Synthesis and photochromism of functionalized benzothiophene-based fulgides and fulgimides

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Earlier unknown fulgides and the corresponding functionalized fulgimides containing a primary amino group were obtained. Their photochromism was examined using spectroscopic methods.

Key words: benzothiophenes, Stobbe condensation, fulgides, fulgimides, photochromism.

Photochromic fulgides and fulgimides have high fatigue resistances and are thermally and chemically stable in both open and closed forms. These properties make them convenient materials for designing optical storage devices, molecular switches, dynamic chemosensors and biosensors, and biological activity controllers.[1—4]

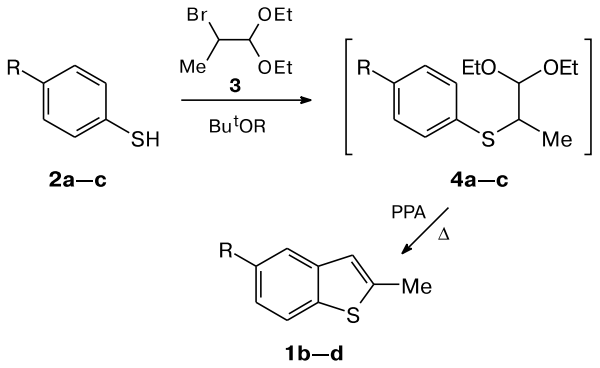
In the literature, this class of photochromic compounds is mainly represented by thiophene, furan, and indole derivatives. It should be noted that only two fulgides with an unsubstituted benzothiophene fragment have been described to date,[5,6] while their analogs with a substituted benzene ring have not been documented at all.

The goal of the present work was to develop methods for the synthesis of (1) photochromic fulgides containing a 5-substituted benzothiophene fragment and (2) the corresponding fulgimides with an unsubstituted primary amino group and to examine their photochromic characteristics. The presence of the reactive functional group enables the fulgimides obtained to be modified or be introduced as a photochromic fragment into other compounds, which extends the area of application of these photochromes.

Results and Discussion

Earlier unknown fulgides and fulgimides were obtained from various 2-methylbenzo[*b*]thiophenes. For instance, 2-methylbenzo[*b*]thiophene (**1a**) was prepared by lithiation of commercial benzothiophene followed by alkylation with dimethyl sulfate according to a known procedure.[7] 5-Substituted 2-methylbenzo[*b*]thiophenes **1b—d** were prepared by reactions of appropriate benzenethiols **2a—c** with 2-bromo-1,1-diethoxypropane (**3**) followed by thermal cyclization of intermediate sulfides **4a—c** in polyphosphoric acid (Scheme 1). The yields of 2-methylbenzo[*b*]thiophenes **1b—d** range from 54 to 69% with respect to the starting mercaptans.

Scheme 1



R = Me (**1b**, **2a**, **4a**), Cl (**1c**, **2b**, **4b**), Br (**1d**, **2c**, **4c**)

The Friedel—Crafts acylation of compounds **1a—d** with acetyl chloride gave 3-acetyl-2-methylbenzo[*b*]thiophenes **5a—d** (Scheme 2). Ketones **5a—c** were used in the Stobbe condensation with diethyl isopropylidenesuccinate **6**.[6] Treatment of the reaction mixture (without isolation or purification of intermediate fulgenates **7a—c** and the corresponding fulgenic acids **8a—c**) with acetyl chloride afforded benzothienylfulgides **9a—c** in 11—19% yields with respect to the corresponding 3-acetylbenzothiophenes (see Scheme 2).

Unlike fulgide **9c**, its bromo analog was not obtained because the Stobbe condensation of 5-bromo-2-methylbenzo[*b*]thiophene **1d** produces a complex mixture of products. The structures of fulgides **9a—c** were confirmed by ^{1}H NMR and mass spectra and elemental analysis data. The ^{1}H NMR spectra show singlets for the methyl groups at δ_H 2.15—2.51 and signals for the aromatic protons of the benzothiophene fragment at δ_H 7.11—7.68.

Fulgides **9a—c** were used in reactions with *N*-Boc-1,4-phenylenediamine **10** as described earlier[8] (Scheme 3).

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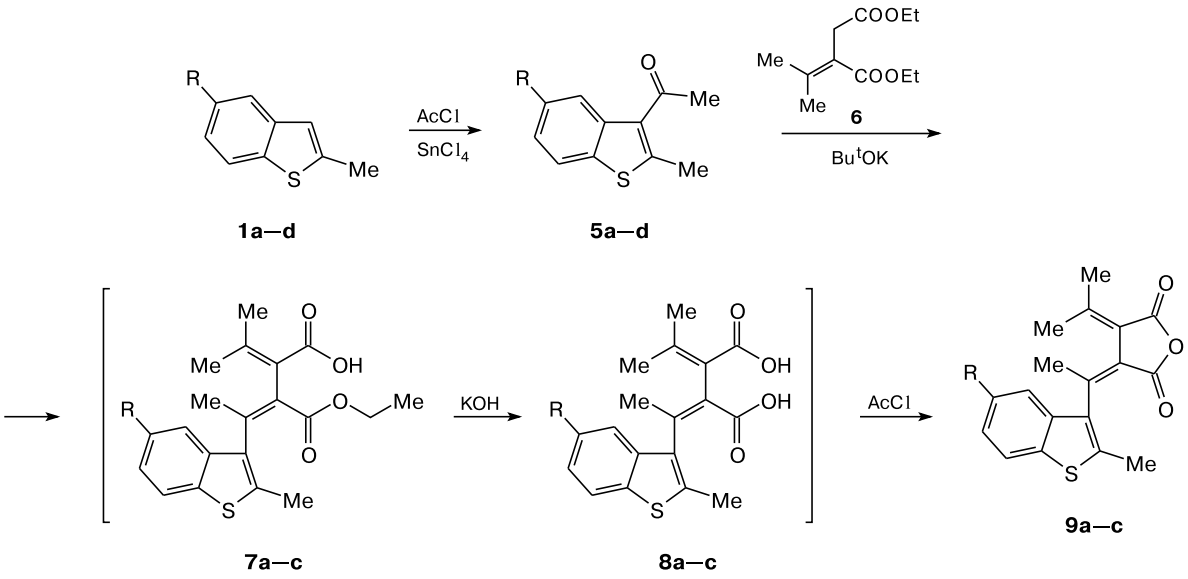
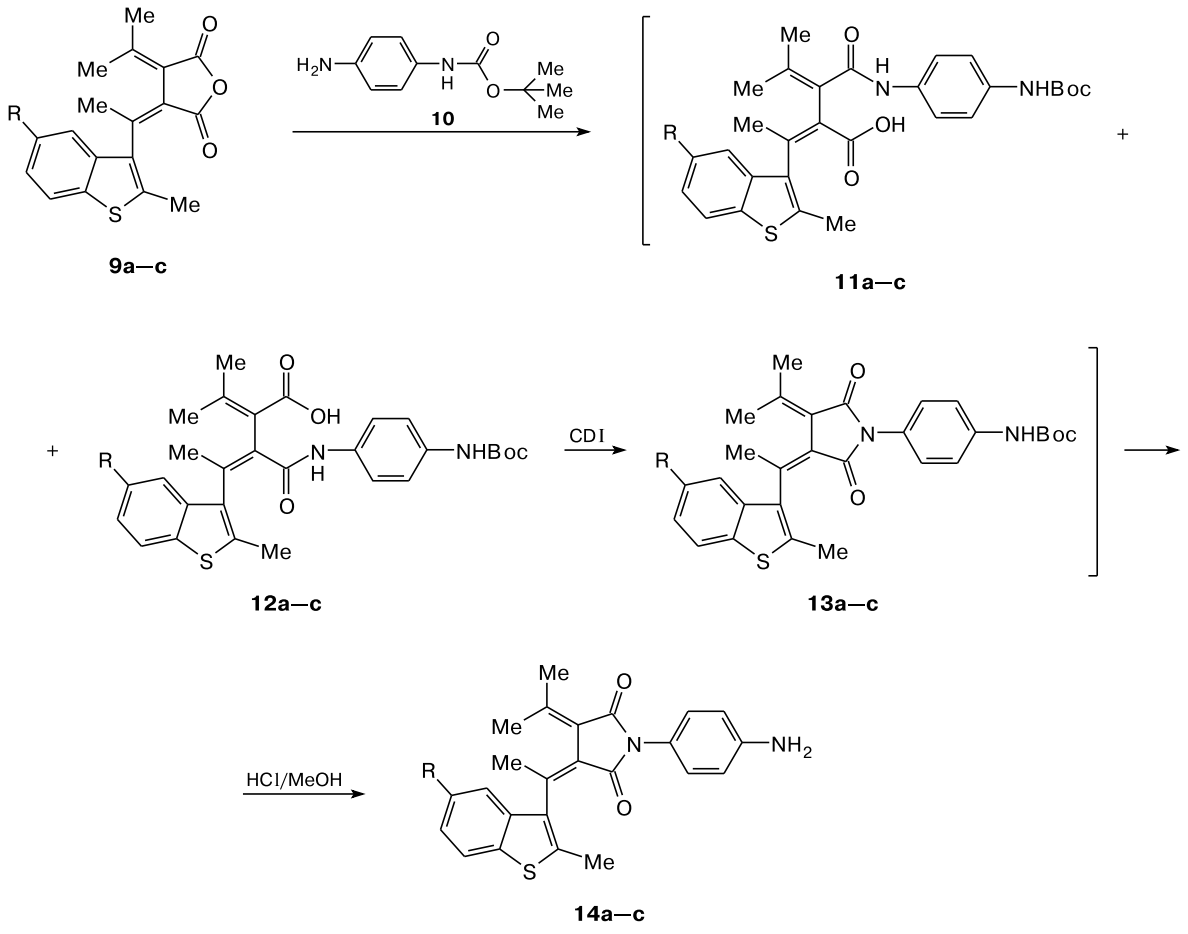
Scheme 2



1, 5, 7—9: R = H (**a**), Me (**b**), Cl (**c**); **1, 5:** R = Br (**d**)

Scheme 3



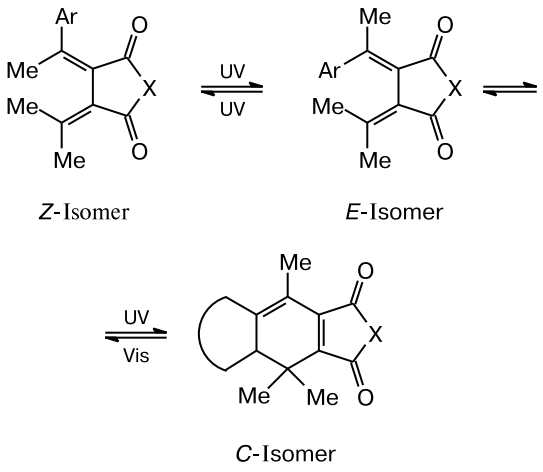
R = H (**a**), Me (**b**), Cl (**c**)

On reflux in benzene for 15—20 h, the resulting mixture of crude amic acids **11a**—**c** and **12a**—**c** was dissolved in THF and stirred with *N*,*N*′-carbonyldiimidazole (CDI) (1.1 equiv.) at room temperature for 5 h. At a final step, the Boc-protection was eliminated from intermediate *N*-Boc-amino fulgimides **13a**—**c** under the action of 5 *M* HCl in ethanol followed by alkalization with a methanolic solution of ammonia. The yields of *N*-(4-aminophenyl)fulgimides **14a**—**c** were 65—71% with respect to the starting fulgide.

The structures of products **14a**—**c** were confirmed by mass and ^{1}H NMR spectra and elemental analysis data. The ^{1}H NMR spectra contain singlets for the methyl groups at δ_H 2.11—2.55 and broadened singlets for the amino group at δ_H 3.56—5.24. Signals for the aromatic protons in the phenyl substituents appear as doublets at δ_H 6.59—7.49.

It is known[1] that fulgides and fulgimides can exist as three isomers (Scheme 4).

Scheme 4



X = O, NR′

All three isomers are in photochemical equilibrium but only the *E*- and *C*-isomers are involved in photochromic transformations. The geometry of the *Z*-isomer precludes its cyclization and an additional portion of the UV light energy is required for the *Z*—*E* isomerization, which inevitably lowers the yield of cyclic photoproducts because *E*—*Z* isomerization is a parallel channel for deactivation of the excited-state energy. The *Z*- or *E*-configuration of fulgides and fulgimides containing an exocyclic isopropylidene substituent can easily be determined from the ^{1}H NMR spectra: this problem was discussed in detail earlier.[9—11] The configurations of such fulgides and fulgimides are determined by the chemical shifts of the signals for the methyl groups in the isopropylidene fragment. For the *Z*-isomers of fulgides and fulgimides, these signals appear at δ_H 1.9—2.5, while the *E*-CH_3 group of the isopropylidene fragment in the *E*-isomer resonates at δ_H 1.3—1.4 because of the shielding effect of the benzothiophene system characteristic only of *E*-isomers of fulgides and fulgimides. The signals for the methyl groups of all the benzothiophene-containing fulgides **9a**—**c** and fulgimides **14a**—**c** appear at δ_H 2.11—2.55, thus suggesting their *Z*-configuration.

We examined the photochromism of fulgides **9a**—**c** and fulgimides **14a**—**c** in acetonitrile using spectroscopic methods (Table 1). Note that spectroscopic data on the photochromism of unsubstituted fulgide **9a** in toluene are available.[6] We recorded electronic absorption spectra of this fulgide in acetonitrile for convenient comparison of its properties with the spectroscopic characteristics of fulgides **9b**—**c** and fulgimides **14a**—**c**.

All the fulgides and fulgimides obtained are photochromes. When their solutions are exposed to monochromated UV light (313 nm), their spectra contain new broad bands in the visible range. The corresponding peaks appear at 480—500 nm (see Table 1). This suggests UV-induced formation of the close (cyclic) forms of these compounds.[12]

For the starting (open) forms of fulgides **9a**—**c**, the absorption bands are similar in shape and peak position (see Table 1). Introduction of both electron-releasing (Me) and electron-withdrawing substituents (Cl) significantly

Table 1. Photochromism of fulgides and fulgimides

Соединение	λ_A (A_A)[a]	λ_B	A_B^{max}
	nm		
9a	341[b]	500	0.060
	231 (1.040), 268 (0.613), 336 (0.137)	490	0.070
9b	234 (1.305), 268 (0.759), 338 (0.161)	500	0.104
9c	237 (1.538), 270 (0.726), 326 (0.184)	490	0.060
14a	235 (1.770), 262 sh, 324 sh	482	0.192
14b	241 (1.245), 266 (1.153), 328 sh	491	0.014
14c	241 (2.050), 266 sh, 322 sh	479	0.203

Note: λ_A and A_A are the absorption peak wavelengths and the corresponding optical densities of the starting (open) form, respectively; λ_B is the peak wavelength of the longer-wavelength absorption of the colored (cyclic) form; A_B^{max} is the optical density of the solution (for a 1-cm-thick layer) at the peak wavelength for the cyclic form in the photostationary state induced by UV irradiation with monochromatized light (313 nm).

[a] The measurements were conducted in acetonitrile ($C = 5 \cdot 10^{-5}$ mol L^{-1}).

[b] Data from Ref. 6. The measurements were conducted in toluene. The cited A_B^{max} value is calculated for $C = 5 \cdot 10^{-5}$ mol L^{-1}.

does not change the band shape or position, as compared to the open form of unsubstituted fulgide **9a**. For instance, the band at 230 nm for compounds **9a—c** shows a slight bathochromic shift (by 3 nm) and the long-wavelength band for compound **9c** shows a hypsochromic shift (by 10 nm) relative to the same band for compound **9a**. The electronic absorption spectrum of compound **9a**, which is typical of this group of compounds, is displayed in Fig. 1, *a*.

The spectra of fulgimides **14a—c** are also similar to each other but contain no distinct absorption bands at 270—330 nm, in contrast to the spectra of the corresponding fulgides. The electronic absorption spectrum of compound **14a**, which is typical of this group of compounds, is displayed in Fig. 1, *b*.

As with the open forms of fulgides, the presence of substituents virtually does not affect the band shape and position in the spectra of the cyclic forms of fulgides **9b—c** compared to unsubstituted fulgide **9a**. Note that the longer-wavelength of the cyclic form of fulgide **9b** (containing an electron-releasing substituent) shows a bathochromic shift by 10 nm relative to the corresponding band of compounds **9a,c**.

The absorption spectra of fulgimides **14** show a slight hypsochromic shift (~10 nm) of the absorption peaks of the cyclic forms compared to the corresponding fulgides **9** (Table 1). In addition, solutions of the cyclic forms of fulgimides **14a,c** in the photostationary state have higher optical densities D_B^{max} than the corresponding fulgides; the opposite pattern is observed for the pair fulgimide **14b**/fulgide **9b**. Fulgimides **14a,c** are most photosensitive among the compounds studied, which is evident from the highest optical densities at the absorption peak wavelength for their cyclic forms in the photostationary state.

Thus, we obtained fulgides and fulgimides containing the 5-substituted benzothiophene ring and found that the presence of the substituents makes insignificant changes in the spectra of these photochromes.

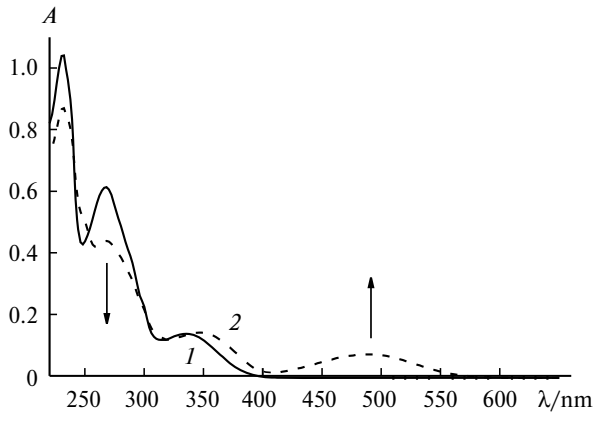


Fig. 1. Electronic absorption spectra $A(\lambda)$ of compounds **9a** (*a*) and **14a** (*b*) in acetonitrile at 298 K for a 1-cm-thick layer: (*1*) the starting open form and (*2*) the photostationary state induced by UV irradiation with monochromatized light (313 nm).

Experimental

^{1}H NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker AM300 spectrometers (300 MHz) in $CDCl_3$ and DMSO-d_6; mass spectra (EI) were recorded on a Finnigan MAT instrument (EI, 70 eV). Melting points were measured on a Boetius hot-stage microscope and are given uncorrected. The course of the reaction was monitored, and the purity of the compounds obtained was checked, by TLC on Merck 60 F_{254} plates.

Commercial benzo[*b*]thiophene, potassium *tert*-butoxide, and *N*,*N*′-carbonyldiimidazole (Acros) were used. Diethyl isopropylidenesuccinate **6** was prepared by condensation of diethyl succinate with acetone in the presence of potassium *tert*-butoxide.[13] 2-Methylbenzo[*b*]thiophene (**1a**),[7] 3-acetyl-2-methylbenzo[*b*]thiophene (**5a**),[14] and *N*-Boc-1,4-phenylenediamine **10** [15] were prepared according to known procedures.

The electronic absorption spectra of the compounds obtained were recorded in solutions on a Lambda 650 two-channel spectrophotometer (Perkin Elmer). In photochemical studies, all solutions were exposed to UV light with $\lambda = 313$ or 365 nm. The light emitted by a DRK-120 mercury-quartz lamp as part of an OI-18A luminescent lighter (LOMO) was monochromated with a set of glass compound light filters. Measurements were carried out in quartz cells (10 mm thick) in the following modes: monochromator step 1 nm, slit width 3 nm, averaging over 3—5 points in each step.

Electronic absorption spectra were recorded in acetonitrile (99% purity, Acros). The concentration of all solutions was $5 \cdot 10^{-5}$ mol L^{-1}.

Synthesis of 5-substituted 2-methylbenzo[*b*]thiophenes 1b—d (general procedure). Potassium *tert*-butoxide (6.4 g, 57.1 mmol) was dissolved in cold anhydrous ethanol (50 mL). Appropriate benzenethiol **2a—c** (51.9 mmol) was added in one portion and the mixture was homogenized by stirring it for 2 h. Then 2-bromo-1,1-diethoxypropane **3** [16] (13.2 g, 62.3 mmol) was added and the reaction mixture was refluxed for 15—25 h until the starting compound was completely consumed (monitoring by TLC). The solvent was removed and the residue was diluted with CH_2Cl_2 and water. Organic material from the aqueous layer was extracted with CH_2Cl_2 (2×50 mL). The combined organic phases were washed with water and brine, dried with anhydrous Na_2SO_4, filtered, and concentrated. Sulfides **4b—d** isolated as light brown oils were employed in the next step without additional purification. Sulfides **4b—d** were added in small portions to a stirred boiling suspension of polyphosphoric acid (30 g) in chlorobenzene (120 mL) for 1 h. The reaction mixture was refluxed for 8—10 h until the starting compound was completely consumed (monitoring by TLC). On cooling, the organic layer was separated by decanting. The brown residue was dissolved in water and the product was extracted with CH_2Cl_2 (3×75 mL). The combined organic phases were washed with water, dried over Na_2SO_4, filtered, and concentrated. The residue was sublimed *in vacuo* (1.2 Torr) to give the corresponding 2-methylbenzo[*b*]thiophene.

2,5-Dimethylbenzo[*b*]thiophene (1b). Yield 4.5 g (54%), white powder, m.p. 43—45 °C (*cf.* Ref. 17: m.p. 45—46 °C).

5-Chloro-2-methylbenzo[*b*]thiophene (1c). Yield 6.5 g (69%), white powder, m.p. 78—82 °C (*cf.* Ref. 17: m.p. 79.5 °C).

5-Bromo-2-methylbenzo[*b*]thiophene (1d). Yield 7.2 g (61%), white powder, m.p. 93—95 °C. ^{1}H NMR ($CDCl_3$), δ: 2.62 (s, 3 H); 6.92 (s, 1 H); 7.35 (dd, 1 H, J_1 = 8.3 Hz, J_2 = 2.0 Hz); 7.61 (d, 1 H, J_1 = 8.3 Hz); 7.79 (d, 1 H, J_2 = 2.0 Hz). Found (%): C, 47.45; H, 3.09; S, 14.18. C_9H_7BrS. Calculated (%): C, 47.60; H, 3.11; S, 14.12.

Synthesis of 3-acetyl-2-methylbenzo[*b*]thiophenes 5a—d (general procedure). Benzothiophene **1a—d** (0.011 mol) and acetyl chloride (1.29 g, 0.016 mol) were dissolved in dry benzene (100 mL) and the mixture was cooled to 5 °C. Then a solution of $SnCl_4$ (4.17 g, 0.016 mol) in dry benzene (30 mL) was added dropwise for 30 min. The reaction mixture was stirred at room temperature for 3 h and acidified with cold 10% aqueous HCl (50 mL). The organic layer was separated, dried over Na_2SO_4, and concentrated *in vacuo*. The residue solidified slowly. Recrystallization from hexane gave 3-acetyl-2-methylbenzo[*b*]-thiophenes **5a—d**.

3-Acetyl-2-methylbenzo[*b*]thiophene (5a). Yield 1.63 g (86%), white crystals, m.p. 68—70 °C (*cf.* Ref. 14: m.p. 69—70 °C).

3-Acetyl-2,5-dimethylbenzo[*b*]thiophene (5b). Yield 1.73 g (77%), white crystals, m.p. 74—76 °C. ^{1}H NMR ($CDCl_3$), δ: 2.48 (s, 3 H); 2.56 (s, 3 H); 2.68 (s, 3 H); 7.17 (dd, 1 H, J_1 = 8.1 Hz, J_2 = 2.0 Hz); 7.61 (d, 1 H, J_1 = 8.1 Hz); 8.00 (d, 1 H, J_2 = 2.1 Hz). Found (%): C, 70.49; H, 5.89; S, 15.65. $C_{12}H_{12}OS$. Calculated (%): C, 70.55; H, 5.92; S, 15.70.

3-Acetyl-5-chloro-2-methylbenzo[*b*]thiophene (5c). Yield 1.73 g (81%), white crystals, m.p. 92—95 °C. ^{1}H NMR ($CDCl_3$), δ: 2.46 (s, 3 H); 2.55 (s, 3 H); 7.14 (dd, 1 H, J_1 = 8.3 Hz, J_2 = 2.1 Hz); 7.61 (d, 1 H, J = 8.3 Hz); 8.38 (d, 1 H, J = 2.1 Hz). Found (%): C, 58.63; H, 4.01; S, 14.15. $C_{11}H_9ClOS$. Calculated (%): C, 58.80; H, 4.04; S, 14.27.

3-Acetyl-5-bromo-2-methylbenzo[*b*]thiophene (5d). Yield 2.76 g (93%), white crystals, m.p. 94—96 °C. ^{1}H NMR ($CDCl_3$), δ: 2.63 (s, 3 H); 2.78 (s, 3 H); 7.43 (dd, 1 H, J_1 = 8.3 Hz, J_2 = 2.0 Hz); 7.57 (d, 1 H, J = 8.3 Hz); 8.41 (d, 1 H, J = 2.0 Hz). Found (%): C, 49.00; H, 3.33; S, 11.85. $C_{11}H_9BrOS$. Calculated (%): C, 49.09; H, 3.37; S, 11.91.

Synthesis of fulgides 9a—c (general procedure). A 500-mL round-bottomed flask fitted with a mechanical stirrer, a dropping funnel, and a reflux condenser was charged with potassium *tert*-butoxide (11 g, 0.098 mol) and anhydrous toluene (250 mL). The resulting suspension was vigorously stirred for 30 min while adding dropwise a solution of appropriate 3-acetyl-2-methylbenzothiophene **5a—c** (0.093 mol) and diethyl isopropylidenesuccinate (**6**) (20 g, 0.093 mol) in dry toluene (50 mL). The reaction mixture was stirred at room temperature for 8 h, poured into water (300 mL), and stirred for 10 min. The aqueous layer was separated and organic material was extracted with toluene (2×50 mL). The extract was acidified with conc. HCl to pH 1 and the product was extracted with ethyl acetate (4×75 mL). The extract was concentrated on a rotary evaporator to a brown oil, which was diluted with ethanol (70 mL) and water (150 mL) and alkalized with KOH (15 g, 0.27 mol). The mixture was refluxed for 6 h, evaporated to dryness, diluted with water (150 mL), and acidified with conc. HCl (20 mL). The resulting viscous dark brown oil was dissolved in CH_2Cl_2 (50 mL) and acetyl chloride (70 mL). The reaction mixture was stirred at room temperature for 3 h and concentrated to dryness on a rotary evaporator. The residue was dissolved in boiling chloroform (15 mL), whereupon light petroleum (35 mL) was added dropwise. On cooling, the crystals that formed were filtered off and washed with light petroleum.

4-Isopropylidene-3-[*Z*-1-(2-methyl-3-benzothienyl)ethylidene]furan-2,5-dione (9a). Yield 19%, white crystals, m.p. 174—176 °C (*cf.* Ref. 6: m.p. 173—176 °C).

3-[*Z*-1-(2,5-Dimethyl-3-benzothienyl)ethylidene]-4-(isopropylidene)furan-2,5-dione (9b). Yield 15%, m.p. 161—163 °C. ^{1}H NMR ($CDCl_3$), δ: 2.16 (s, 3 H, CH_3); 2.22 (s, 3 H, CH_3); 2.42 (s, 3 H, CH_3); 2.43 (s, 3 H, CH_3); 2.51 (s, 3 H, CH_3); 7.11 (m, 2 H, H_{thioph}); 7.64 (d, 1 H, H_{thioph}, J = 8.1 Hz). MS, m/z (I_{rel} (%)): 326 $[M]^+$ (100). Found (%): C, 69.88; H, 5.43; S, 9.75. $C_{19}H_{18}O_3S$. Calculated (%): C, 69.91; H, 5.56; S, 9.82.

3-[*Z*-1-(5-Chloro-2-methyl-3-benzothienyl)ethylidene]-4-(isopropylidene)furan-2,5-dione (9c). Yield 11%, m.p. 187—189 °C. ^{1}H NMR ($CDCl_3$), δ: 2.18 (s, 3 H, CH_3); 2.21 (s, 3 H, CH_3); 2.45 (s, 3 H, CH_3); 2.50 (s, 3 H, CH_3); 7.30 (m, 2 H, H_{thioph}); 7.68 (d, 1 H, H_{thioph}, J = 8.3 Hz). MS, m/z (I_{rel} (%)): 346 $[M]^+$ (100). Found (%): C, 62.36; H, 4.31; S, 9.26. $C_{18}H_{15}Cl_3S$. Calculated (%): C, 62.34; H, 4.36; S, 9.24.

Synthesis of aminophenylfulgimides 14a—c (general procedure). A solution of fulgide **9** (7.2 mmol) and *N*-Boc-1,4-phenylenediamine **10** (1.57 g, 7.54 mmol) in benzene (50 mL) was refluxed for 15—20 h. The solvent was removed on a rotary evaporator and the residue was dissolved in THF (50 mL). Then *N*,*N*′-carbonyldiimidazole (1.28 g, 7.9 mmol) was added and the reaction mixture was stirred at room temperature for 5 h and concentrated on a rotary evaporator. The residue was dissolved with stirring in a 5 *M* methanolic solution of HCl (75 mL) and left at room temperature for 12 h. The reaction mixture was concentrated to dryness on a rotary evaporator and the residue was dissolved in methanol (30 mL) and alkalized with a 5 *M* methanolic solution of ammonia (10 mL). The resulting solution was concentrated to dryness on a rotary evaporator and the residue was diluted with water (100 mL). The product was extracted with ethyl acetate (2×30 mL) and the organic layer was separated, dried over Na_2SO_4, and concentrated. The resulting light yellow oil solidified slowly. Recrystallization from ethyl acetate—hexane gave 4-aminophenylfulgimides **14a—c**.

1-(4-Aminophenyl)-4-isopropylidene-3-[*Z*-1-(2-methyl-3-benzothienyl)ethylidene]pyrrolidine-2,5-dione (14a). Yield 68%, colorless crystals, m.p. 239—241 °C. ^{1}H NMR ($CDCl_3$), δ: 2.16 (s, 3 H, CH_3); 2.21 (s, 3 H, CH_3); 2.45 (s, 3 H, CH_3); 2.52 (s, 3 H, CH_3); 3.58 (br.s, 2 H, NH_2); 6.59 (d, 2 H, H_{ar}, J = 7.5 Hz); 7.0 (d, 2 H, H_{ar}, J = 7.8 Hz); 7.12—7.48 (m, 3 H, H_{thioph}); 7.75 (d, 1 H, H_{thioph}, J = 9.1 Hz). MS, m/z (I_{rel} (%)): 402 $[M]^+$ (100). Found (%): C, 71.65; H, 5.53; N, 6.80. $C_{24}H_{22}N_2O_2S$. Calculated (%): C, 71.62; H, 5.51; N, 6.96.

1-(4-Aminophenyl)-3-[*Z*-1-(2,5-dimethyl-3-benzothienyl)-ethylidene]-4-(isopropylidene)pyrrolidine-2,5-dione (14b). Yield 65%, colorless crystals, m.p. 195—198 °C. ^{1}H NMR ($CDCl_3$), δ: 2.18 (s, 3 H, CH_3); 2.26 (s, 3 H, CH_3); 2.43 (s, 3 H, CH_3); 2.45 (s, 3 H, CH_3); 2.55 (s, 3 H, CH_3); 3.56 (br.s, 2 H, NH_2); 7.14 (m, 2 H, H_{thioph}); 7.66 (d, 1 H, H_{thioph}, J = 8.1 Hz). MS, m/z (I_{rel} (%)): 416 $[M]^+$ (100). Found (%): C, 71.92; H, 5.75; N, 6.61. $C_{25}H_{24}N_2O_2S$. Calculated (%): C, 72.09; H, 5.81; N, 6.73.

1-(4-Aminophenyl)-3-[*Z*-1-(5-chloro-2-methyl-3-benzothienyl)ethylidene]-4-(isopropylidene)pyrrolidine-2,5-dione (14c). Yield 71%, colorless crystals, m.p. 291—293 °C. ^{1}H NMR (DMSO-d_6), δ: 2.11 (s, 3 H, CH_3); 2.12 (s, 3 H, CH_3); 2.39 (s, 3 H, CH_3); 2.42 (s, 3 H, CH_3); 5.24 (br.s, 2 H, NH_2); 6.51 (d, 2 H,

H_{ar}, J = 8.0 Hz); 6.78 (d, 2 H, H_{ar}, J = 8.0 Hz); 7.30 (d, 1 H, J = 8.3 Hz); 7.49 (d, 1 H, J = 8.3 Hz); 7.90 (d, 1 H, H_{thioph}, J = 8.3 Hz). MS, m/z (I_{rel} (%)): 436 $[M]^+$ (100). Found (%): C, 65.83; H, 4.62; N, 6.29. $C_{24}H_{21}ClN_2O_2S$. Calculated (%): C, 65.97; H, 4.84; N, 6.41.

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