Synthesis, structures, and photochromic properties of 2-methylthieno[3,2-*b*][1]benzothiophen-3-ylfulgide

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The novel heterocyclic fulgide, 3-(1-methylethylidene)-4-[1-(2-methylthieno[3,2-*b*]-[1]benzothiophen-3-yl)ethylidene]dihydrofuran-2,5-dione, was obtained and isolated as a *Z*-isomer. Its structure was confirmed by electronic absorption spectroscopy, ^{1}H NMR spectroscopy, and X-ray diffraction analysis. The novel thienothiophene fulgide is photochromic in both solutions and the crystalline state. Its colored cyclic form resists photodegradation and is thermally stable. When benzothiophene is annulated with the thienyl fragment, the long-wavelength absorption peak of the cyclic isomer of the novel fulgide experiences a bathochromic shift compared to the earlier described 3-thienylfulgide. The TD B3LYP/6-311G**-calculated spectroscopic characteristics of the fulgide isomers suggest the formation of their photostationary mixture under irradiation with $\lambda = 365$ nm.

Key words: thieno[3,2-*b*][1]benzothiophene, fulgide, synthesis, structure, photochromism, quantum-chemical calculations, density functional theory.

Because of the high thermal stability of their isomers and the high number of cyclic photochromic transformations, heterocyclic fulgides are a promising class of photochromic compounds for use in optical recording systems.[1] It is known that annulation of the benzene ring additionally stabilizes an aromatic heterocyclic system, thus enhances the resistance of fulgides to photodegradation during photochromic transformations.[2] One can expect that annulation of a heterocyclic aromatic fragment will produce a similar effect.

The goal of the present work was to study the effect of the annulation of benzo[*b*]thiophene fragment with the thienyl ring of 3-thienylfulgide[3,4] on the characteristics of the photochromic system.

Results and Discussion

We developed a procedure for the synthesis of 3-acetyl-2-methylthieno[3,2-*b*][1]benzothiophene containing two methyl groups, which prevent oxidative aromatization of the colored cyclic form of the fulgide. Thermal decarboxylation of thieno[3,2-*b*][1]benzothiophene-2-carboxylic acid (**1**)[5] gave thieno[3,2-*b*][1]benzothiophene (**2**). The Vilsmeier reaction of the latter afforded thieno[3,2-*b*][1]-benzothiophene-2-carbaldehyde (**3**) in high yield. Aldehyde **3** was reduced to 2-methylthieno[3,2-*b*][1]benzothiophene (**4**) according to the Kishner reaction. The Friedel—Crafts acetylation of compound **4** with acetyl chloride in the presence of anhydrous $SnCl_4$ gave 1-(2-methylthieno[3,2-*b*][1]benzothiophen-3-yl)ethanone **5** (Scheme 1).

The Stobbe condensation of ketone **5** with diethyl isopropylidenesuccinate gave earlier unknown (4*Z*)-3-(1-methylethylidene)-4-[1-(2-methylthieno[3,2-*b*][1]benzothiophen-3-yl)ethylidene]dihydrofuran-2,5-dione (**6**) (Scheme 2).

The IR spectra of fulgide **6** contain characteristic bands at 1755 and 1810 cm^{-1} due to two exocyclic carbonyl groups in succinic anhydride. The ^{1}H NMR spectra show high-field signals for four methyl groups and low-field signals for four aromatic protons. The absence of the singlet signal for the ethylidene Me group from the ^{1}H NMR spectrum at δ 2.5 suggests the *Z* configuration of fulgide **6** with respect to the heterylethylidene double bond,[6] which is structurally not ready for a photoinitiated electrocyclic

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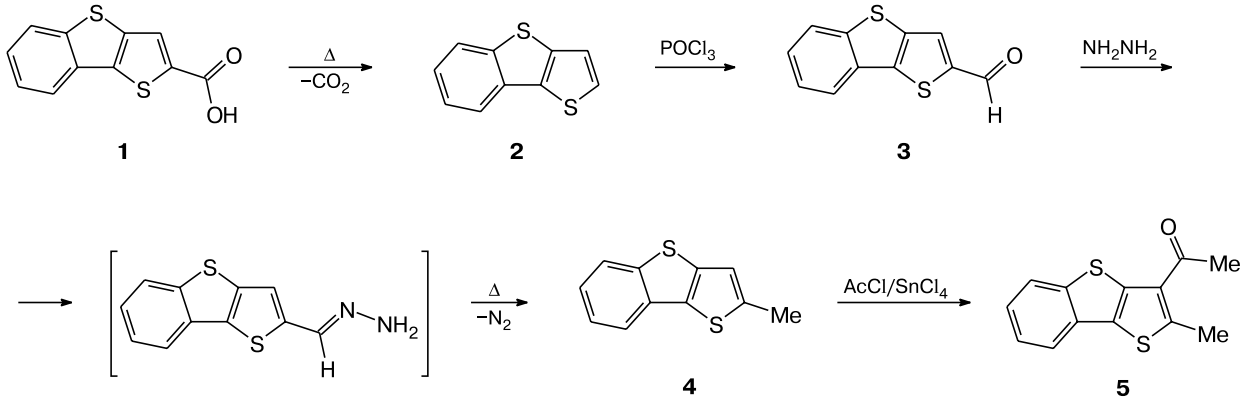
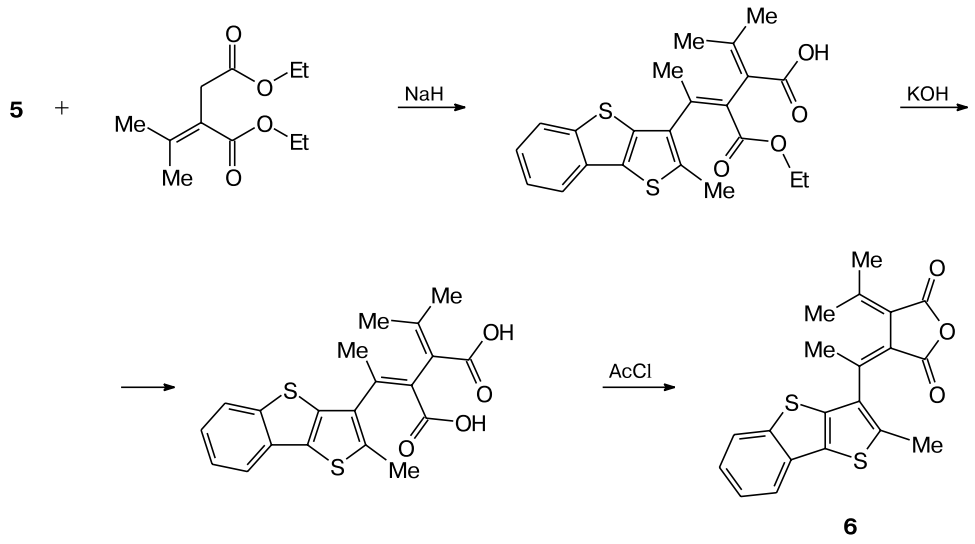
Scheme 1



Scheme 2



reaction. This conclusion was confirmed by X-ray diffraction data. Structure **6** is shown in Fig. 1; selected interatomic distances are given in Table 1.

The atoms of thieno[3,2-*b*][1]benzothiophene fragment are coplanar to within 0.023 Å. The C(5) and C(12)

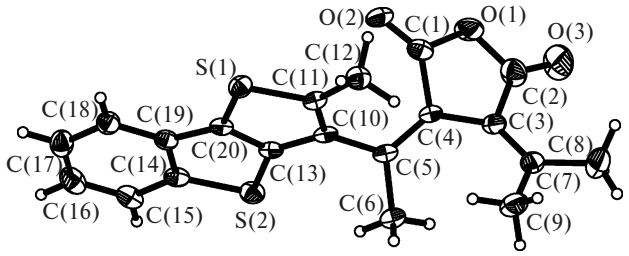


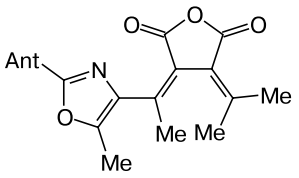
Fig. 1. Structure **6** with atomic thermal displacement ellipsoids (30% probability).

Table 1. Selected interatomic distances (*d*) in structure **6**

Bond	*d*/Å	Bond	*d*/Å
S(1)—C(11)	1.722(4)	S(1)—C(20)	1.723(4)
S(2)—C(13)	1.745(4)	S(2)—C(14)	1.746(4)
O(1)—C(2)	1.395(6)	O(1)—C(1)	1.397(5)
O(2)—C(1)	1.186(5)	O(3)—C(2)	1.191(5)
C(1)—C(4)	1.487(6)	C(2)—C(3)	1.473(6)
C(3)—C(7)	1.349(6)	C(3)—C(4)	1.470(5)
C(4)—C(5)	1.359(5)	C(5)—C(10)	1.470(5)
C(5)—C(6)	1.502(5)	C(7)—C(9)	1.490(6)
C(7)—C(8)	1.505(6)	C(10)—C(11)	1.383(5)
C(10)—C(13)	1.426(5)	C(11)—C(12)	1.495(5)
C(13)—C(20)	1.366(5)	C(14)—C(15)	1.395(6)
C(14)—C(19)	1.419(5)	C(15)—C(16)	1.372(6)
C(16)—C(17)	1.388(6)	C(17)—C(18)	1.382(6)
C(18)—C(19)	1.389(5)	C(19)—C(20)	1.429(5)

atoms deviate from the plane on both sides by 0.063(4) and 0.093(5) Å, respectively. An analysis of the structure of the fulgide fragment containing the C(5) and C(6) atoms shows that the formal plane passes through the O(1), O(2), O(3), C(1), and C(2) atoms to within 0.013 Å; the C(3), C(7), C(8), and C(9) atoms deviate by 0.08(1), 0.62(2), 0.96(2), and 1.00(2) Å, respectively, on one side and the C(4), C(5), C(6), and C(10) atoms deviate by 0.19(1), 0.80(2), 1.52(2), and 0.85(2) Å, respectively, on the other side. Obviously, this is due to the mutual arrangement of the C(6) and C(9) atoms and their hydrogen atoms (the H...H and C(6)...C(9) distances are 2.21 and 3.14 Å, respectively). The angle between the planes of the thieno[3,2-*b*][1]benzothiophene and fulgide fragments calculated as an angle between the perpendiculars to the planes of these fragments is 81°; the torsion angles C(11)—C(10)—C(5)—C(4) and C(10)—C(5)—C(4)—C(1) are −52.4(5)° and −25.1(5)°, respectively; the C(7)—C(11) distance is 5.27 Å.

The mutual arrangement of the fragments of structure **6** and the earlier[7] studied 4-[2-(9-anthryl)-5-methyl]oxazolylfulgide (**7**) is shown in Fig. 2 so that their fulgide fragments coincide (their structures are identical to within the error of determination and have the same orientation relative to the central part of the molecule).



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Note that fulgide **7** also exists as the *Z*-isomer and irradiation of its solutions with λ = 365 nm results in *Z*/*E* isomerization yielding a thermally stable cyclic form; light irradiation with λ = 436 nm produces the starting *E*-isomer.

When considering the structure of the central part of the molecule, note that the shortest distance from the

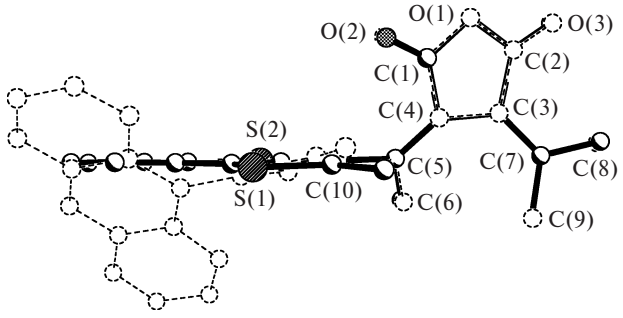


Fig. 2. Mutual arrangement of the fragments of structure **6** and 4-[2-(9-anthryl)-5-methyl]oxazolylfulgide.

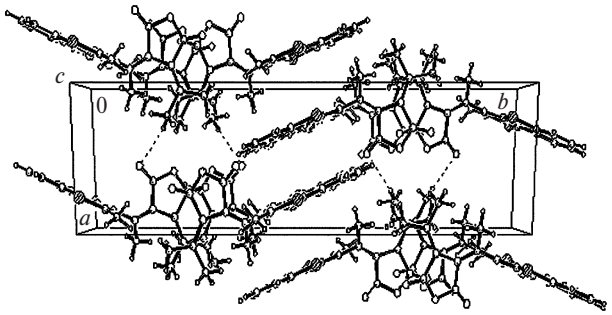


Fig. 3. Arrangement of the molecules of compound **6** along the axis *c*.

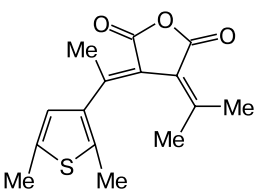
O(2) atom to one of the H atoms at the C(12) atom is 2.707 Å; *i.e.*, no steric interactions occur between these atoms. The C(4)—C(5) and C(3)—C(7) distances are 1.36 and 1.35 Å, which is only slightly longer than an ordinary double bond of this type.

Arrangement of the molecules of compound **6** along the axis *c* is shown in Fig. 3. The shortest distances (2.488 Å) between the fulgide O(2) atoms and one of the H atoms at the C(9) atom, which are related by translations in the unit cell along the axis *a*, are indicated with dashed lines. Using the 6-exp potential with appropriate parameters,[8] we calculated the energies of the intermolecular interactions. The total energy of the crystal lattice of compound **6** was found to be 36.1 kcal mol^{-1}. The major contributions to the energy of the crystal lattice are made by the energies of pair intermolecular interactions: between the molecules related by the center of inversion and translations (011) (15.33 kcal mol^{-1}), (112) (10.72 kcal mol^{-1}), and (111) (6.99 kcal mol^{-1}) and between the molecules related by the helical axis and translations (01−1 and 010) (6.13 kcal mol^{-1}). The volume of the molecule is 259.4 Å^3 and the free volume fraction (the fraction of the free volume per molecule in the unit cell) is K = 176.3 Å^3. This parameter was calculated by the formula $K = (V_{cell} - ZV_{mol})/Z$, where V_{cell} and V_{mol} are the unit cell volume and the molecule volume, respectively; Z is the number of formula units in the unit cell.

In the unit cell with such parameters, the *Z*-isomer can transform itself into the *E*-isomer by rotating about the C(4)—C(5) bond in the solid state, because the molecules in the left- and right-hand chains in Fig. 3 are shifted by half the translation along the plane of the figure. In this case, the photoreaction $E \rightarrow C$ becomes quite possible.

The electronic absorption spectra of fulgide *Z*-**6** in toluene show a long-wavelength absorption peak at 340 nm (Fig. 4, curve *1*).

The molar absorption coefficient ε at the absorption peak is 7340 L mol^{-1} cm^{-1}.



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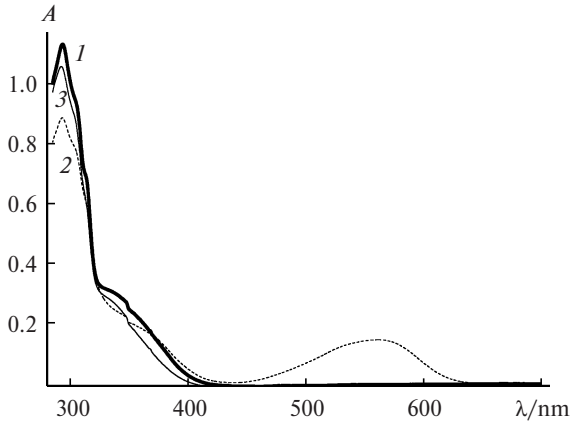


Fig. 4. Electronic absorption spectra of fulgide **6** in toluene ($4 \cdot 10^{-5}$ mol L^{-1}): (*1*) before irradiation; (*2*) photostationary state under light irradiation with λ = 365 nm; (*3*) after subsequent light irradiation with λ = 546 nm.

The spectroscopic characteristics of the *Z*-isomer of fulgide **6** are close to the corresponding parameters of the *Z*-form of thienylfulgide **8** absorbing at 344 nm (ε = 7010 L mol^{-1} cm^{-1}).[3]

Solutions of compound *Z*-**6** in toluene do not fluoresce at room temperature.

When irradiated with UV light corresponding to the long-wavelength absorption peak of the *Z*-form (λ_{exc} = 365 nm), solutions of fulgide *Z*-**6** in toluene became colored and their spectra show an absorption band at 561 nm. This absorption is characteristic of the cyclic *C*-isomers (see Fig. 4, curve *2*); the *C*-isomer of thienylfulgide **8** absorbs at the shorter wavelengths (526 nm).[3] The cyclic form *C*-**6** is thermally stable: the reverse dark reaction $C \rightarrow E$ at 293 K was not observed for 72 h.

The colored form *C*-**6** of 2-methylthieno[3,2-*b*][1]-benzothiophene does not fluoresce in toluene, in contrast to the cyclic isomers of fulgides based on naphtho[1,2-*b*]furan and benzo[*g*]indole we have described earlier.[9]

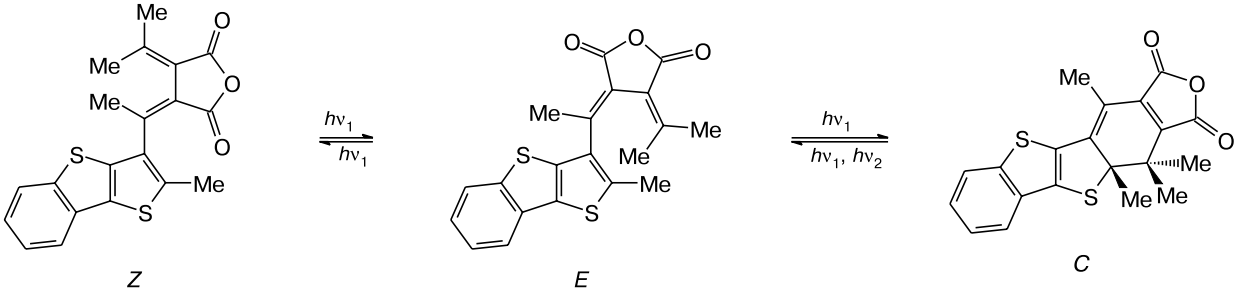
Irradiation of colored solutions of fulgide *C*-**6** with visible light (λ = 546 nm) decolorized them. The decrease in the intensity of the absorption peak of the *C*-form was not accompanied by restoration of the original absorption of the UV-nonirradiated solution (see Fig. 4, curve *3*). At the same time, in subsequent photocoloration—photodecoloration cycles, the spectroscopic characteristics of the colored and decolorized solutions were reproducible. Such changes in the absorption spectra are due to the presence of the isomer *E*-**6** in the irradiated solutions.

Obviously, UV irradiation of solutions of fulgide **6** first initiates the isomerization $Z \rightarrow E$ since cyclic product *C*-**6** cannot be formed directly from the *Z*-form of the fulgide. Because the absorption bands of the isomers *E*-**6** and *Z*-**6** overlap greatly, both the *Z*- and *E*-forms are photoinduced by UV irradiation and the electrocyclic transformation $E \rightarrow C$ becomes possible. We found that the conversion into the colored form remains incomplete even on prolonged irradiation of solutions of fulgide **6**. This can be associated with overlap of the absorption bands due to the transitions $S_0 \rightarrow S_2$ in cyclic isomers *C*-**6** with the absorption bands due to the transitions $S_0 \rightarrow S_1$ in the *E*- and *Z*-isomers. Under the conditions of the reverse photoreaction $C \rightarrow E$ and the photoisomerization $E \rightarrow Z$, UV irradiation produces the photostationary state consisting of the *E*-, *Z*-, and *C*-isomers; their ratio is determined by the wavelength of exciting UV light (Scheme 3). The formation of a mixture of three isomers was confirmed by the ^{1}H NMR spectrum of fulgide *Z*-**6** recorded in deuterated toluene after irradiation with λ = 365 nm. The spectrum contains signals for the methyl groups of all the three isomers. Subsequent full photodecoloration of the solution with visible light gave a mixture consisting only of the isomers *E*-**6** and *Z*-**6**; the content of the *E*-form in the mixture is increased by the amount of the *C*-form in the mixture of three isomers (^{1}H NMR data for the colored solution before and after irradiation with λ = 546 nm).

Fulgide **6** is resistant to photodegradation. After ten photocoloration—photodecoloration cycles, the optical density of the colored solution remained unchanged (Fig. 5).

Fulgide **6** exhibits photochromism in the solid state. When irradiated with UV light (λ_{exc} = 365 nm), goldish yellow crystals of the isomer *Z*-**6** turned dark violet. The electronic absorption spectrum of a solution of dark violet crystals in toluene shows a band at 561 nm. Apparently,

Scheme 3



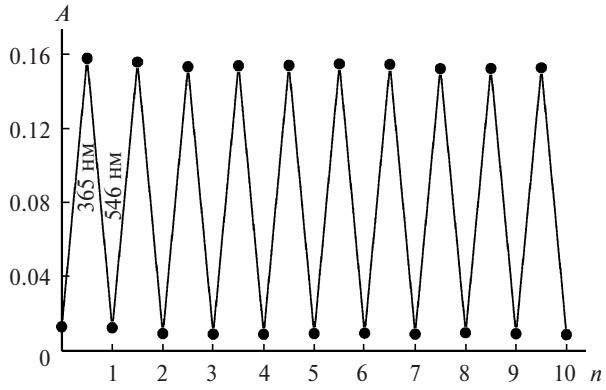


Fig. 5. Change in the optical density of the absorption peak (561 nm) of the *C* form of fulgide **6** in toluene in repeated cycles coloration (light irradiation with λ = 365 nm for 10 min)—decoloration (light irradiation with λ = 546 nm for 10 min); *n* is the number of cycles.

the same sequence of isomerization and cyclization photoreactions $Z \rightarrow E$ and $E \rightarrow C$ occurs in both the solid state and solutions. These crystals turned again yellow upon irradiation with visible light.

To elucidate the nature of the observed absorption bands of fulgide **6**, we performed TD B3LYP/6-311G** calculations of the first three singlet transitions of its isomers whose optimized structures are shown in Fig. 6.

The theoretically predicted structural parameters of the *Z*-isomer agree well with X-ray diffraction data. The largest discrepancy between the experimental and calculated bond lengths does not exceed 0.03 Å. The shorter C—S bonds and the difference in the torsion angles between the planes of the thieno[3,2-*b*][1]benzothiophene and fulgide fragments in the crystal compared to the calculated values for the gas phase can be explained by packing effects. The spectroscopic characteristics of the singlet transitions for the isomers of compound **6** are given in Table 2.

Table 2. DFT-calculated excitation energies (E_{exc}) and the oscillating forces (*f*) of the first three singlet transitions for the *Z*-, *E*-, and *C*-isomers of fulgide **6** (TD B3LYP/6-311G**)

Structure	Transition	E_{exc}/eV	*f*
Z-**6**	$S_0 \rightarrow S_1$	3.13	0.023
	$S_0 \rightarrow S_2$	3.40	0.112
	$S_0 \rightarrow S_3$	3.90	0.005
E-**6**	$S_0 \rightarrow S_1$	3.28	0.009
	$S_0 \rightarrow S_2$	3.52	0.086
	$S_0 \rightarrow S_3$	4.07	0.107
C-**6**	$S_0 \rightarrow S_1$	2.13	0.189
	$S_0 \rightarrow S_2$	3.09	0.122
	$S_0 \rightarrow S_3$	3.50	0.007

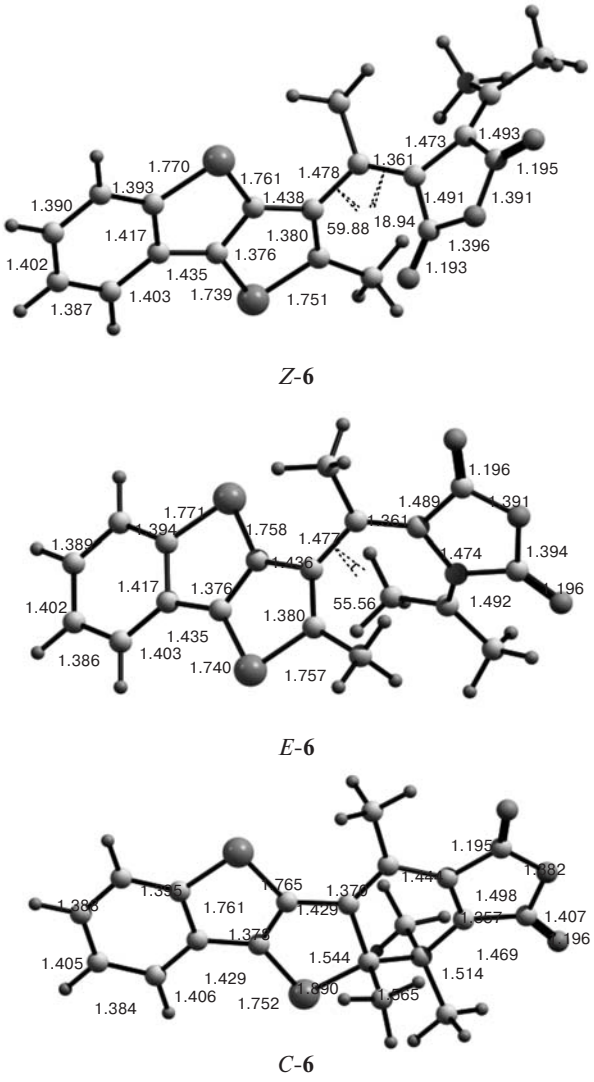


Fig. 6. B3LYP/6-311G**-calculated geometrical parameters of the *Z*-, *E*-, and *C*-isomers of fulgide **6**; bond lengths (Å) and dihedral angles (deg) are indicated.

According to theoretical estimations, the transition $S_0 \rightarrow S_1$ in both the open forms corresponds to the charge transfer band associated with the electron density redistribution between the thieno[3,2-*b*][1]benzothiophene and fulgide fragments. It has low intensity and most likely corresponds to the weakly pronounced shoulder in the long-wavelength part of the spectrum. The second singlet transition of the $\pi \rightarrow \pi^*$ type is responsible for the observed long-wavelength absorption peak at 340 nm (3.65 eV). The deviations of the calculated excitation energies of this transition from the experimental values are 0.25 and 0.13 eV for the structures *Z*-**6** and *E*-**6**, respectively. The short-wavelength absorption band at 300 nm is due to third and higher singlet transitions. As assumed, the absorption bands of the isomers *Z*-**6** and *E*-**6** overlap strongly.

According to our calculations, the long-wavelength peak of the isomer *C*-**6** is due to the transition $\pi \rightarrow \pi^*$; its energy (2.13 eV) is close to the experimental value (2.21 eV; 561 nm). The transition $S_0 \rightarrow S_2$ is less intense than the first one and is contributed by the transition $\pi \rightarrow \pi^*$ and the charge transfer transition. This absorption band of the *C*-isomer overlaps with the charge transfer band in the spectra of the open forms. The third singlet transition of the $n \rightarrow \pi^*$ type for the structure *C*-**6** appears at 355 nm, overlapping with the intense long-wavelength absorption band of the open forms. Thus, according to the calculated data, irradiation with $\lambda = 365$ nm can induce the reverse photoreaction, which can explain the experimentally observed formation of a photostationary mixture of all three isomers (*Z*, *E*, and *C*) of fulgide **6**.

Experimental

Electronic absorption spectra were recorded on a Carry-100 spectrophotometer (Varian). Photolysis of solutions in toluene ($C = 4 \cdot 10^{-5}$ mol L^{-1}) was carried out with a DRSh-250 high-pressure mercury lamp fitted with a set of interference light filters. IR spectra (Nujol) were recorded on a Specord IR-75 instrument. ^{1}H NMR spectra were recorded on a Varian Unity-300 instrument (300 MHz) in $CDCl_3$ with HMDS as the external standard.

Thieno[3,2-*b*][1]benzothiophene-2-carboxylic acid (1) was prepared as described earlier.[5] The yield was 92%, m.p. 265 °C (decomp.).

Thieno[3,2-*b*][1]benzothiophene (2). Acid **1** (2 g, 8.53 mmol) was heated in an open flask at 240—250 °C for 50 min. On cooling, the reaction mixture was dissolved in benzene (120 mL) and the solution was washed with 1% NaOH (25 mL) and water. The benzene layer was separated, dried with $CaCl_2$, treated with activated charcoal (0.5 g), and filtered off. A greater part of the solvent was removed and the product was precipitated with light petroleum. The yield was 88%, m.p. 94—97 °C. Found (%): C, 63.19; H, 3.26. $C_{10}H_6S_2$. Calculated (%): C, 63.12; H, 3.18. ^{1}H NMR, δ: 7.32 (d, 1 H, H arom., J = 5 Hz); 7.32—7.45 (m, 2 H, H arom.); 7.51 (d, 1 H, H arom., J = 5 Hz); 7.84—7.86 (m, 2 H, thiophene).

Thieno[3,2-*b*][1]benzothiophene-2-carbaldehyde (3). A mixture of compound **2** (0.5 mg, 2.60 mmol), *N*-methylformanilide (0.39 g, 2.86 mmol), and $POCl_3$ (0.44 g, 2.86 mmol) was stirred at ~20 °C for 4 h and then heated at 50—55 °C for 0.5 h. On cooling, the reaction mixture was kept for 12 h and treated with water with ice (25 mL). The precipitate that formed was thoroughly triturated with water, filtered off, washed with water several times, and dried in air. The yield was 99%, m.p. 100—102 °C (from ethanol). Found (%): C, 60.39; H, 2.54. $C_{11}H_6O_2S_2$. Calculated (%): C, 60.52; H, 2.77. IR, ν/cm^{-1}: 1770 (C=O). ^{1}H NMR, δ: 7.45—7.53, 7.85—8.00 (both m, 2 H each, H arom.); 8.00 (s, 1 H, H arom.); 10.01 (s, 1 H, CHO).

2-Methylthieno[3,2-b][1]benzothiophene (4). A mixture of aldehyde **3** (450 mg, 2.06 mmol), NaOH (300 mg, 7.5 mmol), and 85% hydrazine hydrate (0.8 mL, 13.5 mmol) was refluxed in diethylene glycol (5 mL) for 3 h. The solution was diluted with water (25 mL) and the product was extracted with chloroform. The extract was washed with water and steam-distilled. The resulting compound **4** was extracted with chloroform and the organic layer was separated and dried with $CaCl_2$. The solvent was evaporated in a rotary evaporator. The yield was 52%, m.p. 39—40 °C. Found (%): C, 64.39; H, 4.16. $C_{11}H_8S_2$. Calculated (%): C, 64.67; H, 3.95. ^{1}H NMR, δ: 2.67 (s, 3 H, Me); 7.45—7.53, 7.85—8.00 (both m, 2 H each, H arom.); 8.05 (s, 1 H, H arom.).

1-(2-Methylthieno[3,2-*b*][1]benzothiophen-3-yl)ethanone (5). Compound **4** (200 mg, 0.98 mmol) was triturated with dry benzene (2 mL) and cooled to 0—5 °C. Acetyl chloride (80 mg, 1.18 mmol) was added with stirring and then $SnCl_4$ (260 mg, 1.2 mmol) was added. The reaction mixture was stirred at ~20 °C for 1 h, 10% HCl (2 mL) was added under cooling, and the solvent was removed in water aspirator vacuum. The residue was filtered off, washed with water, and dried in air. The yield was 83%, m.p. 158—160 °C (from ethanol). Found (%): C, 63.29; H, 4.26. $C_{13}H_{10}OS_2$. Calculated (%): C, 63.38; H, 4.09. IR, ν/cm^{-1}: 1750, 1800 (C=O). ^{1}H NMR, δ: 2.67, 2.92 (both s, 3 H each, Me); 7.30—7.45, 7.75—7.92 (both m, 2 H each, H arom.).

(4*Z*)-3-(1-Methylethylidene)-4-[1-(2-methylthieno[3,2-*b*]-[1]benzothiophen-3-yl)ethylidene]dihydrofuran-2,5-dione (*Z*-6). A solution of compound **5** (2.95 g, 0.012 mol), diethyl isopropylidenesuccinate (2.8 g, 0.013 mol), and diisopropylamine (1.4 mL, 0.01 mol) in THF (20 mL) was added at ~20 °C to a stirred suspension of NaH (0.36 g, 0.015 mol) in THF (10 mL). The reaction mixture was stirred at 30 °C for 2 h. The solvent was removed in water aspirator vacuum. The residue was treated with 10% HCl (10 mL). The precipitate of monoethyl ester that formed was filtered off, and refluxed with 10% KOH (10 mL) in methanol for 2 h. On cooling, the mixture was diluted with water and treated with 10% HCl (30 mL). The precipitate of dicarboxylic acid that formed was filtered off and dried in air. The dicarboxylic acid was dissolved under heating in acetyl chloride (2 mL). The solvent was removed *in vacuo*. The product was purified by column chromatography on silica gel with chloroform as eluent and recrystallized from acetonitrile to give goldish yellow crystals. The yield was 3%, m.p. 211—213 °C. Found (%): C, 65.00; H, 4.12. $C_{20}H_{16}S_2O_3$. Calculated (%): C, 65.19; H, 4.38. IR, ν/cm^{-1}: 1755; 1810 (C=O). UV, λ_{max}/nm (ε): 340 (7340). ^{1}H NMR, δ: 1.29, 1.72, 2.06, 2.23 (all s, 3 H each, Me); 6.92—7.15, 7.34—7.53 (both m, 2 H each, H arom.).

4,10a,11,11-Tetramethyl-10a,11-dihydro[1]benzothiopheno[2′,3′:4,5]thieno[2,3-f][2]benzofuran-1,3-dione (*C*-6) was obtained in a tube of the NMR spectrometer as a mixture with the isomers *Z*-**6** and *E*-**6** upon 3-h irradiation of a solution of fulgide *Z*-**6** in deuterated toluene ($C = 2.4 \cdot 10^{-2}$ mol L^{-1}) with $\lambda_{exc} = 365$ nm. ^{1}H NMR, δ: 1,15, 1.26, 1.42, 2.25 (all s, 3 H each, Me); 6.90—7.15 (m, 4 H, H arom.).

(4*E*)-3-(1-Methylethylidene)-4-[1-(2-methylthieno[3,2-*b*]-[1]benzothiophen-3-yl)ethylidene]dihydrofuran-2,5-dione (*E*-6). ***A.*** The isomer was obtained as described for *C*-**6** as a mixture with the isomers *Z*-**6** and *C*-**6** upon 3-h irradiation of a solution of fulgide *Z*-**6** in deuterated toluene ($C = 2.4 \cdot 10^{-2}$ mol L^{-1}) with $\lambda_{exc} = 365$ nm.

B. The isomer was obtained from the isomer *C*-**6** in a tube of the NMR spectrometer as a mixture with *Z*-**6** upon 3-h irradiation of a solution containing all three isomers in deuterated toluene ($C = 2.4 \cdot 10^{-2}$ mol L^{-1}) with $\lambda_{exc} = 546$ nm. ^{1}H NMR, δ: 0.68, 1.08, 1.54, 2.57 (all s, 3 H each, Me); 6.90—7.15, 7.34—7.53 (both m, 2 H each, H arom.).

X-ray diffraction analysis. A 3D set of reflection intensities were collected and the unit cell parameters of the crystal were determined on a Bruker P-4 automated diffractometer (Mo-Kα radiation, graphite monochromator). Crystals of compound **6** are monoclinic, $C_{20}H_{16}O_3S_2$, M = 368.45; a = 7.772(2) Å, b = 28.634(7) Å, c = 8.235(2) Å, β = 108.00(1)°, V = 1742.9(3) Å^3, Z = 4, ρ_{calc} = 1.404 g cm^{-3}, μ(Mo-Kα) = 0.32 mm^{-1}, space group $P2_1/c$. The intensities of 3658 reflections were measured in the quadrant of reciprocal space (2θ ≤ 50°) in the ω/2θ scan mode for a single crystal 0.1S0.3S0.4 mm. After systematic absences were excluded and the intensities of equivalent reflections were averaged, the working array of measured $F^2(hkl)$ and $\sigma(F^2)$ included 2709 independent reflections; the number of reflections with $F^2 > 4\sigma(F^2)$ was 1764. The structure was solved by the direct method with the SHELXS-97 program[10] and refined by the full-matrix least-squares method on F^2 with the SHELXL-97 program[10] in the anisotropic approximation for non-hydrogen atoms. In the crystal structure **6**, all hydrogen atoms were located from the electron density difference map; the coordinates and isotropic thermal parameters of all the H atoms were refined by the least-squares method in the rider model.[10] The full-matrix refinement was continued until the absolute differences for all 226 variable parameters of structure **6** were less than 0.001σ. Final residuals were R_1 = 0.050 and wR_2 = 0.14 for 1764 observed reflections with $I \geq 2\sigma(I)$ and R_1 = 0.093 and wR_2 = 0.11 for all 2709 measured reflections; GOF = 1.039. The residual maximum and minimum electron densities were 0.247 and –0.258 e Å^{-3}, respectively.

Quantum-chemical calculations. The geometrical parameters of the isomers of fulgide **6** were optimized in terms of density functional theory (DFT) with the B3LYP hybrid exchange-correlation functional[11,12] using the 6-311G** basis set. Spectroscopic characteristics were calculated in terms of TD DFT using the same basis set. All calculations were performed with the Gaussian 03 program package.[13]

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