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PHOTOCHROMIC DIHETARYLETHYLENES. 22*. SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF UNSYMMETRICAL ALKYLTHIO-SUBSTITUTED 1,2-BIS(DITHIENYL)PERFLUOROCYCLOPENTENES*[2]

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Certain unsymmetrical 1,2-bis(dithienyl)perfluorocyclopentenes have been synthesized containing alkylthio, bromo, carboxy, and benzothiazolyl substituents in the thiophene rings. It was shown that on irradiation with UV light they all display photochromic properties, with the exception of the derivative containing an alkylthio group in the reaction center of one of the thiophene rings.

Keywords: unsymmetrical alkylthio-substituted 1,2-bis(dithienyl)perfluorocyclopentenes, 1-(2-ethyl-5-ethylthio-3-thienyl)heptafluorocyclopentene, photo-chromes.

Previously we synthesized vicinally substituted perfluorocyclopentenes (PFCP) **1a,b** in which the fluorinated ring was linked symmetrically with thienyl rings bearing alkyl and alkylthio groups (Scheme 1) [2,3]. We noticed that the presence of alkylthio groups in positions 2 or 5 of the thiophene rings activates the thiophene ring in electrophilic substitution and metallation reactions, which facilitates the subsequent introduction of various substituents into the free positions of the heterocycle. The series of photochromes **1** with substituents in the 4 and 4' positions of the thiophene rings was obtained for the first time by the functionalization of compound **1b** [4].

Unsymmetrical alkylthio-substituted PFCP have been synthesized in the present work having substituents of various nature in the thiophene rings, containing alkylthio groups either in the reaction center of one of the thiophene rings (product **2a**) or in position 5 (products **2b-e**) (Scheme 2), and their photochromic properties have been investigated. A convenient starting material for these purposes was the mono-substitution product of perfluorocyclopentene, 1-(2-ethyl-5-ethylthio-3-thienyl)heptafluorocyclopentene (**3**). We note that dibromide **4d** [4], necessary for its synthesis and described by us previously [4], was obtained successfully in higher yield (~80%) on using a bromide-bromate mixture as brominating agent. The unsymmetrical dithienylPFCP **2a-c** were obtained by the interaction of 1-(2-ethyl-5-ethylthio-3-thienyl)PFCP (**3**) with the appropriate bromides **4a-c**.

* For Part 21 see [1].

*[2] For the anniversary of Academician N. K. Kochetkov.

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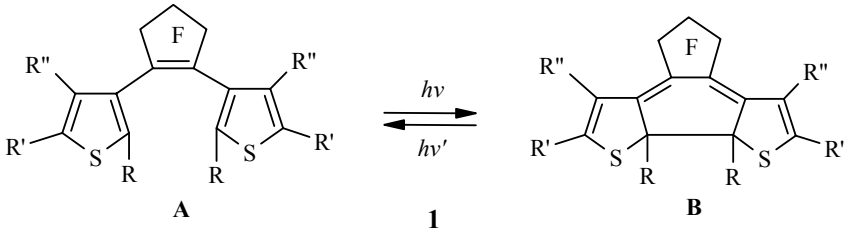
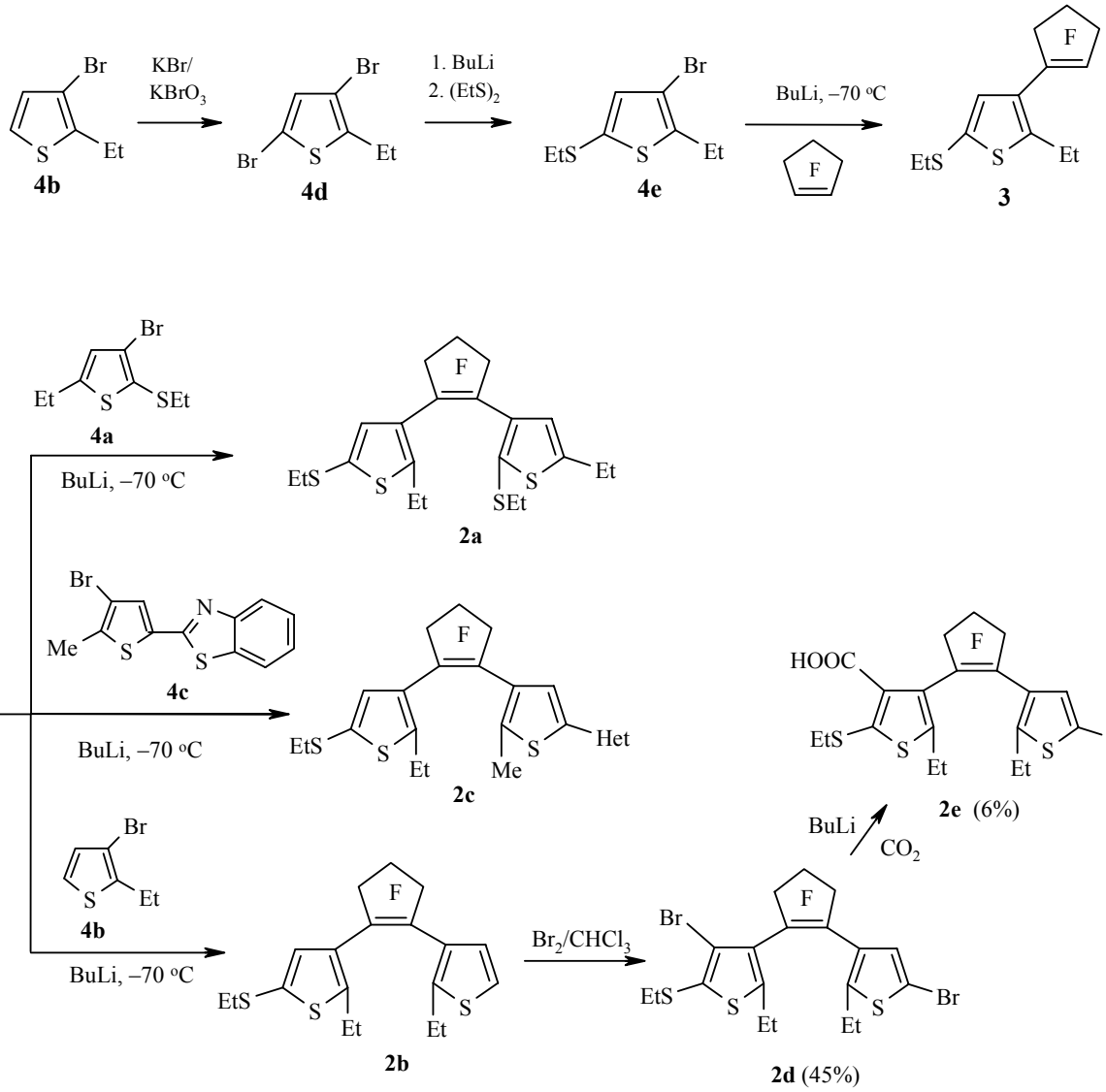
Scheme 1



1 a R = SEt, R' = Et, R" = H; **b** R = Et, R' = SEt, R" = H; **c** R = Et, R' = SEt, R" = Br, CO_2H, CO_2Me, CONHAr

Scheme 2



The PFCP **2b** with one unsubstituted α position was used for the synthesis of new photochromic dithienylethylenes. Reaction with an equimolar quantity of bromine in $CHCl_3$ gave dibromide **2d** in 45% yield, from which the diacid **2e** was successfully isolated (6%) by the sequential action of BuLi and CO_2. The dithienylPFCP **2a-d** were isolated by column chromatography from the reaction mixtures as viscous oils and were characterized by elemental analysis, UV, ^{1}H NMR, ^{19}F NMR, and mass spectra. We note that for compound **2a**, as for **1a**, having respectively an alkylthio group in both or one thiophene ring in position 2, decomposition under electron impact begins with elimination of an ethylthio group (in the mass spectra there are peaks for M-61 [M-SC_2H_5]), while for 2-ethyl-5-ethylthio-substituted **2b** and **1b** elimination of ethyl groups is observed (M-29 and M-58) [3]. This permits the suggestion that the excited molecular ions of compounds **1** and **2** formed on electron impact (as on photochemical action) undergo sigmatropic cyclization into structure **B** (Scheme 1), the initial decomposition of which is linked solely with elimination of the substituent (EtS and Et) in position 2 of the heterocycle.

The photochemical properties of the synthesized compounds were investigated in acetonitrile solution on irradiation with UV light at a wavelength of 313 nm (forward reaction) and 578 nm (reverse reaction). Compounds **2b-e** are photo-chromes. Their typical absorption spectrum is given in Fig. 1 (for dibromide **2d** as example). Isosbestic points were observed for all compounds, coinciding with the execution of the forward and reverse reactions. The dark reaction was absent or very slow. For dibromide **2d** the drop in optical density of the closed form was 8% after 340 h (>14 days). The long wave absorption maxima of the open (**A**) and cyclic (**B**) forms of the compounds investigated are given in Table 1.

TABLE 1. Longwave Absorption Maxima of Forms **A** and **B** for Compounds

Compound	λ_{max}, nm	
	A	**B**
2b	236	551
2c	333	619
2d	244	568

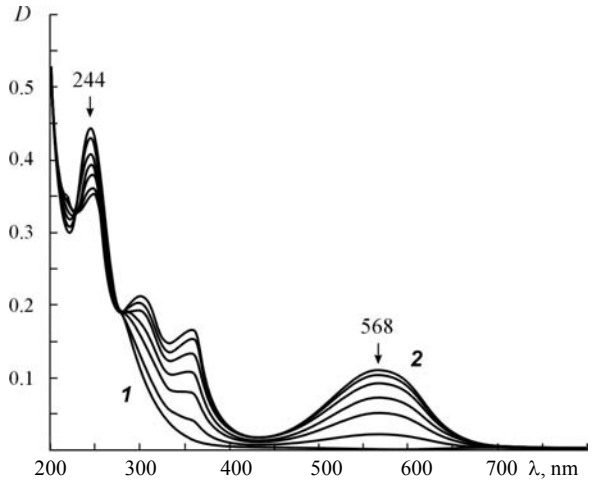


Fig. 1. Change in the absorption spectrum of compound **2d** in acetonitrile on irradiation with UV light, λ = 313 nm (forward reaction) and λ = 578 nm (reverse reaction): 1) absorption spectrum of form **A**; 2) absorption spectrum in the photostationary state (exposure 350 sec). Intermediate spectra were obtained at exposures of 5, 15, 40, 100, and 225 sec.

In the course of our work on the investigation of the effect of substituents at various positions of the thiophene ring on the photochromic properties of alkylthio-substituted 1,2-bis(dithienyl)perfluorocyclopentenes of type **1a,b** [2,3], it was shown that 2-alkylthio derivatives **1a** do not display photochromic properties on irradiation with UV light, while the isomeric 5-alkylthioPFCP **1b** are photochromes.

We have established that compound **2a,** containing an ethylthio group at position 2 in one of the thiophene rings, like bis(ethylthio)-substituted **1a**, does not possess photochromic properties. It is necessary to stress that the analogously constructed dithienyl- [5] and dithiazolylPFCP [6], containing a methoxy group in both or in only one of the heterocyclic rings at the reaction center (position 2), display photochromic properties. The reasons for the anomalous behavior of dithienylethylenes **1a** and **2a** under irradiation conditions require special investigation, however the data obtained by us probably indicate the expediency of constructing photochromes from dithienylethylenes with alkylthio groups in the reactive positions of the thiophene rings.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker WM 250 (250 MHz) instrument in solution in $CDCl_3$ and DMSO-d_6, and the ^{19}F NMR spectra on a Bruker AC 250 (188 MHz) instrument in $CDCl_3$ (standard was $CFCl_3$). Mass spectra were obtained on a Kratos MS 30 instrument at an ionizing energy of 70 eV with direct insertion of samples into the ion source. Column chromatography was carried out on silica gel 70-230 mesh 60 Å (Aldrich), and thin layer chromatography on Silicagel 60 F254 plates (Riedel de Haen). Irradiation with UV light was carried out with a high pressure mercury lamp DPSh 500 using light filters to separate the lines of the mercury spectrum (313 and 578 nm). The intensity of the radiation from the mercury lamp was determined with the aid of an F4 photoelement calibrated by ferrioxalate actinometry [7] for λ = 313 nm and actinometry based on Reinecke's salt [8] for λ = 578 nm. Absorption spectra were recorded on a Shimadzu UV 2101PC spectrophotometer.

3,5-Dibromo-2-ethylthiophene (4d). Bromide-bromate solution (30 ml, equiv. to 1.6 g, 10 mmol Br_2) was added dropwise with stirring to a mixture of 3-bromo-2-ethylthiophene **4b** [9] (1.75 g, 9 mmol) in ether (10 ml) and conc. HCl (10 ml) at 0-3°C. The mixture was stirred for 2 h at 20°C, the ether layer was separated, washed with water, with 5% $NaHCO_3$, with water, dried over $CaCl_2$, and distilled in vacuum. Dibromo compound **4d** (1.94 g, 78.5%) was obtained of bp 110-120°C/10 mm Hg, n_D^{20} 1.6000, which was used for further syntheses. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.27 (3H, t, *J* = 7.10, $\underline{CH_3}CH_2$); 2.72 (2H, q, *J* = 7.10, $\underline{CH_2}CH_3$); 6.85 (1H, s, H-4) corresponding to the data of [4].

3-Bromo-2-ethyl-5-(ethylthio)thiophene (4e) was obtained from bromo compound **4d** by the method of [4] in 75% yield.

1-(2-Ethyl-5-ethylthio-3-thienyl)heptafluorocyclopentene (3). Butyllithium (0.13 g, 2.2 mmol) in hexane (1.5 ml) was added to a solution of 3-bromo-2-ethyl-5-(ethylthio)thiophene **4e** (0.5 g, 2 mmol) in dry ether (3 ml) at -70°C in an atmosphere of Ar and then octafluorocyclopentene (0.26 ml, 2 mmol) was added in two portions after 20 min. The mixture was stirred for 1 h at -70°C, then 1 h at 20°C, cooled to 0°C, and hydrolyzed with dilute HCl (1:10). The organic layer was separated, washed with water to neutral reaction, dried over $CaCl_2$, and the solvent distilled off. The residue (0.6 g dark oil) was chromatographed on a column (eluent hexane) to give 2-ethyl-5-ethylthiothiophene (90 mg), photochromic 1,2-bis(2-ethyl-5-ethylthio-3-thiophenyl)hexafluorocyclopentene **1b** [3] (90 mg: 18%), and heptafluorocyclo-pentene **3** (0.34 g, 46%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.21-1.35 (6H, m, CH_3); 2.60-2.88 (4H, m, CH_2); 7.05 (1H, s, H-4). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm, standard $CFCl_3$: -108.472 (2F, CF_2-5'); 118.02 ($\underline{CF_2}$-CF); -126.94 ($\underline{CF}$-CF_2); 129.80 (CF_2-4'). Mass spectrum, *m/z* (I_{rel}, %): 364 (40) $[M]^+$; 349 (60) $[M-15]^+$; 321 (60). Found, %: C 43.26; H 3.38. $C_{13}H_{11}F_7S_2$. Calculated, %: C 42.86; H 3.04. M 364.28.

1-(5-Ethyl-2-ethylthio-3-thienyl)-2-(2-ethyl-5-ethylthio-3-thienyl)hexafluorocyclopentene (2a). Butyllithium (0.35 g, 0.4 ml, 0.55 mmol) in hexane was added in an atmosphere of Ar to a solution of bromo compound **4a** [10] (0.125 g, 0.5 mmol) in dry ether (3 ml) cooled to -70°C. After 30 min fluoro compound **3** (0.18 g, 0.5 mmol) in dry ether (5 ml) was added and the mixture stirred for 1 h at -70°C, then for 1 h at 20°C, and hydrolyzed with dilute HCl (1:10). After the usual treatment described above for fluoro compound **3** and distilling off the solvent, an oil (0.27 g) was obtained, from which by chromatography on a column (eluent hexane) was isolated unreacted fluoro compound **3** (100 mg), a mixture (90 mg) of bromo compound **4a** with 2-ethyl-5-(ethylthio)thiophene, and PFCP **2a** (30 mg, 11%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.97, 1.12 (6H, both t, *J* = 7.25 $\underline{CH_3}CH_2$); 1.28 (6H, m, $\underline{CH_3}CH_2S$); 2.28 (2H, q, 2-$\underline{CH_2}CH_3$); 2.56 (2H, q, *J* = 7.25, 5-$\underline{CH_2}CH_3$); 2.80 (4H, m, $CH_3\underline{CH_2}S$); 6.82 (1H, s, H-4); 7.09 (1H, s, H-4'). Mass spectrum, *m/z* (I_{rel}, %): 516 (13) $[M]^+$; 455 (32) $[M\text{-}SC_2H_5]^+$; 427 (19); 394 (27) $(M\text{-}2SC_2H_5]^+$. Found, %: C 49.22; H 4.45. $C_{21}H_{22}F_6S_4$. Calculated, %: C 48.82; H 4.29. M 516.66.

1-(2-Ethyl-5-ethylthio-3-thienyl)-2-(2-ethyl-3-thienyl)perfluorocyclopentene (2b) was obtained analogously to compound **2a** from bromo compound **4b** (0.16 g, 0.84 mmol), BuLi (0.9 mmol) in hexane, and fluoro compound **3** (0.3 g, 0.84 mmol). After column chromatography (eluent hexane) PFCP **2b** (0.11 g, 30%) was isolated as a clear oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.97, 1.10 (6H, m, t, $\underline{CH_3}CH_2$); 1.30 (3H, t, *J* = 7.3, $\underline{CH_3}CH_2S$); 2.15-2.35 (4H, m, $\underline{CH_2}CH_3$); 2.80 (2H, q, *J* = 7.3, $S\underline{CH_2}CH_3$); 7.05 (2H, m, H-4,4'); 7.22 (1H, d, *J* = 5.18, H-5). Mass spectrum, *m/z* (I_{rel}, %): 456 (40) $[M]^+$; 427 (30) $[M\text{-}C_2H_5]^+$. Found, %: C 50.30; H 4.29. $C_{19}H_{18}F_6S_3$. Calculated, %: C 49.99; H 3.97. M 456.54.

1-(2-Ethyl-5-ethylthio-3-thienyl)-2-[5-(2-benzothiazolyl)-2-methyl-3-thienyl]hexafluorocyclopentene (2c). Butyllithium (0.32 g, 0.5 mmol) in hexane was added with vigorous stirring in an atmosphere of Ar to a suspension of bromo compound **4c** [11] (0.15 g, 0.48 mmol) in dry THF (5 ml), freshly distilled over $LiAlH_4$, at -70°C. After 30 min a solution of fluoro compound **3** (0.18 g, 0.5 mmol) in dry ether (1 ml) was added, the mixture was stirred for 2 h at -70°C, 2 h at 20°C, and then hydrolyzed with dilute HCl (1:10). The mixture was evaporated on a rotary evaporator, the residue was dissolved in benzene, washed with water to neutral reaction, and dried over $CaCl_2$. The benzene was distilled off, and the residue, an oil (0.3 g), was chromatographed on a column (eluent benzene). Product **2c** (oil, 0.128 g, 46%) was obtained. ^{1}H NMR spectrum (DMSO-D_6), δ, ppm (*J*, Hz): 0.88 (3H, t, $\underline{CH_3}CH_2$); 1.20 (3H, t, *J* = 7.3, $\underline{CH_3}CH_2S$); 2.10 (1H, s, CH_3); 2.38 (2H, q, $\underline{CH_2}CH_3$); 2.85 (2H, q, *J* = 7.3, CH_2S); 7.15 (1H, s, H-4); 7.48-7.52 (2H, m, H-5', H-6' arom.); 7.80 (1H, s, H-4'); 8.0, 8.15 (2H, both d, *J* = 8.4, H-4', H-7' arom.). Mass spectrum, *m/z* (I_{rel}, %): 575 (100) $[M]^+$. Found, %: C 52.45; H 3.56. $C_{25}H_{19}F_6NS_4$. Calculated, %: C 52.16; H 3.33. M 575.66.

1-[(4-Bromo-2-ethyl-5-ethylthio-3-thienyl)-2-(5-bromo-2-ethyl-3-thienyl)]hexafluorocyclopentene (2d). Bromine (0.16 g, 1 mmol) in $CHCl_3$ (1 ml) was added gradually to a boiling solution of PFCP **2c** (0.456 g, 1 mmol) in $CHCl_3$ (3 ml). The mixture was boiled for 12 h, and left for 12 h at 20°C. The mixture was washed with 10% $NaHCO_3$ solution, with water, dried over $CaCl_2$, and the solvent distilled off. The residue, an oil (0.34 g), was chromatographed on a column (eluent hexane) and dibromo compound **2d** (0.26 g, 43%) was obtained. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.90-1.10 (6H, m, $\underline{CH_3}CH_2$); 1.30 (3H, m, $\underline{CH_3}CH_2S$); 2.55, 2.70, 2.85 (about 2H, q, *J* = 7.3, $\underline{CH_2}CH_3$, $\underline{CH_2}S$); 6.90 (1H, s, H-3). Mass spectrum, *m/z* (I_{rel}, %): 612 (for ^{79}Br isotope) (64) $[M]^+$; 533 (85) $[M\text{-}Br]^+$; 454 (55) $[M\text{-}2Br]^+$. Found, %: C 37.44; H 2.83. $C_{19}H_{16}Br_2F_6S_3$. Calculated, %: C 37.15; H 2.63. M 614.33. On interacting PFCP **2c** with 2 mole Br_2 the yield of dibromo compound **2d** was 55%.

1-[(4-Carboxy-2-ethyl-5-ethylthio-3-thienyl)-2-(5-carboxy-2-ethyl-3-thienyl)]hexafluorocyclopentene (2e). A solution of BuLi (0.34 mmol) in hexane was added with vigorous stirring in an atmosphere of Ar to a solution of dibromo compound **2d** (0.1 g, 0.32 mmol) in dry ether (5 ml) cooled to -70°C. After 1 h the solution was poured onto dry ice in ether, left for 12 h at 20°C, and hydrolyzed with water (4 ml). The organic layer was separated, extracted with 10% NaOH, the combined aqueous fractions were acidified with dilute HCl (1:1), the precipitated solid was filtered off, washed with water, dried, and diacid **2e** (10 mg: 6%) was obtained;

mp 182-184°C (EtOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 0.95, 1.15 (3H, both t, *J* = 7.3, $\underline{CH_3}CH_2$); 1.28 (3H, m, $\underline{CH_3}CH_2S$); 2.53, 2.75, 2.82 (2H, q, *J* = 7.3, $\underline{CH_2}CH_3$, $\underline{CH_2}S$); 7.75 (1H, s, H-3). Mass spectrum, *m/z* (I_{rel}, %): 544 (100) $[M]^+$. Found, %: C 46.57; H 3.61. $C_{21}H_{18}F_6O_4S_3$. Calculated, %: C 46.32; H 3.33. M 544.56.

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