18 x 10^{-4} *M*) upon irradiation with lights in the uv and visible regions.

product which absorbs in the long wavelength visible region. The observed λ_{max} of 605 nm for the colored product **5** may still be somewhat low to afford adequate compatibility with semiconductor lasers, and so, it may be necessary to further extend the conjugation profile of the molecule, perhaps by introduction of suitable functional groups at the 5-position of the furan ring. Such an endeavor is currently in progress.

In order to increase the yield for the bleaching reaction of the colored cyclized product **9** of the promising laser-compatible fulgide **8**, the isopropylidene group of the latter was replaced with an adamantyl group to form the fulgide **10**. Unfortunately, fulgide **10** failed to undergo electrocyclic ring-closure upon irradiation with a uv light. A tentative explanation has been offered for the observed failure of ring-closure. In view of the lack of physicochemical data for **8** in the literature, it has been resynthesized and the missing spectral, physical, and analytical data have been provided.

EXPERIMENTAL

The nmr spectra were recorded at 300 MHz. The data are reported in the following format: Chemical shift (all relative to TMS), multiplicity (s = singlet, d = doublet, dt = double triplet, dd = double doublet, t = triplet, q = quartet, m = multiplet, b = broad, coupling constants, integration and assignment). The mass spectral analyses were performed by the Mass Spectral Facility, Department of Biochemistry, Michigan State University. Elemental microanalyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. 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); dimethylformamide and dimethyl sulfoxide were dried over calcium oxide (s) and then distilled at reduced pressure from calcium hydride and were subsequently stored over molecular sieves (type 3Å); methylene and ethylene dichloride were distilled from calcium hydride and were stored over molecular sieves (type 3Å); diethyl ether was distilled from sodium and benzophenone. 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.

(*E*)-4(3)-Adamantylidene-5-dicyanomethylene-3(4)-[1-(2,5-dimethylfuryl)ethylidene]tetrahydrofuran-2-one **4** and **4a**.

A mixture of (*E*)-4-adamantylidene-3-[1-(2,5-dimethyl-3-furyl)ethylidene]tetrahydrofuran-2,5-dione (**6**) [5] (0.9 g, 2.5 mmoles) and malononitrile (0.19 g, 2.5 mmoles) was dissolved in tetrahydrofuran (10 ml). Diethylamine (0.37 g, 5.0 mmoles) was added to the solution dropwise at room temperature, and the mixture was stirred 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 a mixture of **7** and **7a**, yield 0.95 g (67%), mp 130-132°; ^{1}H nmr (deuteriochloroform): δ 1.16-2.34 (m, 12 H, adamantyl H's), 1.42 (t, 12 H, 4 CH_3), 2.18 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 2.94 (br s, 1 H, adamantyl H), 3.13 (q, 8 H, CH_2), 3.47 (br s, 1 H, adamantyl H), 5.72 (s, 1 H, furan H), 8.95 (br s, 4 H, NH_2).

The above mixture of **7** + **7a** (0.57 g, 1.0 mmole) was added to a solution of acetyl chloride (8.0 ml) in ethylene dichloride (8.0 ml), and the resultant mixture was stirred at room temperature for 2.5 hours. The solvent was removed using a rotary evaporator, and the residue was triturated with 50 ml of methanol. The solid which separated was filtered *in vacuo*, washed with methanol, and dried to afford a mixture of **4** and **4a**, yield 310 mg (87%), mp 156-157°; ^{1}H nmr (deuteriochloroform): δ 1.60-2.05 (m, 24 H, adamantyl H's), 2.07 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.38 (br s, 1 H, adamantyl H), 2.68 (br s, 1 H, adamantyl H), 4.03 (br s, 1 H, adamantyl H), 4.16 (br s, 1 H, adamantyl H), 5.76 (s, 1 H, furan H), 5.84 (s, 1 H, furan H).

Anal. Calcd. for $C_{25}H_{24}N_2O_3$: C, 74.98; H, 6.04; N, 7.00. Found: C, 74.74; H, 6.05; N, 6.94.

Bis(3-bromo-2,4-dimethylphenyl)methane (**12**).

Method A.

A dry three-necked flask was charged with 2-bromo-*m*-xylene (3.9 g, 21 mmoles) and chloromethyl methyl ether (3.8 g, 47 mmoles). Concentrated sulfuric acid (98%) (1.25 g) was added dropwise at 5-10° with stirring. The mixture was stirred at room temperature overnight, and poured over crushed ice (5 g). The resulting oil was extracted with chloroform (2 x 5 ml), and the combined organic layer was washed with water and dried over anhydrous magnesium sulfate. The mixture was filtered and the filtrate was evaporated on a rotary evaporator to obtain a white solid. The solid was recrystallized from hexane, yield 1.8 g (45%), mp 95-96°; ^{1}H nmr (deuteriochloroform): δ 2.36 (s, 6 H, 2 CH_3), 2.41 (s, 6 H, 2 CH_3), 3.96 (s, 2 H, CH_2), 6.68 (d, J = 7.8 Hz, 2 H, 2 Ar-H's), 6.98 (d, J = 7.5 Hz, 2 H, 2 Ar-H's).

Method B.

A dry three-necked flask was charged with 2-bromo-*m*-xylene (0.8 g, 4.3 mmoles) and chloromethyl methyl ether (0.76 g, 9.4 mmoles). Fuming sulfuric acid (>20% sulfur trioxide) (0.25 g, ~2.5 mmoles) was added dropwise at -5° with stirring. The mixture was stirred at room temperature overnight, and poured over crushed ice (10 g). The resulting oil was washed with water, and recrystallized from hexane, yield 0.38 g (46%), mp 95-96°. The ^{1}H nmr spectral data of this compound was identical to that of **12** obtained by Method A above.

Bis(3-bromo-5-chloromethyl-2,4-dimethylphenyl)methane (**13**).

Method A.

A dry three-necked flask was charged with chloromethyl methyl ether (1.1 g, 14 mmoles) and compound **12** (0.38 g, 1.0 mmole). The reaction mixture was cooled to -5°, and fuming sulfuric acid (>20% sulfur trioxide) (0.2 g, ~2.0 mmoles) was added dropwise, and heated to reflux for 6 hours. After cooling, the reaction mixture was poured over crushed ice, and the solid separated was filtered and recrystallized from hexane, yield 0.28 g (59%), mp 151-153°; ^{1}H nmr (deuteriochloroform): δ 2.37 (s, 6 H, 2 CH_3), 2.53 (s, 6 H, 2 CH_3), 3.97 (s, 2 H, CH_2), 4.54 (s, 4 H, 2 CH_2Cl's), 6.75 (s, 2 H, 2 Ar-H's).

Anal. Calcd. for $C_{19}H_{20}Br_2Cl_2$: C, 47.63; H, 4.21; Br, 33.36; Cl, 14.80. Found: C, 47.75; H, 4.27; Br, 33.22; Cl, 14.74.

Method B.

A dry three-necked flask was charged with concentrated sulfuric acid (98%) (0.15 g, 1.5 mmoles) and chloromethyl methyl ether (0.8 g, 9.9 mmoles). The reaction mixture was heated to reflux, and 2-bromo-*m*-xylene (0.4 g, 2.2 mmoles) was added. The mixture was continued to reflux for an additional 3 hour period, and then poured over crushed ice. The resulting oil was extracted with chloroform, and the organic layer was washed with water, and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, the residue was purified by silica gel column chromatography, using a mixture of hexane:ethyl acetate (10:1) as an eluent. Appropriate fractions were pooled and evaporated to obtain **13** as a white solid which was recrystallized from hexane, yield 0.3 g (57%), mp 150-152°. The ^{1}H nmr spectral data of this compound was identical to that of **13** obtained by Method A above.

2-Bromo-4,6-bis(chloromethyl)-*m*-xylene (**14**).

Fuming (>20% sulfur trioxide) sulfuric acid (10.0 g, >0.1 mole) was placed in a dry three-necked flask. The flask was cooled in an ice-bath, and chloromethyl methyl ether (32.0 g, 0.4 mole) was added with stirring. After 10 minutes, the cold bath was removed, and the reaction mixture was allowed to heat to refluxing temperature. 2-Bromo-*m*-xylene (18.5 g, 0.1 mole) was added dropwise during a period of 2 hours, and the reaction mixture was heated at reflux for 6 hours, followed by stirring at room temperature overnight. Ice (20 g) was added with stirring, and the mixture was filtered, and the residue was washed with hexanes (2 x 10 ml). The solid was recrystallized with 200 ml of hexanes to obtain white needles of **14** (17.3 g, 62%), mp 104-106° (lit [6] 113-117°); ^{1}H nmr (deuteriochloroform): δ 2.52 (s, 6 H, 2 CH_3), 4.60 (s, 4 H, 2 CH_2), 7.23 (s, 1 H, Ar-H).

2-Bromo-4,6-bis(*O,O*-diethylphosphonylmethyl)-*m*-xylene (**18**).

A dry three-necked flask was charged with 2-bromo-4,6-dichloromethyl-*m*-xylene (17.0 g, 0.06 mole) and triethyl phosphite (26.0 g, 0.156 mole). The mixture was heated under nitrogen atmosphere in an oil-bath at 110-120° for 2 hours. The bath temperature was then raised to 130-135°, and the heating was continued for another 10 hours. The reaction mixture was cooled in an ice-bath, and washed with hexanes (3 x 25 ml). The residual oil was dissolved in ether (150 ml), washed with water (2 x 50 ml), and dried over anhydrous magnesium sulfate. Filtration and solvent evaporation under reduced pressure afforded **18** as a brown oil (24.2 g, 83%), which was directly employed in the next step.

2-Bromo-4,6-bis(*p*-diethylaminostyryl)-*m*-xylene (**19**).

A dry, 300 ml, three-necked flask was purged with dry nitrogen, and charged with sodium hydride (60% dispersion in mineral oil) (4.0 g, (0.1 mole) and dry tetrahydrofuran (100 ml). The mixture was stirred, and a solution containing **18** (24.0 g, 0.048 mole) and *p*-diethylaminobenzaldehyde (17.0 g, 0.09 mole) in dry tetrahydrofuran (20 ml) was added dropwise over a period of 1 hour. The reaction mixture was warmed to 60°, and stirred for 0.5 hour. When the evolution of gas ceased, the reaction mixture was heated to reflux for 0.5 hour. It was concentrated by removal of about 60 ml of tetrahydrofuran, and the concentrate was poured over crushed ice. The mixture was extracted with methylene chloride (3 x 80 ml), and the combined extracts dried over anhydrous magnesium sulfate. The filtration and solvent evaporation gave a solid which was recrystallized from benzene-ethanol to afford **19** as a yellow solid, yield 13.7 g (54%), mp 162-164° (lit [6] 154-156°); ^{1}H nmr (deuteriochloroform): δ 1.2 (t, J = 6.9 Hz, 12 H, 4 ethyl CH_3's), 2.52 (s, 6 H, 2 Ar-CH_3's), 3.42 (q, J = 6.9 Hz, 8 H, 4 ethyl CH_2's), 6.67 (d, J = 8.4 Hz, 4 H, Ar-H's), 6.89 (d, J = 15.9 Hz, 2 H, styryl CH), 7.11 (d, J = 15.9 Hz, 2 H, Styryl CH), 7.40 (d, J = 8.4 Hz, 4 H, Ar-H's), 7.64 (s, 1 H, Ar-H).

2,6-Dimethyl-3,5-bis(*p*-diethylaminostyryl)benzaldehyde (**20**).

A hexane solution (2.5 *M*) of butyllithium (12 ml, 0.03 mole) was added dropwise at -75°, under nitrogen atmosphere, to a solution of **19** (5.0 g, 0.0094 mole) in tetrahydrofuran (75 ml) over a period of 10 minutes. The mixture was stirred for 0.5 hour, and then 2.5 ml of dimethylformamide was added. The reaction mixture was further stirred for 4 hours at -75 to -20°, followed by 2 hours at room temperature. It was poured over 50 g of ice-water, and the oil separated was extracted with benzene (2 x 40 ml and 1 x 20 ml), and the combined extracts washed with water (3 x 30 ml) and dried over anhydrous magnesium sulfate. The filtration and evaporation of the solvent gave a yellow solid which was recrystallized from benzene-methanol (1:1, 100 ml) to obtain **20** as a pale yellow solid, yield 4.3 g (95%), mp 178-181° (lit [6] 168-169°); ^{1}H nmr (deuteriochloroform): δ 1.17 (t, 12 H, 4 ethyl CH_3's), 2.52 (s, 6 H, 2 Ar-CH_3's), 3.41 (q, 8 H, 4 ethyl CH_2's), 6.68 (d, J = 8.7 Hz, 4 H, Ar-H's), 6.92 (d, J = 15.9 Hz, 2 H, styryl CH), 7.10 (d, J = 15.9 Hz, 2 H, styryl CH), 7.42 (d, J = 8.7 Hz, 4 H, Ar-H's), 7.84 (s, 1 H, Ar-H), 10.66 (s, 1 H, CHO).

(*E*)-4-Isopropylidene-3-[2,6-dimethyl-3,5-bis(*p*-diethylaminostyryl)benzylidene]tetrahydrofuran-2,5-dione (**8**).

A hexane solution (2.5 *M*) of butyllithium (2.0 ml, 5.0 mmoles) was added dropwise at -75°, under nitrogen, to a solution of diisopropylamine (0.7 ml, 5.0 mmoles) and bipyridyl (5.0 mg) in tetrahydrofuran (50 ml). Diethyl 2-isopropylidenesuccinate (**21a**) [7] (0.5 g, 2.3 mmoles) was then added at -75°, and the mixture was stirred for 1 hour, followed by addition of the aldehyde **20** (1.0 g, 2.1 mmoles). The solution was warmed to room temperature over a 2 hour period, and further stirred for 1 hour. The reaction mixture was then poured over 30 g of ice-water, acidified with 6 *N* hydrochloric acid, and the *p*H was adjusted to 7-8 with a solution of sodium bicarbonate. The solution was extracted with ether (3 x 25 ml), and the combined extracts dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give 1.5 g of **22a** as a yellow solid.

The above half-ester **22a** was mixed with potassium hydroxide (1.18 g), ethanol (2.0 ml), and 2-propanol (9.0 ml), and the mixture was heated to reflux for 3 hours. It was poured over 20 g of ice-water, and the mixture was extracted with chloroform (3 x 15 ml). The combined extracts were dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated on a rotary evaporator to yield 1.0 g of the dicarboxylic acid **23a**.

The above diacid **23a** (0.5 g) was mixed with acetic anhydride (10 ml), and the mixture heated to reflux for 1 hour. The mixture was evaporated on a rotary evaporator under reduced pressure, and the residue was dissolved in 10 ml of chloroform, followed by addition of 20 ml of hexanes. The mixture was heated at 50° for 2 minutes, the supernatent solution was separated and allowed to stand at room temperature for 0.5 hour when the crystals of **8** formed, yield 0.1 g (20% overall, starting from **20**), mp 194-196°; ^{1}H nmr (deuteriochloroform): δ 1.21 (t, 12 H, 4 ethyl CH_3's), 2.22 (s, 6 H, 2 Ar-CH_3's), 2.39 (s, 3 H, isopropylidene CH_3), 2.61 (s, 3 H, isopropylidene CH_3), 3.40 (q, 8 H, 4 ethyl CH_2's), 6.67 (d, J = 8.1 Hz, 4 H, Ar-H's), 6.94 (d, J = 15.9 Hz, 2 H, styryl CH), 7.11 (d, J = 15.9 Hz, 2 H, styryl CH), 7.41 (d, J = 8.1 Hz, 4 H, Ar-H's), 7.50 (s, 1 H, olefinic CH), 7.75 (s, 1 H, Ar-H).

Anal. Calcd. for $C_{40}H_{46}N_2O_3 \cdot H_2O$: C, 77.39; H, 7.79; N, 4.51. Found: C, 77.53; H, 7.61; N, 4.60.

(*E*)-4-Adamantylidene-3-[2,6-dimethyl-3,5-bis(*p*-diethylaminostyryl)benzylidene]tetrahydrofuran-2,5-dione (**10**).

A hexane solution (1.6 *M*) of butyllithium (1.0 ml, 1.6 mmoles) was added dropwise at -10°, under nitrogen, to a solution of diisopropylamine (0.28 ml, 2.0 mmoles) and bipyridal (2.0 mg) in tetrahydrofuran (20 ml). Dimethyl 2-adamantylidenesuccinate (**21b**) [5] (0.33 g, 1.2 mmoles) was then added at -78°, and the mixture was stirred for 2 hours at the same temperature, followed by addition of the aldehyde **20** (0.5 g, 1.04 mmoles). The reaction mixture was stirred at -78° for an additional 3 hour period, and further stirred at room temperature for 16 hours. The reaction mixture was then poured over 40 g of ice-water, acidified with 6 *N* hydrochloric acid, and the *p*H was adjusted to 5-6 with a solution of sodium bicarbonate. The solution was extracted with ether (3 x 15 ml), and the combined extracts dried over anhydrous magnesium sulfate. After filtration, the solvent was removed under reduced pressure to give 0.7 g of **22b** as a yellow solid.

The above half-ester **22b** was mixed with potassium hydroxide (1.0 g) and ethanol (13.0 ml), and the mixture was heated to reflux for 3.5 hours. It was cooled to room temperature, 15 ml of ice-water was added, and the *p*H adjusted to 5-6. The mixture was extracted with ether (3 x 15 ml). The combined extracts were dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated on a rotary evaporator to yield 0.8 g of the dicarboxylic acid **23b**.

The above diacid **23b** (0.8 g) was mixed with acetic anhydride (20 ml), and the mixture was heated to reflux for 0.5 hour. After removing the solvent, the residue was purified by silica gel chromatography, using a mixture of petroleum ether (bp 40-60°):ethyl acetate (5:1) as an eluting solvent. The appropriate fractions were pooled and evaporated to obtain **10** as a yellow solid, yield 0.27 g (37% overall, starting from **20**), mp 140-142°; ^{1}H nmr (deuteriochloroform): δ 1.21 (t, 12 H, 4 ethyl CH_3's), 1.57 (s, 3 H, CH_3), 2.00-2.17 (m, 12 H, adamantyl H's), 2.28 (s, 3 H, CH_3), 3.40 (q, 8 H, 4 ethyl CH_2's), 3.57 (br s, 1 H, adamantyl H), 4.50 (br s, 1 H, adamantyl H), 6.68 (d, J = 7.8 Hz, 4 H, Ar-H's), 6.94 (d, J = 15.9 Hz, 2 H, styryl CH), 7.11 (d, J = 16.2 Hz, 2 H, styryl CH), 7.68 (s, 1 H, olefinic CH), 7.42 (d, J = 8.4 Hz, 4 H, Ar-H's), 7.75 (s, 1 H, Ar-H).

Anal. Calcd. for $C_{47}H_{54}N_2O_3 \cdot H_2O$: C, 79.17; H, 7.92; N, 3.93. Found: C, 79.49; H, 7.91; N, 3.88.

Acknowledgments.

This research was supported by grants from the Martin Marietta Technologies, Inc. and the Maryland Industrial Partnerships program (# 1307.13). Mass spectral data were obtained at the Michigan State University Mass Spectrometry Facility which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health.

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