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SYNTHESIS OF PHOTOCHROMIC BISFULGIMIDES BY THE CONDENSATION OF (3*Z*)-3-[1-(2,5-DIMETHYL-3-THIENYL)-ETHYLIDENE]-4-ISOPROPYLIDENE-2,5-FURANDIONE WITH AROMATIC DIAMINES

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The first representatives of thiophene derivatives with two fulgimide fragments in one molecule have been obtained by the condensation of (3Z)-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidene-2,5-furandione with aromatic diamines. The photochromic properties of the obtained compounds have been investigated and the effect of a spacer, linking the two fulgimide fragments, on the reaction rates of photocoloration and photodecoloration of these compounds has been studied.

Keywords: 3-acetyl-2,5-dimethylthiophene, fulgides, fulgimides, Stobbe condensation, photochromism.

Fulgimides of the thiophene series are considered at the present time as one of the promising classes of photochromic compounds. They possess photochemical characteristics valuable in practice, such as thermal irreversibility and high chemical stability, which enables these compounds to be considered as components for constructing molecular switches, and also systems of recording, storage, and treatment of information [1-5].

The aim of the present work was the preparation of thiophene fulgimides, not reported in the literature, containing two fulgimide fragments in one molecule linked by various aromatic bridges, and clarification of the effect of the spacer on their photochromic properties.

The approach developed by us to the synthesis of this type of compounds includes the preparation of (3*Z*)-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidene-2,5-furandione (**1**) (Scheme 1), which is described in the literature [6]. Compound **1** is then converted into the desired products by interaction with aromatic diamines.

Hemiester **5** was obtained by the Stobbe condensation of 3-acetyl-2,5-dimethylthiophene (**3**), obtained by the acylation of 2,5-dimethylthiophene (**2**) according to Friedel-Crafts, with diethyl isopropylidenesuccinate (**4**) in the presence of *t*-BuOK as base. It should be noted that the use of *t*-BuOK as base in this reaction, in place of NaOEt reported in the literature [7], enabled a purer product to be obtained. Subsequent alkaline

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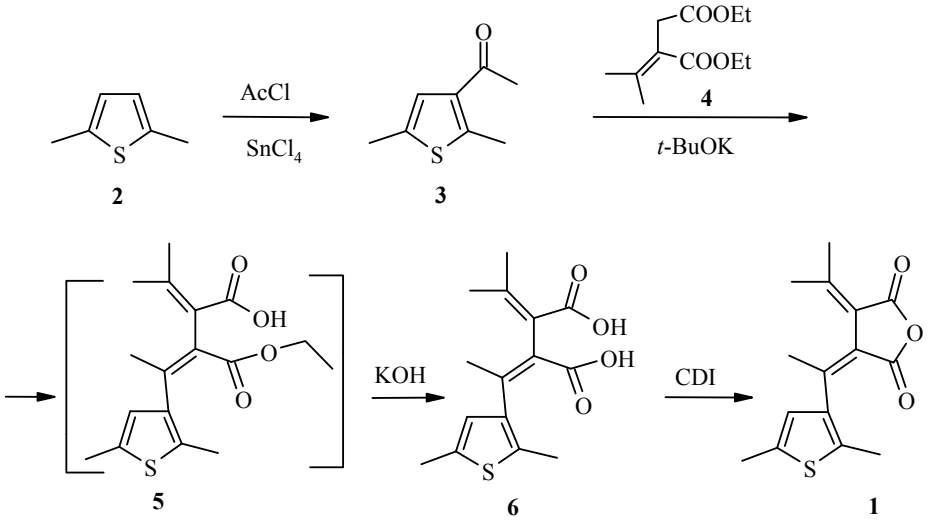
hydrolysis of the hemiester with alcoholic KOH solution led to a mixture of (*Z*)- and (*E*)-isomers of 3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidenesuccinic acid (**6**) in a ratio of approximately 1:1. Cyclization of the diacid **6** formed with N,N'-carbonyldiimidazole at room temperature led to compound **1** in 77% yield (Scheme 1).

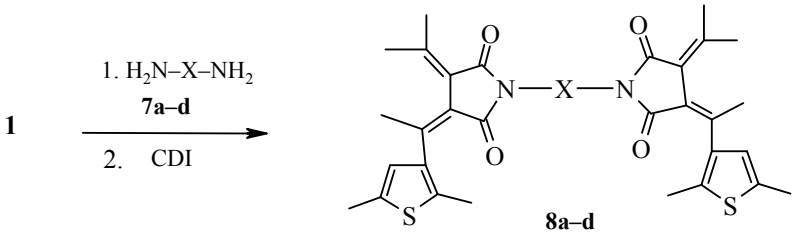
Scheme 1

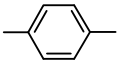
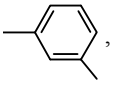
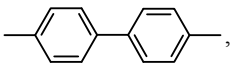
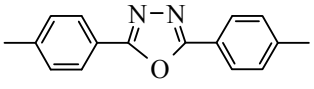


CDI – N,N'-carbonyldiimidazole

The interaction of fulgide **1** and aromatic diamines **7a-d** on boiling in benzene for 25-30 h led to the preparation of a mixture of intermediately formed regioisomeric bisamido acids. Cyclization of the latter without first purification by the method developed previously by us [8] using N,N'-carbonyldiimidazole under mild conditions at room temperature, unlike the procedures applied previously [2, 4], led to the corresponding bisfulgimides **8a-d** in 36-52% yield (Scheme 2).

Scheme 2

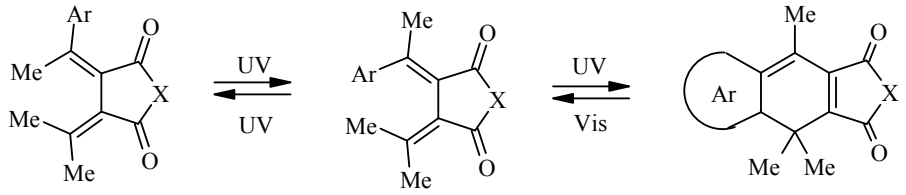


a X =  , **b** X =  , **c** X =  , **d** X = 

The structures of all the synthesized compounds were confirmed by the results of elemental analysis, data of ^{1}H NMR and IR spectroscopy, and also mass spectrometry. In the IR spectra of these compounds characteristic bands were present for amide carbonyl groups at 1710 and 1755 cm^{-1}, corresponding to the alkylidenesuccinimide [9]. Signals were observed in the ^{1}H NMR spectra for the 10 methyl groups as singlets in the region δ 2.02-2.50 ppm, and signals appeared for the protons of the thiophene fragment as a singlet at δ 6.56 ppm. The signals of the aromatic protons of phenyl substituents were present as doublets in the range δ 6.59-7.49 ppm.

It is known that fulgides and fulgimides exist in three isomeric forms [1] (Scheme 3).

Scheme 3



(*Z*)-isomer (*E*)-isomer (*C*)-isomer

X = O, NR^4

All three isomers are in photochemical equilibrium although photochromic conversions only occur between the open (*E*) and cyclic (*C*) forms. The (*Z*)-form cannot undergo cyclization because of its geometry, and energy of UV radiation is consumed additionally in its conversion into the (*E*)-isomer, which is seemingly an inevitable problem leading to a reduction in the quantum yield of cyclization when using fulgides and their derivatives. The (*Z*)- or (*E*)-configuration of fulgides and fulgimides, containing an exocyclic isopropylidene substituent, may readily be determined on the basis of ^{1}H NMR spectra. This problem has been investigated in detail in the literature [10, 11]. The configurations of similar fulgides and fulgimides are determined from the chemical shift of the methyl groups of the isopropylidene fragment.

The (*Z*)-isomers of fulgides and fulgimides are characterized by the signals of CH_3 groups of the isopropylidene fragment displayed in the δ 1.9-2.5 ppm region. However the (*E*)-CH_3 group of the isopropylidene fragment of (*E*)-isomer gives a signal at δ 1.3-1.4 ppm, which is caused by the deshielding action of the thiophene ring, displayed only in the (*E*)-isomers of fulgides and fulgimides. The signals of the methyl groups of all the fulgimides synthesized by us (compounds **8a-d**) lie in the range δ 2.02-2.50 ppm, which indicates their (*Z*)-configuration.

Intense peaks were present in the mass spectra of compounds **8a-d** for the molecular ion (*I* = 72-87%) and for the $[M\text{-}CH_3]^+$ fragment (100%). Peaks with *m/z* 189 (72%) and 217 (64%) also had high intensity, but their identification was unsuccessful due to the complex decomposition of these compounds under conditions of electron impact for mass spectrometry.

TABLE 1. Spectral Kinetic Characteristics* of Fulgimides **8a-d** in Toluene

Compound	λ_A^{max}, nm	λ_B^{max}, nm	ΔD_B^{max}	k_{AB}/k_{BA}
8a	330	528	1.2	0.7
8b	335	530	0.9	0.6
8c	335	530	1.5	0.4
8d	310	530	1.1	0.4

*λ_A^{max} and λ_B^{max} are the wavelengths of the absorption band maxima of the initial (open) **A** and photoinduced (cyclic) **B** form; D_B^{max} is the photoinduced change of optical density at the wavelength of the absorption band maximum of the photoinduced form **B** on UV irradiation through a UVS-2 filter; k_{AB}/k_{BA} is the ratio of the rate constants of photocoloration and photodecoloration of the photochromic compounds.

According to the results of the photochemical investigations of the synthesized compounds, given in Table 1, all the compounds have the same absorption maximum for the open (**A**) and cyclic (**B**) isomers, with the exception of compound **8d** (Fig. 1) in which the absorption maximum of the open form is displaced towards the short wave region by 25 nm.

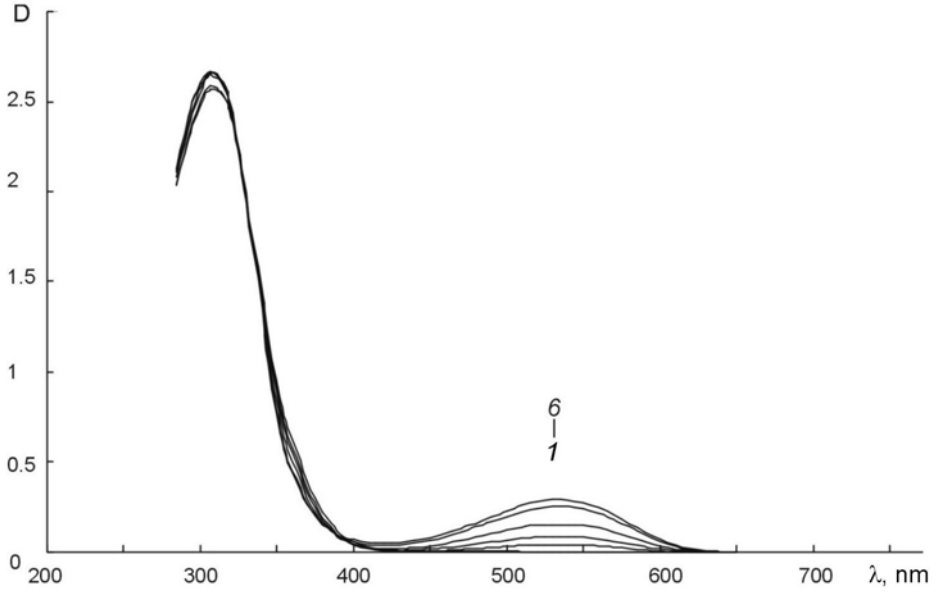


Fig. 1. Absorption spectra of fulgimide **8d** in toluene before (*1*) and after irradiation at 313 nm for 1 (*2*), 2 (*3*), 4 (*4*), 8 (*5*), and 12 (*6*) min.

This indicates that the phenyl rings and the 1,3,4-oxadiazole ring do not in fact participate in conjugation with the two fulgimide fragments.

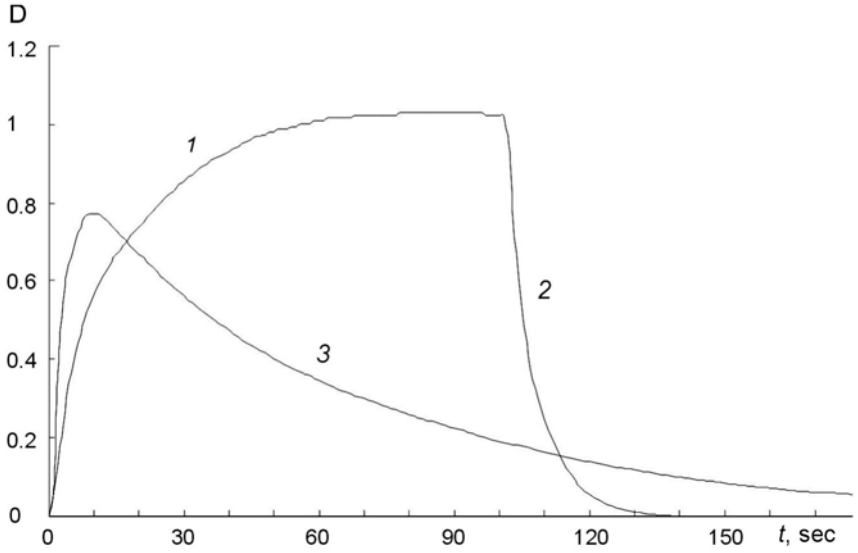


Fig. 2. Kinetics of photocoloration under the action of 313 nm radiation (*1*), photodecoloration under the action of 546 nm radiation (*2*), and photodecomposition under the action of unfiltered mercury lamp radiation (*3*) of solutions of fulgimide **8d** in toluene.

Judging by the change in optical density in the photoinduced state at the absorption maximum wavelength of the cyclic isomer the light sensitivity of the compounds does not depend on the structure of the spacer connecting the two fulgimide fragments, with the exception of structure **8c**.

Analysis of the ratio of the photocoloration and photodecoloration constants of compounds **8a-d** indicates that an increase in the length of the spacer leads to an increase in the intensity of photodecoloration of the compounds in comparison with the intensity of photocoloration of them, achieving maximum values for the compound with the greatest length of spacer, *viz*. fulgimide **8d** (Fig. 2).

In the course of the work carried out, previously unreported photochromic fulgimides of the thiophene series containing two fulgimide fragments in one molecule, linked by bridges of various length, have been obtained. The photochromic properties of the obtained compounds and the effect of the spacer linking the two fulgimide fragments on the rate of the photocoloration and photodecoloration reactions of these compounds have been investigated.

EXPERIMENTAL

The IR spectra were taken on a Perkin-Elmer-577 instrument (KBr disks). The ^{1}H NMR spectra were recorded on a Bruker WM-250 (250 MHz) spectrometer in $CDCl_3$, the mass spectra (EI) were taken on a Kratos MS-30 instrument with direct insertion of samples into the ion source, ionizing voltage 70 eV, emission current 0.1 mA, temperature in ionization chamber 250°C. Melting points were measured on a Boetius microscope stage. Analysis of reaction mixtures and a check on the purity of isolated products was carried out by TLC on Silufol UV-254 plates, eluent was ethyl acetate–petroleum ether (bp 40-70°C) in a 3:1 ratio.

Commercially available 2,5-dimethylthiophene, potassium *tert*-butylate, and N,N'-carbonyldiimidazole (Acros) were used in the work. 3-Acetyl-2,5-dimethylthiophene (**3**) [12] and 2,5-di(*p*-aminophenyl)-1,3,4-oxadiazole (**7d**) [13] were obtained by known methods.

Investigation of the photochromic properties of compounds **8a-d** was carried out in toluene solution. The concentration of compounds in solution was $2\cdot10^{-4}$ M. Measurement was carried out in a cuvette of 2 mm thickness. Absorption spectra of the open and cyclic forms were measured on a Shimadzu UV-vis or Carey (Varian) spectrophotometers over the spectral range 200-800 nm. The cyclic form was obtained after photoexcitation of a solution with radiation from a DRSh-250 mercury lamp through a UV light filter isolating radiation of λ 313 nm. Photodecoloration of a solution was achieved on irradiating with filtered radiation of λ 546 nm. The kinetics of photocoloration of solutions of fulgimides were measured at the wavelength of the absorption band maximum on irradiating previously decolored solutions of these compounds with the same radiation. The kinetics of photodecoloration were measured on irradiation of previously colored solutions of these compounds with irradiation by the mercury lines of a DRSh-250 lamp, isolated with the aid of the appropriate glass filters.

Diethyl 3-Isopropylidenesuccinate (4). Potassium *tert*-butylate (31 g, 275 mmol) was dissolved with heating in *tert*-butanol (300 ml) and a mixture of dry acetone (19 ml, 250 mmol) and diethyl succinate (52 ml, 313 mmol) was added during 1 h to the boiling solution. The reaction mixture was then boiled for 2 h, after which the solvent was distilled off, water (200 ml) was added to the residue, and extracted with ether. The aqueous layer was separated, acidified with hydrochloric acid to acid reaction, and extracted with ether. The organic layer was separated, the ether distilled off, and ethyl alcohol (200 ml) and sulfuric acid (1 ml) were added to the residue. The mixture was boiled for 12 h. After esterification, the ethyl alcohol was evaporated on a rotary evaporator, water (200 ml) was added to the residue, and the mixture was extracted with methylene chloride. The residual mobile oil after evaporation of the solvent was then vacuum distilled. Yield of compound **4** 29.5 g (56%); bp 118-120°C (8 mm Hg), n_D^{22} 1.4538 (lit. bp 100-102°C (2 mm Hg), n_D^{20} 1.4550 [7]).

(3*Z*)-3-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-4-isopropylidenesuccinic Acid (6). Potassium *tert*-butylate (11 g, 100 mmol) in dry toluene (250 ml) was placed into a round-bottomed flask fitted with a reflux condenser, a dropping funnel, and a magnetic stirrer. A solution of compound **4** (20 g, 90 mmol) and 3-acetyl-2,5-dimethylthiophene (**3**) (14.4 g, 90 mmol) in dry toluene (50 ml) was added dropwise during 30 min to the resulting suspension. The reaction mixture was stirred at room temperature for 8 h. The solvent was then distilled, water (250 ml) was added to the residue, and the mixture was extracted with ether (2×100 ml). The aqueous layer was separated, and acidified with HCl to a weakly acidic reaction, and then extracted with chloroform (3×70 ml). The organic layer was separated, dried over $CaCl_2$, and the solvent evaporated on a rotary evaporator. The residue, hemiester **5**, was dissolved in 10% ethanolic KOH solution (100 ml), and hydrolyzed for 7 h. The solvent was then distilled off to dryness, water (100 ml) was added to the residue, and the solution acidified to weakly acidic reaction. Diacid **6** was extracted with chloroform, the solvent removed, dried over $CaCl_2$, and the solvent distilled on a rotary evaporator. The residue was a dark-brown viscous oil. Petroleum ether (200 ml) and diethyl ether (30 ml) were added to it. The precipitated crystals were filtered off, washed on a Schott filter with petroleum ether, and dried in a vacuum desiccator. Diacid **6** (11.98 g, 44%) was obtained as white crystals; mp 203-205°C (lit. mp 204-205°C [6]).

(3*Z*)-3-[1-(2,5-Dimethyl-3-thienyl)ethylidene-4-isopropylidene-2,5-furandione (1). Diacid **6** (11.98 g, 41 mmol) was dissolved with stirring in dry THF (50 ml) and N,N'-carbonyldiimidazole (120 mmol) was added to the resulting solution. The reaction mixture was stirred at room temperature for 3 h. The solvent was then distilled off on a rotary evaporator, water (100 ml) was added to the residue, and the mixture extracted with methylene chloride. The solvent was evaporated, petroleum ether (20 ml) was added to the residue, and the mixture placed in the refrigerator (0-5°C) for 1 h. The precipitated crystals were filtered off on a Schott filter, and washed with petroleum ether. After recrystallization from a chloroform–petroleum ether (1:2) mixture, anhydride **1** (8.72 g, 77%) was obtained as pale-yellow crystals; mp 155-156°C (lit. mp 155-156°C [6]).

Interaction of (3*Z*)-3-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-4-isopropylidene-2,5-furandione (1) with Aromatic Diamines (General Method). Fulgide **1** (1 g, 3.6 mmol) was added to a solution of diamine **7a-d** (1.8 mmol) in dry benzene (30 ml) and the reaction mixture was boiled for 25-30 h. At the end of boiling the precipitated crystals of amido acid were filtered off and used further without additional purification. The isolated crystals were suspended in dry tetrahydrofuran (30 ml) and N,N'-carbonyldiimidazole (8 mmol) was added. The reaction mixture was stirred for 5 h at room temperature. The solvent was then distilled off on a rotary evaporator, water (100 ml) was added to the residue, and the mixture was extracted with ethyl acetate. After distilling off the solvent, the obtained amorphous solid was purified by column chromatography on silica gel with a petroleum ether–ethyl acetate (2:1) mixture.

(Z)-1,4-Phenylenebis{3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidene}pyrrolidine-2,5-dione (8a). Light-yellow crystals of compound **8a** (0.43 g, 38%) were obtained; mp 258-260°C (chloroform–petroleum ether). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.04 (6H, s, $2CH_3$); 2.12 (6H, s, $2CH_3$); 2.34 (6H, s, $2CH_3$); 2.41 (6H, s, $2CH_3$); 2.49 (6H, s, $2CH_3$); 6.56 (2H, s, 2H-4 thioph.); 7.40 (4H, s, H arom.). Mass spectrum, *m/z* (I_{rel}, %): 624 $[M]^+$ (87). Found, %: C 69.20; H 5.81; S 10.26. $C_{36}H_{36}N_2O_4S_2$. Calculated, %: C 68.91; H 5.80; S 10.17.

(*Z*)-1,3-Phenylenebis{3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidene}pyrrolidine-2,5-dione (8b). Light-yellow crystals of compound **8b** (0.4 g, 36%) were obtained; mp 174-178°C (chloroform–petroleum ether). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.02 (6H, s, $2CH_3$); 2.11 (6H, s, $2CH_3$); 2.33 (6H, s, $2CH_3$); 2.41 (6H, s, $2CH_3$); 2.48 (6H, s, $2CH_3$); 6.56 (2H, s, 2H-4 thioph.); 7.31-7.47 (4H, m, H arom). Mass spectrum, *m/z* (I_{rel}, %): 624 $[M]^+$ (72). Found, %: C 69.20; H 5.81; S 10.26. $C_{36}H_{36}N_2O_4S_2$. Calculated, %: C 68.97; H 5.78; S 10.19.

(*Z*)-4,4'-Biphenylenebis{3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidene}pyrrolidine-2,5-dione (8c). White crystals of compound **8c** (0.61 g, 49%) were obtained; mp >260°C (chloroform–petroleum ether). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.04 (6H, s, $2CH_3$); 2.12 (6H, s, $2CH_3$); 2.34 (6H, s,

2CH_3); 2.41 (6H, s, 2CH_3); 2.49 (6H, s, 2CH_3); 6.56 (2H, s, 2H-4 thioph.); 7.38 (4H, d, J = 8.2, H arom.); 7.60 (4H, d, J = 8.2, H arom). Mass spectrum, *m/z* (I_{rel}, %): 700 $[M]^+$ (81). Found, %: C 71.97; H 5.75; S 9.15. $C_{42}H_{40}N_2O_4S_2$. Calculated, %: C 71.84; H 5.71; S 8.98.

(*Z*)-4,4'-(2,5-Diphenylene-1,3,4-oxadiazolyl)bis{3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-isopropylidene}pyrrolidine-2,5-dione (8d). White crystals of compound **8d** (0.72 g, 52%) were obtained; mp 180-183°C (chloroform–petroleum ether). ^{1}H NMR spectrum, δ, ppm (J, Hz): 2.04 (6H, s, 2CH_3); 2.12 (6H, s, 2CH_3); 2.34 (6H, s, 2CH_3); 2.40 (6H, s, 2CH_3); 2.49 (6H, s, 2CH_3); 6.56 (2H, s, 2H-4 thioph.); 7.58 (4H, d, J = 8.8, H arom); 8.16 (4H, d, J = 8.8, H arom.). Mass spectrum, *m/z* (I_{rel}, %): 768 $[M]^+$ (76). Found, %: C 68.73; H 5.24; S 8.34. $C_{44}H_{40}N_4O_5S_2$. Calculated, %: C 68.61; H 5.30; S 8.17.

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