## Novel photochromic dithienylperfluorocyclopentenes with rhodanine fragments: synthesis and spectroscopic properties

M. M. Krayushkin,<sup>a\*</sup> B. V. Lichitskii,<sup>a</sup> A. A. Dudinov,<sup>a</sup> O. Yu. Kuznetsova,<sup>a</sup> I. V. Platonova,<sup>b</sup> and V. A. Barachevskii<sup>b</sup>

 <sup>a</sup>N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5328. E-mail: mkray@ioc.ac.ru
 <sup>b</sup>Photochemistry Center, Russian Academy of Sciences, 7a ul. Novatorov, 119421 Moscow, Russian Federation. Fax: +7 (495) 936 1255. E-mail: barva@photonics.ru

Novel photochromic dithienylperfluorocyclopentenes with rhodanine fragments **1a**—**c** were obtained and their spectrokinetic characteristics were examined. The open-chain and cyclic forms of these compounds absorb at longer wavelengths compared to known symmetrical dithienylperfluorocyclopentenes. The influence of the substituent nature on the photochromism of these compounds was studied.

**Key words:** synthesis, photochromism, sulfur-containing diarylethenes, dithienylethenes, rhodanines, photocoloration, photodecoloration, photodegradation.

Photochromic dihetarylethenes undergoing UV-induced reversible cyclization are of considerable interest for the design of photosensitive functional materials,<sup>1</sup> optical storage devices,<sup>2</sup> and various photoswitches.<sup>3</sup>

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The goal of the present work was to obtain novel photochromic dithienylethenes **1a**—**c** containing rhodanine fragments and study their spectrokinetic characteristics.

## **Results and Discussion**

The target dithienylethenes 1a-c were obtained from photochromic dialdehyde<sup>4</sup> 2 and various rhodanine derivatives 3a-c (Scheme 1). It should be noted that with such bases as sodium acetate in acetic anhydride or *N*-methylmorpholine, the reaction under study proceeded incompletely, giving a complex mixture of products. Good yields of compounds 1a-c were achieved only in the presence of catalytic amounts of ethylenediamine diacetate.

Products 1a-c are crystalline solids; their structures were confirmed by elemental analysis and NMR spectroscopy. The <sup>1</sup>H NMR spectra show characteristic signals for the equivalent protons at  $\delta$  7.70–7.72 for the thiophene fragment and at  $\delta$  7.89–8.05 for the methine protons.

Photochromic dihetarylethenes are known<sup>1</sup> to undergo UV-induced reversible valence isomerization between two thermally stable forms **A** and **B** (Scheme 2).

The results of a comparative spectrokinetic study of the photochromic transformations of dithienylethenes **1a**-**c** in acetonitrile for their equal concentrations  $(C=2 \cdot 10^{-4} \text{ mol } \text{L}^{-1})$  are given in Table 1 and Figs 1 and 2.



R = H(a), Me(b), Ph(c)

*i*. Ethylenediamine diacetate.

An analysis of the curves in Figs 1 and 2 shows that these compounds undergo reversible phototransformations when exposed to visible and UV radiation. It should be noted that the absorption bands of the open-chain and

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Table 1. Spectrokinetic characteristics of the photochromic transformations of dithienylethenes **1a**–**c** in acetonitrile

Com- pound	λ <sub>B</sub> <sup>max</sup> /nm	$\Delta D_{\mathbf{B}}^{\mathrm{ph}}$	$\tau_{1/2}/s$	$\lambda_{\mathbf{A}}^{\max}$ /nm	D <sub>A</sub>
1a	727	0.50	2000	284 390 405	0.73 1.72 1.72
1b	734	0.44	2500 (37.5%)	284 392 407	0.51 1.32 1.33
1c	740	0.62	2000 (28.5%)	288 393 407	0.80 2.01 2.01

*Note.* Hereafter,  $\lambda(\sigma)^{max}$  and  $\lambda_{\mathbf{B}}^{max}$  are the absorption peak wavelengths for the open-chain (**A**) and cyclic forms (**B**), respectively;  $D_{\mathbf{A}}$  is the peak optical densities of the open-chain form;  $\Delta D_{\mathbf{B}}^{\mathrm{ph}}$  is the largest photoinduced change in the peak optical density for the cyclic form in photoequilibrium;  $\tau_{1/2}$  is the time required for unfiltered radiation to halve the largest photoinduced change in the peak optical density for the peak optical density for the cyclic form in photoequilibrium.



(especially) cyclic forms of these diarylethenes experience bathochromic shifts compared to most other known sym-



**Fig. 1.** Electronic absorption spectra of compound **1c** in acetonitrile: (1) no irradiation, (2) irradiation with UV light through a UFS-1 light filter, (3) further irradiation with visible light through a KS-10 light filter, and (4) reirradiation with UV light through a UFS-1 light filter.



**Fig. 2.** Photocyclization kinetic curves of compound **1c** in acetonitrile: (1) irradiation of the open-chain form with UV light through a UFS-1 light filter, (2) dark storage, and (3) photorecyclization upon irradiation of the cyclic form with visible light through a KS-10 light filter.

metric derivatives.<sup>1</sup> Such a considerable bathochromic shift of the absorption band of the cyclic form has been observed earlier only for some symmetric perfluorocyclopentene<sup>4</sup> and tetrahydrothiophene<sup>5</sup> derivatives, as well as for asymmetric diarylethenes containing an electron-releasing substituent in one thienyl fragment and an electron-withdrawing substituent in the other.<sup>1</sup> Apparently, these experimental results can be attributed to the conjugation between the electron-releasing endocyclic S atom of the rhodanine fragment in one part of the photochromic molecule and the electron-withdrawing carbonyl group in the other rhodanine ring. It is also worth noting that the long-wavelength absorption bands of the openchain form are very much the same as the UV spectra of rhodanine derivatives of thiophene containing no photochromic fragment.<sup>6</sup>

It follows from Table 1 that introduction of a phenyl fragment into rhodanine derivative **1a** results in a bathochromic shift of the absorption band of the cyclic form, which is due to the increased conjugation in the dithienylethene molecule.

All the compounds studied are comparably photosensitive to UV light, which is evident from numerically close photoinduced changes in the optical density of the absorption peak of the cyclic form  $\Delta D^{\text{ph}}$ . Data on the photodegradation of diarylethenes exposed to unfiltered radiation of an LC-4 illuminator (Hamamatsu) show that they are not easily prone to irreversible phototransformations.

Similar results were obtained for photochromic polymer films based on poly(methyl methacrylate) and the aforesaid diarylethenes (C = 0.25 wt.% of the dry polymer weight). The difference is that the absorption bands of both the open-chain and cyclic forms experience additional bathochromic shifts (Table 2).

**Table 2.** Spectrokinetic characteristics of the photochromic transformations of dithienylethenes 1a-c in a poly(methyl methacrylate) film (C = 0.25 wt.% of the dry polymer)

Com- pound	λ <sub>B</sub> <sup>max</sup> /nm	$\Delta D_{\mathbf{B}}^{\mathrm{ph}}$	$\tau_{1/2}/s$	$\lambda_A^{max}$ /nm	D <sub>A</sub>
1a	745	0.40	3650	285	0.52
				392	1.25
				410	1.29
1b	747	0.71	4150 (40%)	283	0.86
				393	1.31
				412	1.32
1c	750	0.30	3250	290	0.51
				396	1.21
				412	1.24

To sum up, we obtained for the first time novel dithienylperfluorocyclopentenes with rhodanine fragments that undergo photochromic transformations in acetonitrile. The spectrokinetic characteristics of the photochromic transformations depend on the structures of the rhodanine substituents.

## Experimental

<sup>1</sup>H NMR spectra were recorded on Bruker AM-300 instruments (300 MHz) in DMSO- $d_6$ . Melting points were measured on a Boetius hot stage and are given uncorrected. The course of the reactions was monitored and the purity of the compounds obtained was checked by TLC (Silica gel 60 F254 plates (Merck), ethyl acetate—hexane (1 : 3)).

Spectrokinetic studies were performed in acetonitrile (Kriokhrom) and toluene (Aldrich). The working concentration of solutions was  $C = 2 \cdot 10^{-4}$  mol L<sup>-1</sup>.

Spectrokinetic studies of the photocoloration, photodecoloration, and photodegradation of dithienylethenes in solution were carried out on a Cary 50 bio spectrophotometer (Varian) in 0.2-cm-thick quartz cells; samples were irradiated with filtered and unfiltered light of an LC-4 illuminator (Hamamatsu, Japan).

Rhodanine **3a** is available from Acros. Dialdehyde **2** was prepared as described earlier,<sup>7</sup> m.p. 180–182 °C (*cf.* Ref. 7: m.p. 182 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.20 (s, 6 H, Me); 7.20 (s, 2 H, CH); 10.10 (s, 2 H, CH<sub>ald</sub>). Rhodanines **3b** (see Ref. 8) and **3c** (see Ref. 9) were prepared according to known procedures.

Synthesis of rhodanine derivatives of dithienylperfluorocyclopentenes 1a—c (general procedure). A mixture of dialdehyde 2 (0.174 g, 0.41 mmol), rhodanine 3 (0.82 mmol), and ethylenediamine diacetate (2 mg, 0.01 mmol) in a mixture of benzene (15 mL) and acetic acid (4 mL) was refluxed with a Dean—Stark trap for 10 h. After the reaction was completed (monitoring by TLC,  $R_f$  0.60), the solvent was removed and the residue was dissolved in ethyl acetate (50 mL) and washed with water (2×50 mL). Krayushkin et al.

The organic layer was dried over  $Na_2SO_4$  and concentrated; the residue was recrystallized from ethanol.

(5E,5'E)-5,5'-[(3,3,4,4,5,5-Hexafluorocyclopent-1-ene-1,2-diyl)-4,4'-bis(5-methylthiophen-2-ylmethylidene)]bis(2-thioxo-1,3-thiazolidin-4-one) (1a). Yield 78%, m.p. >300 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), & 2.08 (s, 6 H, 2 Me); 7.70 (s, 2 H, CH<sub>Het</sub>); 7.89 (s, 2 H, CH); 13.85 (s, 2 H, NH). Found (%): C, 42.84; H, 2.05; N, 4.78. C<sub>23</sub>H<sub>12</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>. Calculated (%): C, 42.19; H, 1.85; N, 4.28.

 $\begin{array}{l} (5E,5`E)-5,5'-[(3,3,4,4,5,5-Hexafluorocyclopent-1-ene-\\ 1,2-diyl)-4,4'-bis(5-methylthiophen-2-ylmethylidene)]bis(3-me-\\ thyl-2-thioxo-1,3-thiazolidin-4-one) (1b). Yield 65\%, m.p. >300 °C. \\ {}^{1}{\rm H}\ {\rm NMR}\ ({\rm DMSO-d}_6),\ \delta:\ 2.11\ ({\rm s},\ 6\ {\rm H},\ 2\ {\rm Me});\ 3.39\ ({\rm s},\ 6\ {\rm H},\ 2\ {\rm Me});\ 7.72\ ({\rm s},\ 2\ {\rm H},\ {\rm CH}_{\rm Het});\ 8.05\ ({\rm s},\ 2\ {\rm H},\ {\rm CH}).\ {\rm Found}\ (\%): \\ {\rm C},\ 44.70;\ {\rm H},\ 2.56;\ {\rm N},\ 4.78.\ C_{25}{\rm H}_{16}{\rm F}_6{\rm N}_2{\rm O}_2{\rm S}_6.\ {\rm Calculated}\ (\%): \\ {\rm C},\ 43.98;\ {\rm H},\ 2.36;\ {\rm N},\ 4.10.\end{array}$ 

 $(5E,5^{2}E)-5,5^{2}-[(3,3,4,4,5,5-Hexafluorocyclopent-1-ene-1,2-diyl)-4,4^{2}-bis(5-methylthiophen-2-ylmethylidene)]bis(3-phe-nyl-2-thioxo-1,3-thiazolidin-4-one) (1c). Yield 65%, m.p. >300 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>), & 2.11 (s, 6 H, 2 Me); 7.42 (d, 4 H, H arom.,$ *J*= 7.2 Hz); 7.50-7.60 (m, 6 H, H arom.); 7.72 (s, 2 H, CH<sub>Het</sub>); 8.05 (s, 2 H, CH). Found (%): C, 52.43; H, 2.69; N, 3.89. C<sub>35</sub>H<sub>20</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>S<sub>6</sub>. Calculated (%): C, 52.10; H, 2.50; N, 3.47.

**Preparation of films.** Poly(methyl methacrylate) (10%, 100 mg) was added to a solution of a photochrome (0.25 mg) in chloroform (1 mL). The resulting formulation (0.25% photochrome with respect to the dry polymer) was placed in a Dacron tub ( $2.5 \times 2.5$  cm) and allowed to dry completely. The Dacron substrate was removed from the dried film. The film thickness was 100–150 µm.

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