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Synthesis and photochromic properties of thiosemicarbazide and thiocarbazate derivatives of dithienylperfluorocyclopentene

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A number of new thiosemicarbazide and thiocarbazate derivatives of dithienylperfluorocyclopentene have been synthesized. Spectral-kinetic study of photochemical transformations of these compounds was performed. All the compounds obtained exhibit photochromic properties. Dependencies of spectral characteristics of two thermally stable forms and kinetic properties of photocoloration and photodegradation processes from the nature of substituents affecting the conjugated bonds length in the molecules were found.

Key words: synthesis, photochromism, sulfur-containing diarylethenes, photocoloration, photobleaching, photodegradation.

Thermally irreversible photochromic compounds from the class of diarylethenes (DAE) possessing unique thermal stability of the photoinduced form remain the most promising for the use in various fields of photonics,[1] in particular, for development of registration media for optical memory with superhigh information capacity,[2] photoswitches of various types.[3] Development of photoactive coordination compounds is one of important problems in the creation of optoelectronic devices.[4] Photocontrolled systems of this type with the use of photochromic organic compounds and nanoparticles of noble metals are of special interest. For accomplishing efficient molecular interaction of photochromic compounds with nanoparticles of noble metals, as a rule, derivatives of photochromic compounds with thiol groups are used, that creates certain difficulties in accomplishing their synthesis.[5—7]

In the present work, results of spectral-kinetic study of photochromic transformations in the series of sulfur-containing DAE without thiol substituents are represented for the first time.

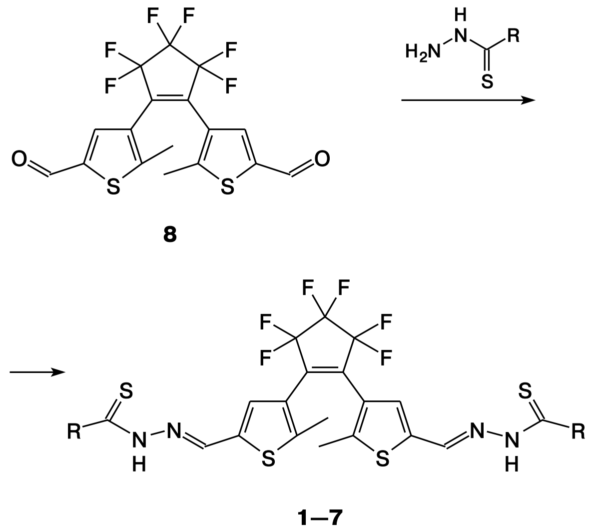
Experimental

^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz) in DMSO-d$_6$. Melting points were measured on a Boetius heating stage and uncorrected. Reaction course and purity of compounds obtained were monitored by TLC (Merck Silica gel 60 F254 plates, eluent: ethyl acetate—hexane).

Diarylethenes **1—7** were obtained from dithienylperfluorocyclopentene **8** and different thiosemicarbazide derivatives or methyl dithiocarbazate (Scheme 1). Aldehyde **8** was obtained according to the procedure described earlier.[8]

A mixture of aldehyde **8** (0.06 g, 0.14 mmol) and the corresponding thiosemicarbazide or methyl dithiocarbazate

Scheme 1



8

1—7

R = NH$_2$ (**1**), NHPh (**2**), 4-MeC$_6$H$_4$NH (**3**), 2-MeC$_6$H$_4$NH (4), 4-FC$_6$H$_4$NH (**5**), 2-FC$_6$H$_4$NH (**6**), SMe (**7**)

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Table 1. Yields, melting points, ^{1}H NMR spectroscopic (DMSO-d$_6$) and elemental analysis data for compounds **1—7**

Compound	Yield (%)	M.p. /°C	Found/Calculated (%) C	H	N	Molecular formula	^{1}H NMR (δ, *J*/Hz)
1	68	254—256	40.12 39.99	2.94 2.83	14.86 14.73	$C_{19}H_{16}F_6N_6S_4$	1.98 (s, 6 H, 2 CH$_3$); 7.57 (s, 2 H, CH$_{Het}$); 8.34 (s, 2 H, CH); 13.32 (s, 2 H, NH$_2$)
2	62	>300	51.70 51.51	3.41 3.35	11.80 11.63	$C_{31}H_{24}F_6N_6S_4$	1.98 (s, 6 H, 2 CH$_3$); 7.15 (m, 2 H, arom.); 7.39 (m, 4 H, arom.); 7.57 (m, 4 H, arom., 2 H, CH$_{Het}$); 8.28 (s, 2 H, CH); 9.80 (s, 2 H, NH); 11.89 (s, 2 H, NH)
3	54	>300	52.85 52.79	3.89 3.76	11.24 11.19	$C_{33}H_{28}F_6N_6S_4$	1.92 (s, 6 H, 2 CH$_3$); 2.29 (s, 6 H, 2 CH$_3$); 7.12 (d, 4 H, arom., *J* = 7.2); 7.42 (d, 4 H, arom., *J* = 7.2); 7.54 (s, 2 H, CH$_{Het}$); 8.28 (s, 2 H, CH); 9.72 (s, 2 H, NH); 11.87 (s, 2 H, NH)
4	56	>300	52.96 52.79	3.87 3.76	11.32 11.19	$C_{33}H_{28}F_6N_6S_4$	1.98 (s, 6 H, 2 CH$_3$); 2.21 (s, 6 H, 2 CH$_3$); 7.12—7.38 (m, 8 H, arom.); 7.52 (s, 2 H, CH$_{Het}$); 8.28 (s, 2 H, CH); 9.68 (s, 2 H, NH); 11.86 (s, 2 H, NH)
5	66	>300	49.28 49.07	3.15 2.92	11.39 11.08	$C_{31}H_{22}F_8N_6S_4$	1.92 (s, 6 H, 2 CH$_3$); 7.18 (m, 4 H, arom.); 7.51 (m, 4 H, arom.); 7.54 (s, 2 H, CH$_{Het}$); 8.28 (s, 2 H, CH); 9.81 (s, 2 H, NH); 11.90 (s, 2 H, NH)
6	60	>300	49.19 49.07	3.22 2.92	11.27 11.08	$C_{31}H_{22}F_8N_6S_4$	1.92 (s, 6 H, 2 CH$_3$); 7.13—7.30 (m, 6 H, arom.); 7.54 (s, 2 H, CH$_{Het}$); 7.58—7.64 (m, 2 H, arom.); 8.28 (s, 2 H, CH); 9.72 (s, 2 H, NH); 12.05 (s, 2 H, NH)
7	64	>300	40.13 39.86	2.99 2.87	8.94 8.85	$C_{21}H_{18}F_6N_4S_6$	1.92 (s, 6 H, 2 CH$_3$); 2.48 (s, 6 H, 2 CH$_3$); 7.58 (s, 2 H, CH$_{Het}$); 8.36 (s, 2 H, CH); 13.32 (s, 2 H,NH)

(0.29 mmol) in ethanol (3 mL) was refluxed for 4 h. Then the reaction mixture was cooled, a precipitate formed was filtered off. Basic physico-chemical characteristics of compounds **1—7** obtained are given in Table 1.

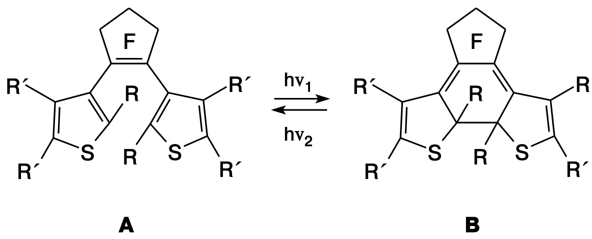
Dimethyl sulfoxide (DMSO) was used for obtaining solutions of photochromic DAE. A working concentration of these solutions was 2 • 10^{-4} mol L^{-1}.

Spectral-kinetic studies of the processes of DAE photocoloration, photobleaching, and photodegradation in solution were performed using Varian Cary 50 bio spectrophotometer in 0.2-cm quartz cuvettes. Irradiation was made by filtered and nonfiltered light of the Hamamatsu LC-4 lamp.

Results and Discussion

It is known that photochromic DAE perfluorocyclopentene derivatives undergo reversible isomerization between two thermally stable forms:[1] open (**A**) and cyclic (**B**) (Scheme 2).

Scheme 2



Results of comparative spectral-kinetic studies of photochromic transformations of DAE in DMSO at the same concentration of compounds in solution (2 • 10^{-4} mol L^{-1}) are given in Figs 1—3, as well as in Table 2.

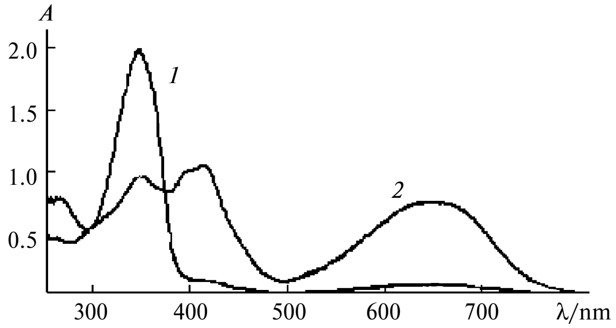


Fig. 1. Absorption spectra for compound **1** in DMSO before (*1*) and after irradiation by the UV light through a light filter UFS-1 (*2*).

Typical absorption spectra of the starting open and photoinduced cyclic forms are shown in Fig. 1, whereas

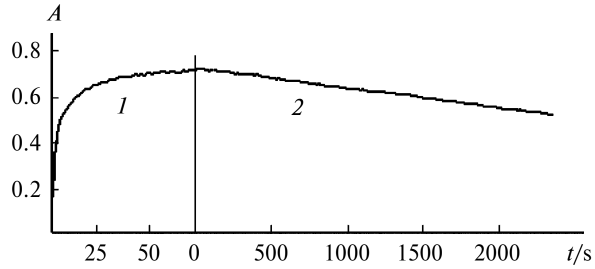


Fig. 2. Kinetics of the photocoloration under influence of the UV light through a light filter UFS-1 (*1*) and photobleaching under influence of the visible light through a light filter OS-12 (*2*) for the solution of compound **1** on the wavelength 660 nm in DMSO.

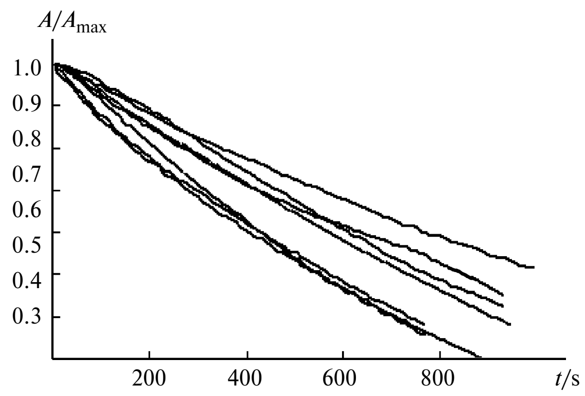


Fig. 3. The $A/A_{\max}$ value versus irradiation time with nonfiltered light for the DAE derivatives studied in DMSO solution.

Table 2. Spectral-kinetic characteristics of photochromic transformations of DAE in DMSO

Compound	$\lambda_{\mathbf{A}}^{\max}$	$\lambda_{\mathbf{B}}^{\max}$	$\Delta A_{\mathbf{B}}^{\mathrm{phot}}$	$k_{\mathbf{A-B}}/\mathrm{s}^{-1}$	$\tau_{1/2}^{\mathrm{photodeg}}/\mathrm{s}$
	nm				
1	340	648	0.8	0.82	570
2	350	660	0.6	0.47	760
3	350	650	1.0	0.39	985
4	347	650	0.8	0.47	1015
5	345	655	0.7	0.47	590
6	345	660	0.9	*	890
7	360	657	0.6	0.29	550

Note: $\lambda_{\mathbf{A}}^{\max}$ and $\lambda_{\mathbf{B}}^{\max}$ are the wavelengths of the absorption band maxima for the open (**A**) and cyclic (**B**) forms; $\Delta A_{\mathbf{B}}^{\mathrm{phot}}$ is the maximum change of the photoinduced optical density in the absorption band maximum of the cyclic form (**B**) under influence of the UV irradiation in the photoequilibrium state; $k_{\mathbf{A-B}}$ is the rate constant of phototransformation of the open form (**A**) to the cyclic form (**B**) under influence of the UV irradiation; $\tau_{1/2}^{\mathrm{photodeg}}$ is the time for the $\Delta A_{\mathbf{B}}^{\mathrm{phot}}$ value to decrease by a factor of 2 under influence of the nonfiltered irradiation.
* $k_1 = 0.72$, $k_2 = 0.17$.

kinetics of the reversible photoinduced transformations between these forms, in Fig. 2.

From Table 2, it follows that introduction of an aryl fragment onto amino derivative **1** in all the cases leads (compounds **2**—**6**) to a bathochromic shift of the absorption bands of both the open and cyclic forms, which is due to the increase of conjugation in the DAE molecules containing the aryl substituent. Introduction of a methyl group at different positions of the benzene ring (compounds **3** and **4**) results in the hypsochromic shift of the absorption band of the cyclic form, which apparently is due to the lowering conjugation because of electron-donating effect of the methyl substituent. Replacement of the methyl groups with the fluorine atoms (compounds **5** and **6**) leads to the opposite effect, which confirms influence of the electronic factor.

The largest bathochromic shift of the absorption band of the open form is found for compound **7**, in which the amino group was exchanged for the methylsulfanyl group.

All the compounds studied possess comparable light sensitivity to the UV irradiation, which is indicated by the close to each other $\Delta A_{\mathbf{B}}^{\mathrm{phot}}$ values. For the most compounds, the phototransformation process of the open form to cyclic is described by the exponential curve. Amino-substituted DAE **1**, apparently possessing the lowest steric hindrance in photoisomerization, is characterized by the highest rate constant.

Attention should be paid to a decrease in the efficiency of DAE photodegradation after introduction of methyl substituents onto the aryl fragment. Fluorination, as well as replacement of the amino group with the methylsulfanyl group, on the contrary, reduce stability of compounds to the irreversible photochemical transformations (see Fig. 2). *o*-Methylphenyl-substituted DAE **4** possesses the highest stability to the photodegradation (see Fig. 3).

In conclusion, the synthetic and spectral-kinetic studies performed resulted in the first synthesis of seven new sulfur-containing DAE, which undergo photochromic transformations in DMSO solution. Spectral-kinetic characteristics of photochromic transformations depend on the structures of the sulfur-containing substituents.

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