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Photochromic 1,2-dihetarylethenes with perfluorocyclopentene bridge: synthesis and spectral and kinetic study

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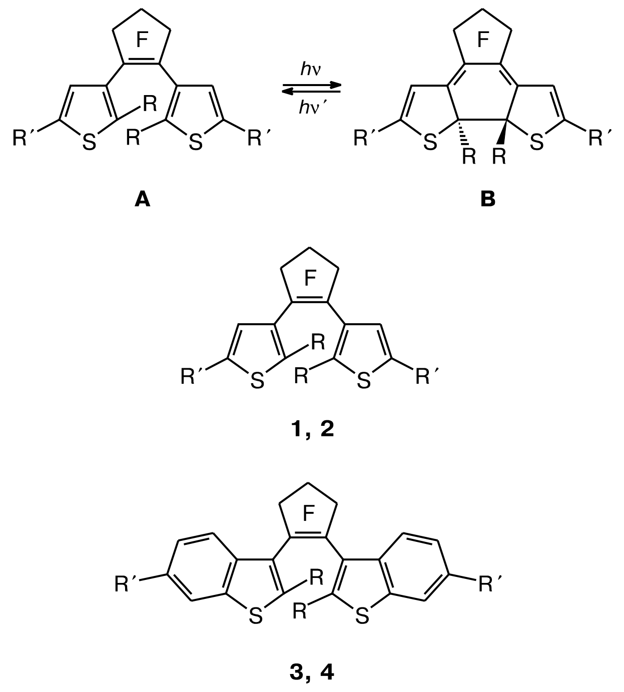
A spectral and kinetic study was carried out of some substituted 1,2-dithienylperfluorocyclopentenes and 1,2-bis(benzo[b]thienyl)perfluorocyclopentenes suitable for use as photosensitive components of photochromic recording media for optical memory. The introduction of nitro groups into the benzothienyl moieties dramatically decreases photodegradation and increases the fatigue resistance of these photochromes.

Key words: dithienylethenes, photochromism, kinetics of phototransformations.

Photochromic 1,2-dithienylethenes with a perfluorocyclopentene bridge are promising photosensitive components of optical memory devices.[1—3] They exhibit a high fatigue resistance and can undergo repeated hexatriene—cyclohexadiene photochemical transformations involving the formation of thermally stable open (**A**) and cyclic (**B**) forms (Scheme 1).

Scheme 1



1: R = C_6H_{13}, R´ = H
2: R = Et, R´ = SEt
3: R = CH_2OMe, R´ = H
4: R = CH_2OMe, R´ = NO_2

The photochromic properties of 1,2-dithienylethenes strongly depend on the nature of substituents in the thiophene ring and on the character of conjugation of the thiophene ring with other heterocyclic compounds.[4,5] In this connection search for "structure—property" relationships for photochromic compounds is topical.

The aim of this study was to synthesize photochromic dihetarylethenes **1—4** with the perfluorocyclopentene bridge linked to substituted thienyl or benzothienyl moieties and to perform a comparative analysis of their spectral and kinetic characteristics.

Photochromic products **1** and **2** were obtained following known procedures[6,7] while photochromes **3** and **4** were synthesized from 2-hydroxymethylbenzothiophene (**5**) following Scheme 2.

2-Methoxymethylbenzothiophene (**6**) is formed by boiling a sodium salt of 2-hydroxymethylbenzothiophene (**5**) with methyl iodide in THF. The interaction of ether **6** with excess bromine in THF at room temperature results in a high yield of 3-bromo-2-methoxymethylbenzothiophene (**7**). The reaction of compound **7** with Bu^nLi in THF at –70 °C and subsequent reaction with octafluorocyclopentene leads to photochromic 1,2-bis([2-methoxymethylbenzo[*b*]thiophene-3-yl])-3,3,4,4,5,5-

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Scheme 2

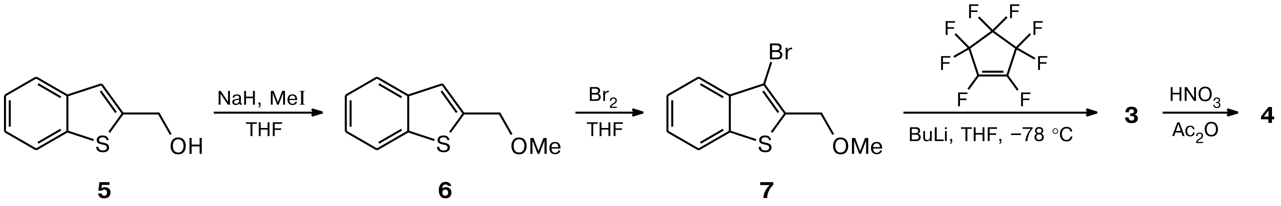

Table 1. Spectral and kinetic characteristics of perfluorocyclopentenes **1—4** in toluene

Compound	$\lambda^{\mathbf{A}}_{\max}$	$\lambda^{\mathbf{B}}_{\max}$	$A^{\mathbf{B}}_{\max}$	$k_{\mathbf{AB}}$	$k_{\mathbf{BA}}$	$t_{0.5}^{\mathrm{pd}}$ /s
	nm			s^{-1}		
1	300	532	0.37	0.18	0.09	120
2	<300	540	0.77	0.42	0.35	50
3	295, 320 п	360, 520	0.90	2.40	1.60	160
4	300, 340 п	545	0.44	0.13	0.10	600

Note. $\lambda^{\mathbf{A}}_{\max}$ and $\lambda^{\mathbf{B}}_{\max}$ are the absorption maxima wavelengths of the open (**A**) and cyclic (**B**) forms, respectively; sh is shoulder or inflection of the curve in the absorption spectrum; $A^{\mathbf{B}}_{\max}$ is the photoinduced optical density at the absorption maximum of the cyclic form **B**; $k_{\mathbf{AB}}$ and $k_{\mathbf{BA}}$ are respectively the rate constants for photocoloration and photobleaching determined under irradiation through the UFS-2 + ZhS-3 (photocoloration) and ZhS-18 + PS-7 (photobleaching) combinations of light filters from a "Colored optical glass" kit (GOST 9411-66); and $t_{0.5}^{\mathrm{pd}}$ is the photodecomposition time of the compound, determined by the twofold changes in the $A^{\mathbf{B}}_{\max}$ value.

hexafluorocyclopent-1-ene (**3**). Nitration of **3** with a mixture of nitric acid and acetic anhydride affords the photochromic product **4**.

The key spectral and kinetic characteristics of the compounds under study (in toluene) are presented in Table 1 and in Figs 1 and 2.

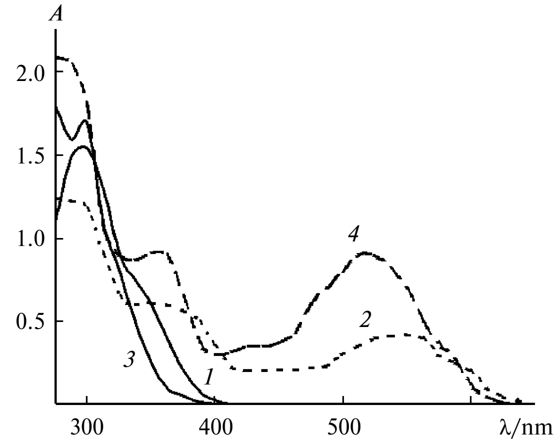

Fig. 1. Absorption spectra of dihetarylethenes **1** (*1*, *2*) and **2** (*3*, *4*) in toluene before (*1*, *3*) and after (*2*, *4*) UV irradiation.

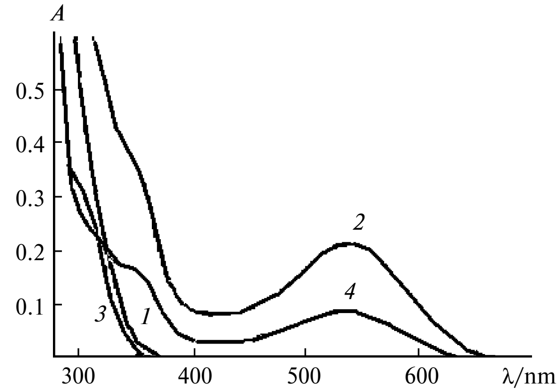

Fig. 2. Absorption spectra of dihetarylethenes **3** (*1*, *2*) and **4** (*3*, *4*) in toluene before (*1*, *3*) and after (*2*, *4*) UV irradiation.

The photoinduced changes in the absorption spectra of compounds **1** and **2** in toluene are shown in Fig. 1.

The cyclic form of dihetarylethene **1** is characterized by an absorption band at $\lambda = 532$ nm. The absorption spectrum of compound **2** differs insignificantly in spite of different substituents (see Table 1). However, the absorption maxima of the cyclic forms of both compounds experience a bathochromic shift compared with the spectrum of a related compound with R = Me and R′ = H ($\lambda^{\mathbf{B}}_{\max}$ = 508 nm).[8]

Analysis of the data in Table 1 shows that compound **2** is characterized by higher photosensitivity (photoinduced optical density is more than twice as high as for dihetarylethene **1**). The rate constant for the photocoloration of compound **2** is also higher than for compound **1**. Dihetarylethene **1** exhibits a higher resistance to irreversible phototransformations, which is more than twice as high as that of compound **2** (see Table 1).

The cyclic form of compound **3** is characterized by the absorption band with a maximum at $\lambda = 520$ nm (see Table 1 and Fig. 2, curve *2*), which is very similar to the position of the absorption maximum for a related compound with R = Me and R′ = H ($\lambda^{\mathbf{B}}_{\max}$ = 517 nm).[9] The introduction of nitro groups into the benzothiophene moiety (dihetarylethene **4**) causes a bathochromic shift of the absorption band of the open form (see Table 1, Fig. 2, curve *1*) and of the absorption maximum of the cyclic form to $\lambda = 545$ nm (see Table 1, Fig. 2, curve *4*).

The photosensitivity of compound **3** to UV radiation approaches the value measured for compound **2** (*cf.* the corresponding $A^{\mathbf{B}}_{\max}$ values in Table 1). The photocoloration and photobleaching rates are higher for compound **3** rather than **2**. The introduction of nitro groups into the benzothienyl moieties (compound **4**) causes a twofold decrease in the photoinduced optical density compared to dihetarylethene **3** and a dramatic decrease in the rate constants for photocoloration and photobleaching (see Table 1).

The thienyl derivatives of the dihetarylethenes under study exhibit a relatively low fatigue resistance. In contrast, the benzothienyl derivatives **3** and **4** are characterized by the lowest efficiency of photodegradation in toluene. This first of all concerns compound **4**, which is highly stable to irreversible photochemical transformations (see Table 1). It was also established that the use of polar acetonitrile instead of toluene (a solvent of low polarity) makes the compounds less stable to irreversible photochemical transformations.

The photoinduced cyclic forms of dithienylethenes **1—4** exhibit high thermal stability, which are retained in solutions kept in the dark for more than a month. This is indicated by the absence of any changes in the photoinduced optical density during this time interval.

Thus, the dihetarylethenes synthesized in this work are comparable in most of the spectral and kinetic parameters with the known thienyl-containing dihetarylethenes with a perfluorocyclopentene bridge. Therefore, they can be used as photosensitive components of photochromic recording media for optical memory applications. The introduction of nitro groups into the benzothienyl moieties leads to an abrupt decrease in the efficiency of photodegradation and, as a consequence, to an increase in the fatigue resistance of these photochromes.

Experimental

^{1}H NMR spectra were recorded with a Bruker WM 250 spectrometer operating at 250 MHz in $CDCl_3$ and DMSO-d$_6$. The mass spectra were obtained using a Kratos MS-30 instrument with a direct inlet system at an ionizing voltage of 70 eV. Column chromatography was performed on silica gel 70—230 mesh 60 A (Aldrich) and TLC was performed on Silicagel 60 F254 (Riedel de Haen) plates. 2-Hydroxymethylbenzothiophene (**5**) was purchased from Acros.

Spectral studies were carried out using toluene (A.C.S. spectrophotometric grade) as solvent. The concentrations of compounds in solutions were $2 \cdot 10^{-4}$ mol L^{-1}. Measurements were carried out in a cell 3 mm thick.

Absorption spectra of the open and cyclic forms of photochromic compounds were recorded with a Shimadzu UV—Vis spectrophotometer in the 200—800 nm spectral range. The cyclic forms were obtained by photoexcitation of the solutions by a DRSh-250 mercury lamp through a light filter selecting light with $\lambda = 313$ nm.

The photocoloration kinetics were studied by irradiating dihetarylethene solutions at the absorption maximum wavelength of the cyclic forms (the solutions were pre-bleached by exposure to the same radiation). The photobleaching kinetics were studied by irradiating pre-colored solutions of these compounds with the DRSh-250 lamp in the visible region (necessary spectral lines were selected with corresponding glass filters).

The kinetic curves of photodecomposition of the photochromes were used to assess their fatigue resistances under the action of intense light. Photodegradation of solutions was characterized by the time taken to halve the optical density at the absorption maximum of the cyclic form under continuous irradiation with unfiltered light of the DRSh-250 lamp.

The kinetics of thermally induced isomerization of the photoinduced form of dihetarylethenes (**B**) were studied by periodically recording the absorption spectra of the solutions (with a few day intervals). During the time interval between measurements the solutions were kept in the dark.

2-Methoxymethylbenzo[*b*]thiophene (6). To a solution of compound **5** (1 g, 6.08 mmol) in anhydrous THF (30 mL), a suspension of sodium hydride (0.48 g, 18 mmol) in paraffin (90%) was added, followed by adding MeI (1.28 g, 9 mmol) with sturring and the mixture was refluxed for 1 h (TLC monitoring). The reaction mixture was cooled, poured into water, and extracted with ethyl acetate (3×30 mL). The combined extracts were dried with $MgSO_4$, the solvent was evaporated, and oil-like residue was chromatographed on silica gel with petroleum ether—ethyl acetate (5 : 1) mixture as eluent. The yield was 0.84 g (78%), oil-like substance. Found (%): C, 67.52; H, 5.63; S, 17.68. $C_{10}H_{10}OS$. Calculated (%): C, 67.38; H, 5.65; S, 17.99. M 178.25. Mass-spectrum, *m/z*: 178 [M]$^+$. ^{1}H NMR (DMSO-d$_6$), δ: 3.27 (s, 3 H, MeO); 4.69 (s, 2 H, CH_2O); 7.25—7.55 (m, 3 H, CH arom.); 7.75—7.95 (m, 2 H, CH arom.).

3-Bromo-2-methoxymethylbenzo[*b*]thiophene (7). To a solution of compound **6** (1 g, 5.6 mmol) in THF (50 mL), a solution of bromine (0.16 g, 10 mmol) in THF (20 mL) was added with stirring for 3 h. The reaction mass was stirred for an additional 1 h and poured into water (100 mL). The solution was extracted with ether (3×40 mL), the combined extracts were washed with 0.5 *M* aqueous NaOH (200 mL), dried with $MgSO_4$, the solvent was evaporated, and the oil-like residue was chromatographed on silica gel with petroleum ether—ethyl acetate (10 : 1) mixture as eluent. The yield was 1.22 g (85%), m.p. 76—78 °C. Found (%): C, 46.82; H, 3.51; Br, 30.45; S, 12.39. $C_{10}H_9BrOS$. Calculated (%): C, 46.71; H, 3.53; Br, 31.07; S, 12.47. M 257.15. Mass-spectrum, *m/z*: 256/258 [M]$^+$. ^{1}H NMR (DMSO-d$_6$), δ: 3.40 (s, 3 H, MeO); 4.75 (s, 2 H, CH_2O); 7.40—7.55, 7.70—8.00 (both m, 2 H, CH arom.).

1,2-Bis(2-methoxymethylbenzo[*b*]thiophene-3-yl)-3,3,4,4,5,5-hexafluoro-1-cyclopentene (3). A solution of compound **7** (1 g, 3.9 mmol) in anhydrous THF (40 mL) was cooled to −78 °C in dry argon atmosphere and a 1.6 *M* solution of butyllithium in hexane (3.65 mL, 5.85 mmol) was added. The reaction mass was stirred at −78 °C for 2 h, octafluorocyclopentene (0.41 g, 1.95 mmol) was added at the same temperature, and the mixture was stirred for an additional 3 h. The reaction mass was heated to room temperature and poured into water (100 mL). The solution was extracted with ethyl acetate (3×30 mL), the combined extracts were dried with $MgSO_4$, the solvent was evaporated, and the oil-like residue was chromatographed on silica gel with petroleum ether—ethyl acetate (5 : 1) mixture as eluent. The yield was 0.58 g (56%), m.p. 102—104 °C. Found (%): C, 56.73; H, 3.42. $C_{25}H_{18}F_6O_2S_2$. Calculated (%): C, 56.81; H, 3.43. M 528.53. Mass-spectrum, *m/z*: 528 $[M]^+$. ^{1}H NMR ($CDCl_3$), δ: 3.06 and 3.45 (s, 6 H, 2 MeO); 4.00—4.70 (m, 4 H, 2 CH_2O); 7.15—7.85 (m, 8 H, CH arom.).

1,2-Bis(6-nitro-2-methoxymethylbenzo[*b*]thiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-ene (4). A solution of compound **3** (0.5 g, 0.95 mmol) in a mixture of glacial acetic acid (10 mL) and acetic anhydride (5 mL) was cooled to 10 °C and fuming nitric acid (0.5 mL) was added in such a fashion that the temperature was maintained at 10 °C. The reaction mixture was stirred for 1 h, then allowed to stay for 12 h at room temperature, and poured on ice. The residue precipitated was chromatographed on silica gel with petroleum ether—ethyl acetate (6 : 1) mixture as eluent. Nitro derivative **4** was obtained (0.38 g, 65%), m.p. 136—138 °C (from hexane). Found (%): C, 48.60; H, 2.62; N, 4.62. $C_{25}H_{16}F_6N_2O_6S_2$. Calculated (%): C, 48.55; H, 2.61; N, 4.53. M 618.53. Mass-spectrum, *m/z*: 618 $[M]^+$. ^{1}H NMR ($CDCl_3$), δ: 3.26 and 3.49 (s, 6 H, 2 MeO), 4.10—4.80 (m, 4 H, 2 CH_2O); 7.50—8.40 (m, 6 H, CH arom.).

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