Coumarinyl(thienyl)thiazoles as new fluorescent molecular photoswitches*

A. Yu. Bochkov,[a] V. N. Yarovenko,[b] V. A. Barachevskii,[c] B. V. Nabatov,[b] M. M. Krayushkin,[b] S. M. Dolotov,[a] V. F. Traven´,[a] and I. P. Beletskaya[d]*

[a]*D. I. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya pl., 125047 Moscow, Russian Federation. E-mail: traven@muctr.ru*
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation.*
[c]*Photochemistry Center of the Russian Academy of Sciences, 7a ul. Novatorov, 119421 Moscow, Russian Federation*
[d]*A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119071 Moscow, Russian Federation*

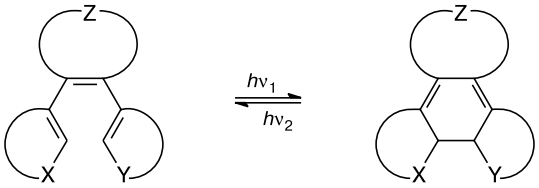
A number of new photochromic 3-(4-phenylthiazol-5-yl)- and 3-(4-hetarylthiazol-5-yl)-coumarins has been synthesized. These compounds possess properties of molecular photoswitches providing a reversible change of the fluorescence intensity in the visible region of the spectrum upon alternating irradiation of their solutions with the visible and UV light. Irradiation with the UV light ($\lambda < 400$ nm) leads to their electrocyclization and loss of fluorescence, whereas irradiation of the cyclic form with the visible light ($\lambda > 400$ nm) returns the system to the state with the original absorption and fluorescence spectra. Switching of fluorescence is also observed in polymer matrices.

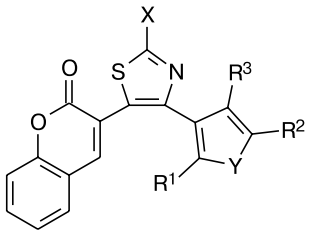
Key words: photochromism, dihetarylethenes, 3-hetarylcoumarins, 4,5-dihetarylthiazoles, molecular switches, photomodulation of fluorescence.

The interest to dihetarylethenes prone to photoinduced electrocyclic reactions (Scheme 1) is caused by the possibility of their use as materials for optoelectronics, in particular, for the development of light-sensitive recording media with the ultrahigh informational capacity for the three-dimensional optical memory.[1,2] Introduction of a bridged double bond into a cycle fixes its *cis*-configuration, that increases the quantum yields of the photocyclization reaction. The dihetarylethenes containing fragments of cyclopentene and perfluorocyclopentene as the ethene bridge are the most studied.[1] In addition, examples of dihetarylethenes in which the hetaryl fragments are bonded by a hetarene "bridge",[3] in particular, the thiazole one[4—7] are also known. Among dihetarylethenes, derivatives containing at least one thiophene fragment conjugated with the C=C double bond possess especially valuable photochromic characteristics.

In the recent years, structures of photochromic compounds able to function as molecular photoswitches, which upon the action of light reversibly change not only color, but also other properties, for example, fluorescence,

Scheme 1





are under intensive study.[8] Such systems can be used, in particular, for the development of photochromic recording media with non-destructive readout of recorded information.[9—15]

* Dedicated to Academician A. I. Konovalov on his 75th birthday.

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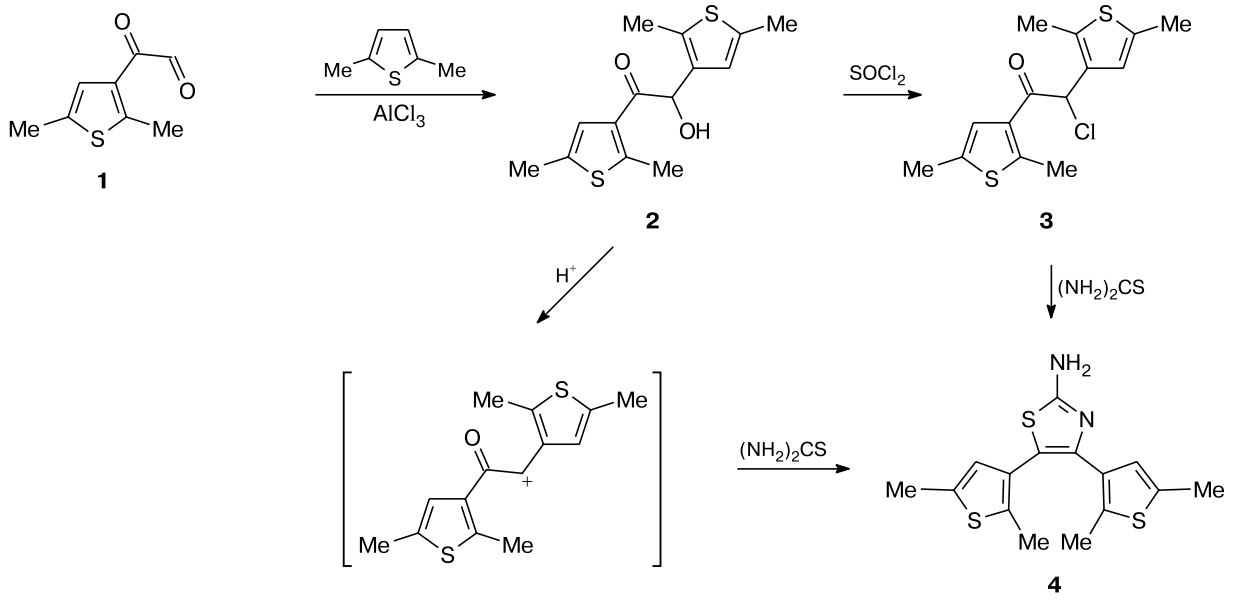
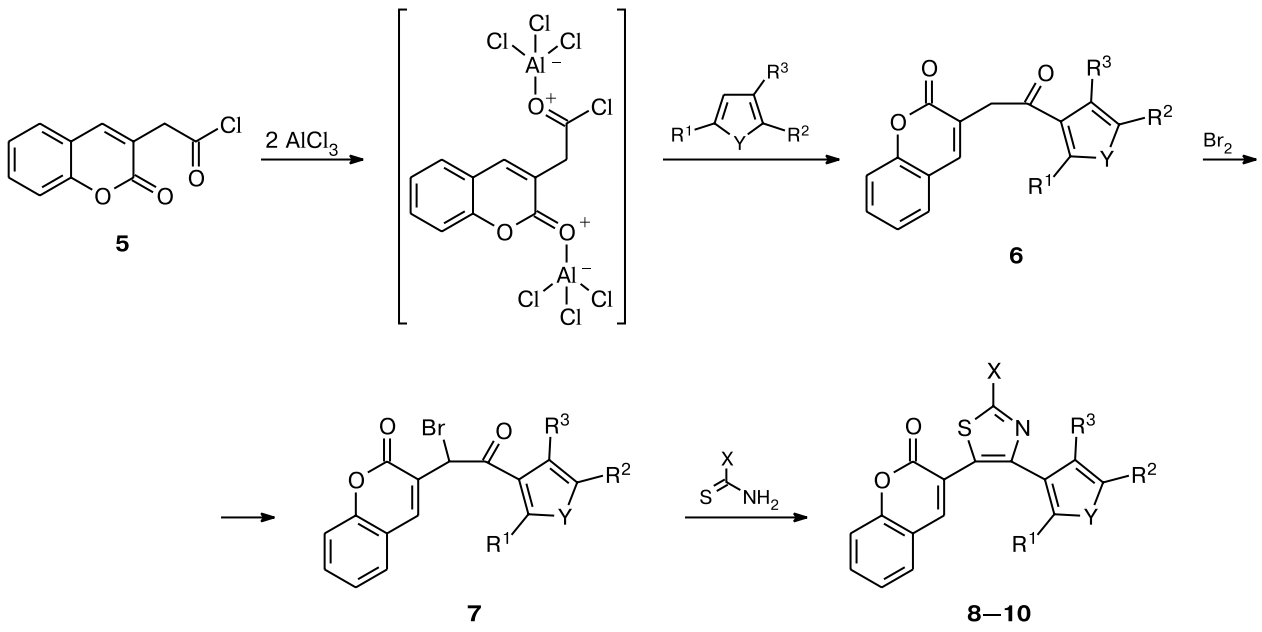
During study of coumarin derivatives capable to the photoinduced change of fluorescence,[16–18] we obtained a number of new unsymmetrical dihetarylethenes possessing properties of fluorescent photoswitches. These dihetarylethenes contain a coumarin fragment at position 5 of the thiazole "bridge" and the thiophene or benzothiophene fragment at position 4 (see Scheme 1). Such compounds possess an intensive fluorescence which reversibly changes under the action of the visible and UV light.

Earlier,[4] we have described the synthesis of dithienylthiazoles (Scheme 2). The Friedel—Crafts reaction of thienylglyoxal **1** with 2,5-dimethylthiophene afforded acyloin **2**, which further was converted into α-chloroketone **3** by the standard method. The subsequent reflux

Scheme 2



Scheme 3



6a, 7a, 8a—e: Y = HC=CH; $R^1 = R^2 = R^3 = H$
6b, 7b, 9a—e: Y = S; $R^1 = R^2$ = Me, R^3 = H
6c, 7c, 10a—e: Y = S; R^1 = H, R^2, R^3 = —HC=CH—CH=CH—
8—10: X = Me (**a**), Ph (**b**), 4-$OMeC_6H_4$ (**c**), NH_2 (**d**), NHPh (**e**)

of a methanol solution of **3** and thiourea led to 2-amino-4,5-dithienylthiazole **4**. Later, we have shown[5] that acyloin **2** can be converted into thiazole **4** in one step by the reaction with thiourea in trifluoroacetic acid.

The realization of Scheme 2 for the coumarin derivatives turned out to be somewhat difficult. The oxidation of 3-acetylcoumarin upon treatment with SeO_2 did not lead to 3-coumarinylglyoxal, the coumarin analog of compound **1**. Therefore, we have chosen an alternative approach to the synthesis of 3-(thienylthiazolyl)coumarins (Scheme 3).

Ethanones **6** turned out to be available by the Friedel—Crafts acylation of benzene, 2,5-dimethylthiophene, and 2-methylbenzothiophene with 3-coumarinylacetyl chloride (**5**). Earlier,[19] an approach to the preparation of the acyl chloride from 3-coumarinylacetic acid by the prolonged reflux of the acid in excess thionyl chloride has been described. However, this method is inconvenient since a significant resinification of the reaction mixture was observed in the course of the reaction. We applied more mild conditions: a solution of 3-coumarinylacetic acid in dichloromethane was kept with excess thionyl chloride for 12 h at room temperature. After the solvent was evaporated, a crystalline acyl chloride was obtained, which was used in the acylation reaction. The acylation of benzene with acyl chloride **5** in the presence of $AlCl_3$ at 50 °C for 3 h leads to ketone **6a** in 75% yield. The reaction of the acyl chloride with 2,5-dimethylthiophene and 2-methylbenzothiophene was carried out at reduced temperatures (−5—10 °C). Ethanones **6b** and **6c** were obtained in 71 and 61% yields, respectively. The structures of compounds **6a—c** were confirmed by elemental analysis, ^{1}H NMR spectroscopic, and mass spectrometric data. It should be noted that to successfully carry out the acylation reaction with participation of acyl chloride **5**, the use of a large amount of aluminum chloride turned out to be necessary, in contrast to the analogous reactions with participation of aliphatic and aromatic acyl chlorides. When 1.1 mole of $AlCl_3$ per 1 mole of acyl chloride **5** was used, we failed to isolate the desired acylation products **6a—c**. It was found that the formation of these products begins only when more than 2 moles of $AlCl_3$ per 1 mole of acyl chloride **5** are present in the reaction mixture. Obviously, this can be explained by the fact that the first mole of $AlCl_3$ is consumed in the complex formation with the lactone fragment of coumarin, whereas the second, in the activation of the acyl chloride function in accordance with the standard scheme of the Friedel—Crafts acylation. It is known[20] that coumarins form complexes with Lewis acids, in particular, with $AlCl_3$.

The reaction of ethanones **6a—c** with bromine in dichloromethane at room temperature afforded α-bromoketones **7a—c** in 83—92% yield. Thiazoles **8—10** were obtained by reflux of methanol solutions of α-bromoketones **7a—c** with compounds containing thioamide fragment. We used thioamides of acetic, benzoic, and 4-methoxybenzoic acids, as well as thiourea and phenylthiourea. The yields of thiazoles **8—10** were 54—94%. 3-(4-Phenylthiazol-5-yl)coumarins **8** and 3-(4-hetarylthiazol-5-yl)coumarins **9** and **10** synthesized were characterized by elemental analysis, ^{1}H NMR spectroscopy, and mass spectrometry data.

Table 1. Spectral characteristics of the starting and photoinduced forms of 3-(4-arylthiazol-5-yl)coumarins **8—10**

Compound	λ^{abs}_{max} /nm	ε	λ^{fl}_{max}/nm (I_{fl} (rel. units))	λ^{photo}_{max} /nm	A^{photo}_{max}
8a	338	7400	426 (230)	—	—
8b	362	9360	445 (80)	—	—
8c	390	7440	458 (410)	—	—
8d	392	6880	474 (165)	—	—
8e	402	8780	552 (360)	—	—
9a	350	7300	504 (125)	500	0.22
9b	374	14100	501 (295)	517	0.22
9c	382	16300	510 (280)	515	0.30
9d	398	7400	543 (7)	496	0.28
9e	410	13400	551 (50)	500	0.25
10a	365	3200	466 (125)	481	0.06
10b	376	5450	468 (75)	502	0.04
10c	378	5400	473 (260)	502	0.04
10d	406	6450	505 (220)	480	0.21
10e	390	8530	490 (215)	495	0.10

Note. λ^{abs}_{max} and λ^{fl}_{max} are the absorption and fluorescence band maxima, respectively; ε/L cm^{-1} mol^{-1} is the coefficient of molar extinction; λ^{photo}_{max} is the wavelength of the absorption maximum of the photoinduced form; A^{photo}_{max} is the value of optical density in the absorption band maximum of the photoinduced form in the photostationary state.

Spectral properties of the compounds synthesized were studied in acetonitrile. The results of spectral and kinetic studies of thiazoles **8—10** are given in Table 1.

In the absorption spectra of each thiazole **8a—e**, two partially overlapping absorption bands are recorded in the region 300—410 nm (Fig. 1, curve *1*). In the sequence of com-

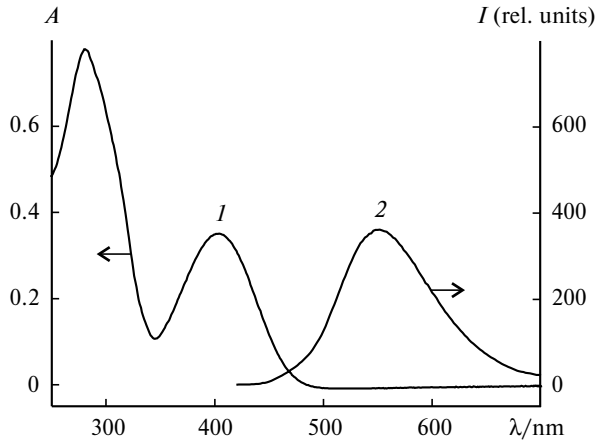


Fig. 1. Absorption (*1*) and emission spectra (*2*) of compound **8e**.

pounds **8a** (X = Me), **8b** (X = Ph), **8c** (X = 4-$MeOC_6H_4$), **8d** (X = NH_2), **8e** (X = NHPh), a bathochromic shift of the long-wave absorption band maximum is observed, which is caused, apparently, by the enhancement of donor properties of substituents in this sequence. 3-(4-Phenylthiazol-5-yl)coumarins **8** fluoresce in the visible region of the spectrum, the emission maxima are in the region 420—550 nm (see Fig. 1, curve *2*) and they are also bathochromiccally shifted in the sequence **8a—e** (see Table 1).

Absorption and fluorescence spectra of compounds **9** before irradiation are analogous in its form to the absorption spectra of compounds **8**. In the sequence of compounds **9a—e**, a bathochromic shift of the absorption and fluorescence band maxima is also observed. However, in contrast to compounds **8**, the presence of the amino group at position 2 of the thiazole ring (compounds **9d,e**) leads to a significant decrease in the intensity of fluorescence in comparison with 2-aryl- and 2-alkylthiazoles **9a—c**.

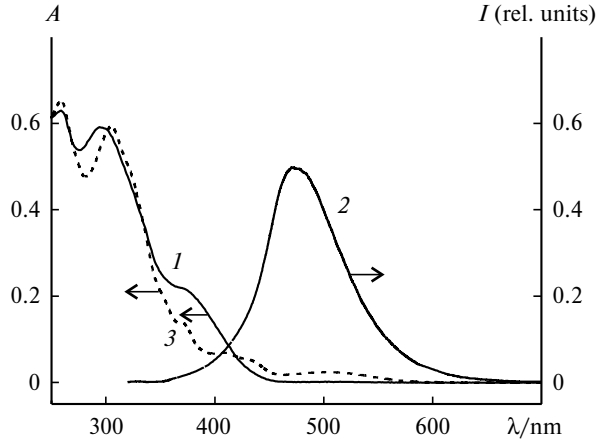


Fig. 2. Absorption (*1*) and emission spectra (*2*) of the initial form and absorption spectrum of the photoinduced form (*3*) of compound **10c**.

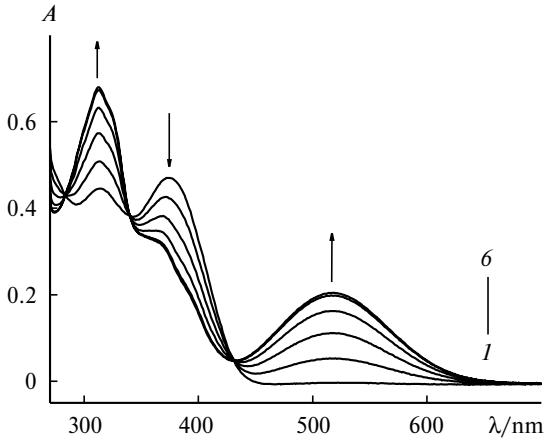


Fig. 3. Absorption spectra of compound **9b** in solution before (*1*) and after irradiation with light of 365 nm in wavelength for 1 (*2*), 2 (*3*), 4 (*4*), 8 (*5*), and 12 s (*6*).

In the absorption spectra of compounds **10**, two overlapping absorption bands in the region 280—400 nm (Fig. 2, curve *1*) can be also highlighted. In the spectra of 2-phenyl-substituted thiazoles **10b,c**, the overlapping is especially pronounced in comparison with analogous compounds **8b,c** and **9b,c** (Fig. 3, curve *1*), that leads to the appearance of a shoulder in the absorption spectrum. The absorption and emission bands in the spectra of compounds **10a—e** are additionally bathochromically shifted in comparison with compounds **8** and **9**.

Photochemical transformatons of compounds **8—10** were studied by irradiation of their acetonitrile solutions with the filtered light of mercury-xenon lamp. The irradiation with the wavelength corresponding to the long-wave absorption band maximum of the starting forms of compounds **8—10** was separated using composite glass light filters.

Irradiation of solutions of 3-(4-phenylthiazol-5-yl)coumarins **8** with the UV light did not cause any changes in the spectra, that suggests the absence of the electro-cyclization reaction (see Scheme 1). Conversely, compounds **9** and **10** turned out to be capable of photoinduced changes in both the absorption and the fluorescence spectra. The irradiation of solutions of the open forms of compounds **9** with the filtered UV light leads to a decrease in intensity of the absorption band in the region 350—400 nm and to the appearance of the absorption band in the visible region of the spectrum (496—517 nm), the intensity of which grows with time (see Fig. 3, curves *2—6*). The intensity of fluorescence on photoirradiation of compounds **9a—e** decreases by 3—6 times (Fig. 4) with the positions of the fluorescence band maxima remaining unchanged (see Table 1). The retention of the fluorescence maxima positions suggests that only the initial form of these compounds causes their fluorescence.

The irradiation of the photoinduced cyclic forms of compounds **9** with light of the wavelength corresponding

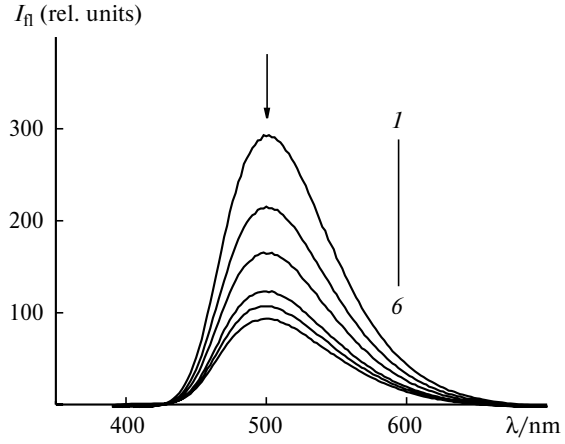
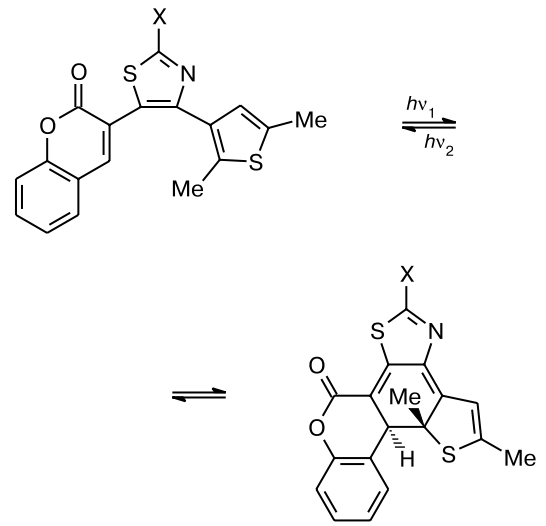


Fig. 4. Fluorescence spectra of compound **9b** in solution before (*1*) and after irradiation with light of 365 nm in wavelength for 1 (*2*), 2 (*3*), 4 (*4*), 8 (*5*), and 12 s (*6*).

Scheme 4



to their absorption maximum in the visible region leads to the reverse phototransformatons of the closed form into the open one with virtually complete recovery of the absorption and fluorescence spectra of the compound initial form. The photochromic transformations of compounds **9** observed are explained by the photoinduced electrocyclic reaction (Scheme 4), rather than, for example, by the [2+2]-cyclodimerization of compounds **9** at the 3—4 double bond of the coumarin fragment.

The explanation suggested confirms the fact of the appearance of a long-wave absorption in the EAS, that corresponds to an increase in the chain of conjugation on passing from the open form to the closed. In addition, the growth of the absorption intensity in the region 500 nm on irradiation of the starting forms follows the first order kinetics, rather than the second order, which would have been the case for the photoinduced reaction of a [2+2]-cycloaddition (Fig. 5).

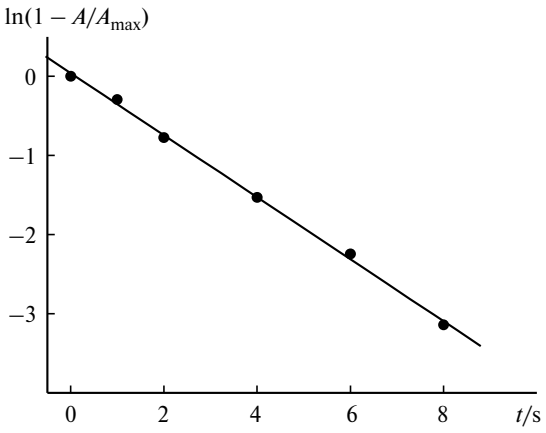


Fig. 5. Optical density changes on coloring of compound **9b** in solution in coordinates of the first order reaction.

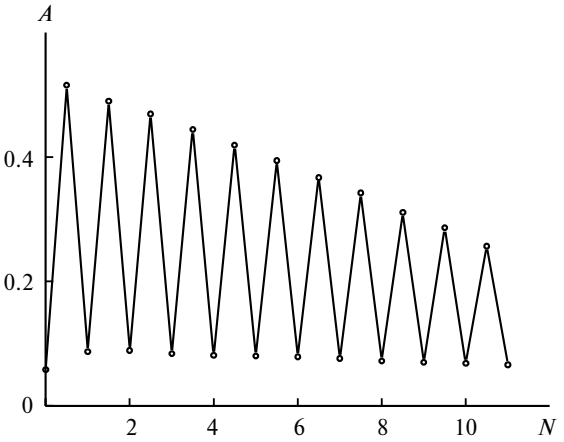


Fig. 6. Fatigue resistance of phototransformations (optical density at 516 nm) of compound **9b** in solution (acetonitrile); here and on Fig. 7 *N* means the cycle number.

Compounds **9** are able to undergo repeated mutually reversible phototransformations depicted by Scheme 4. However, already after 10—12 cycles of phototransformations, the optical density in the absorption maximum of the colored form is lower 50% of the initial value (Fig. 6).

The photocyclization reactions of compounds **9** turned out to be thermally reversible. After irradiation of solutions with the UV light until the photostationary state is reached, a slow decrease in the value of optical density in the absorption band maximum of the photoinduced cyclic form was observed on keeping the solutions in the dark. The rate of spontaneous bleaching in the dark depends on the nature of substituent in the thiazole ring. Compound **9b** having the phenyl substituent completely decolorizes for 8 days, whereas other compound decolorize only partially for this time. Probably, the donor substituents (methyl, *p*-methoxyphenyl, and phenylamino groups) stabilize the closed form of compounds **9**. The effect mentioned is the strongest in the case of phenylamino group **9e**: the optical density in the absorption band maximum of the closed form of compound **9e** decreases by only 27% for 8 days. This agrees with the fact that the closed forms of dithienylethenes connected by the azole bridges are thermally unstable.[4–7] The time of 50% conversion of the closed form **4** into the open one is only several hours. From the data obtained it follows that the introduction of the coumarin fragment into the conjugated system of thienylthiazole significantly increases the thermal stability of the closed form.

On the prolonged irradiation of solutions of compounds **9** with the nonfiltered light of a mercury-xenon lamp, a photodecomposition is observed. The photodecomposition rate depends on the nature of substituent at position 2 of the thiazole ring. Compounds containing methyl and *p*-methoxymethyl substituents turned out to be the least light-resistant. The complete decomposition was observed after irradiation for 80—120 s.

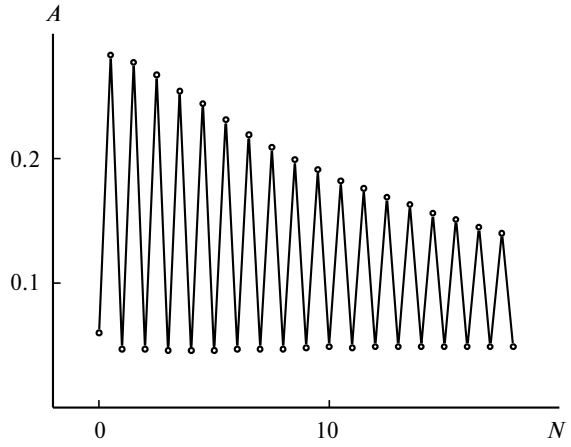


Fig. 7. Fatigue resistance of phototransformations (optical density at 516 nm) of compound **9b** in the PMMA film.

In the case of 2-methylbenzothiophene derivatives **10**, the irradiation with the UV light leads also to the appearance of a new absorption band in the visible region (see Fig. 2, curve *2*). However, its intensity is considerably lower than that for the colored closed forms of compounds **9**. Irradiation of the colored forms of compounds **10** with the visible light leads to the disappearance of the absorption band in the visible region, however, the absorption spectrum of the initial open form is not completely recovered, that can suggest the more efficient photodecomposition of these compounds in comparison with compounds **9**.

Earlier,[17,21] we have shown that the introduction of spiropyrans of the coumarin series into the poly(methyl methacryate) significantly increases stability of the photoinduced form in comparison with the solution. We studied also the phototransformatons of compounds **9** in the poly(methyl methacrylate) film. The spectral changes observed on irradiation of the film with the visible and UV light are similar to the changes in solution. The positions of the absorption and fluorescence bands are virtually unchanged relatively to the solution in acetonitrile. However, the introduction of 3-(4-hetarylthiazol-5-yl)coumarins into the polymer matrix allowed us to increase the fatigue resistance of phototransformations: a 50% decrease in optical density in the absorption maximum of the cyclic form was observed after 18 cycles of phototransformatons (Fig. 7). In addition, the stability in the dark of the cyclic forms in the polymer is significantly higher than in solution: the optical density in the absorption maximum of the closed form of the film, irradiated with the UV light until the photostationary state, decreases by 50% for 30 days (compound **9b**).

In conclusion, a number of differences between 3-(4-arylthiazol-5-yl)coumarins studied in this work and dithienylthiazoles described earlier[4,5] should be highlighted. Introduction of the coumarin fragment gave to the new thiazoles pronounced fluorescent properties, changing on irradiation. In addition, it turned out to be possible to increase the stability in the dark of the closed form up to several days instead of several hours, which was reported earlier, by the variation of the substituent at position 2 of the thiazole ring in the coumarin derivatives.[4] Additional increase in the thermal stability of the closed forms of 3-(4-arylthiazol-5-yl)coumarins can be successfully achieved by their incorporation into the poly(methyl methacrylate) film.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$ and $(CD_3)_2SO$. Melting points were measured on a Boetius heating block. Mass spectra (EI) were recorded on a Kratos MS-30 instrument (70 eV) with the direct injection of a substance into the ion source. Thin-layer chromatography was performed on Merck 60 F_{254} plates.

A single-beam CARY UV 50 spectrophotometer (Varian) was used for the recording of absorption spectra of solutions. Fluorescence spectra of solutions were recorded on a CARY ECLIPSE spectrofluorimeter (Varian). Absorption and fluorescence spectra were recorded in 1-cm thick cuvettes. Acetonitrile (HPLC grade, Acros) was used as the solvent. Concentration of solutions for the absorption and fluorescence spectra recording was $4 \cdot 10^{-5}$ mol L^{-1}.

For the photochemical studies of solutions, the visible and UV filtered irradiation of a Hamamatsu LC-4 gas-discharge mercury-xenon lamp, separated using composite glass light filters from the standard set of colored glasses, was used.

The synthesis of compounds **6a—c** was described by us earlier.[22]

Bromination of 3-(2-aryl-2-oxoethyl)coumarins (general procedure). Bromine (1 mmol) was added to a solution of ketone **6a—c** (1 mmol) in dichloromethane (15 mL) and the mixture was kept for ~14 h. The next day, the solvent was evaporated, the residue was chromatographed on a short column with silica gel (eluent, dichloromethane).

3-(1-Bromo-2-oxo-2-phenylethyl)-2*H*-chromen-2-one (7a). The yield was 89%, white crystals, m.p. 143—144 °C. Found (%): C, 59.34; H, 3.32. $C_{17}H_{11}BrO_3$. Calculated (%): C, 59.50; H, 3.23. ^{1}H NMR ($CDCl_3$), δ: 6.66 (s, 1 H, CHBr); 7.35—8.13 (m, 9 H arom.); 8.26 (s, 1 H, H(4) coumarin). MS, *m/z* (I_{rel} (%)): 344 $[M]^+$ (5), 263 $[M - Br]^+$ (3), 235 (7), 218 (3), 207 (12), 191 (22), 178 (18), 130 (33), 114 (12), 108 (100), 89 (8), 78 (98), 63 (28), 51 (97), 38 (37).

3-[1-Bromo-2-(2,5-dimethyl-3-thienyl)-2-oxoethyl]-2*H*-chromen-2-one (7b). The yield was 92%, white crystals, m.p. 122—123 °C. Found (%): C, 54.29; H, 3.58; S, 8.31. $C_{17}H_{13}BrO_3S$. Calculated (%): C, 54.12; H, 3.47; S, 8.50. ^{1}H NMR ($CDCl_3$), δ: 2.44 (s, 3 H, Me(5) thiophene); 2.70 (s, 3 H, Me(2) thiophene); 6.33 (s, 1 H, CHBr); 7.17 (s, 1 H, H(4) thiophene); 7.33—7.38 (m, 2 H, H(5)—H(8) coumarin); 7.54—7.61 (m, 2 H, H(6)—H(7) coumarin); 8.23 (s, 1 H, H(4) coumarin). MS, *m/z* (I_{rel} (%)): 377 $[M]^+$ (1), 298 $[M - Br]^+$ (6), 269 (7), 217 (25), 139 (100), 111 (27).

3-[1-Bromo-2-(2-methylbenzo[*b*]thiophen-3-yl)-2-oxoethyl]-2*H*-chromen-2-one (7c). The yield was 83%, white crystals, m.p. 147—149 °C. Found (%): C, 58.25; H, 3.28; S, 7.63.

$C_{20}H_{13}BrO_3S$. Calculated (%): C, 58.12; H, 3.17; S, 7.76. ^{1}H NMR ($CDCl_3$), δ: 2.88 (s, 3 H, Me); 6.48 (s, 1 H, CHBr); 7.33—8.52 (m, 9 H arom.). MS, *m/z* (I_{rel} (%)): 413 $[M]^+$ (4), 255 (100), 227 (30), 175 (76), 149 (49).

Preparation of thiazoles 8—10 (general procedure). A solution of bromoketone **7** (0.25 mmol) and the corresponding thioamide (0.3 mmol) in methanol (25 mL) was refluxed for 3 h, cooled, and poured in aqueous K_2CO_3 (2 g in water (150 mL)). The crystals formed were filtered off.

3-(2-Methyl-4-phenyl-1,3-thiazol-5-yl)-2*H*-chromen-2-one (8a). The yield was 70%, white crystals, m.p. 167—168 °C. Found (%): C, 71.53; H, 4.20; N, 4.29; S, 10.15. $C_{19}H_{13}NO_2S$. Calculated (%): C, 71.45; H, 4.10; N, 4.39; S, 10.04. ^{1}H NMR (DMSO-d_6), δ: 3.45 (s, 3 H, Me); 7.34—7.68 (m, 9 H arom.); 7.98 (s, 1 H, H(4) coumarin). MS, *m/z* (I_{rel} (%)): 319 $[M]^+$ (100), 304, $[M - Me]^+$ (24), 291 (31), 277 (20), 250 (21), 221 (35), 205 (13), 189 (24).

3-(2,4-Diphenyl-1,3-thiazol-5-yl)-2*H*-chromen-2-one (8b). The yield was 96%, yellow crystals, m.p. 157—158 °C. Found (%): C, 75.71; H, 3.84; N, 3.57; S, 8.36. $C_{24}H_{15}NO_2S$. Calculated (%): C, 75.57; H, 3.96; N, 3.67; S, 8.41. ^{1}H NMR ($CDCl_3$), δ: 7.19—8.34 (m, 15 H arom.). MS, *m/z* (I_{rel} (%)): 381 $[M]^+$ (100), 353 (25), 277 (27), 250 (22), 221 (52), 205 (21), 189 (42), 176 (16).

3-[2-(4-Methoxyphenyl)-4-phenyl-1,3-thiazol-5-yl]-2*H*-chromen-2-one (8c). The yield was 90%, yellow crystals, m.p. 196—197 °C. Found (%): C, 72.77; H, 4.30; N, 3.35; S, 7.91. $C_{25}H_{17}NO_3S$. Calculated (%): C, 72.97; H, 4.16; N, 3.40; S, 7.79. ^{1}H NMR ($CDCl_3$), δ: 3.88 (s, 3 H, OMe); 6.96—8.01 (m, 14 H arom.). MS, *m/z* (I_{rel} (%)): 411 $[M]^+$ (100), 278 (34), 250 (23), 221 (27), 205 (9), 189 (14).

3-(2-Amino-4-phenyl-1,3-thiazol-5-yl)-2*H*-chromen-2-one (8d). The yield was 68%, yellow crystals, m.p. 193 °C (decomp.). Found (%): C, 67.52; H, 3.85; N, 8.59; S, 10.18. $C_{18}H_{12}N_2O_2S$. Calculated (%): C, 67.48; H, 3.78; N, 8.74; S, 10.01. ^{1}H NMR ($CDCl_3$), δ: 5.19 (br.s, 2 H, NH_2); 7.15—7.59 (m, 10 H arom.). MS, *m/z* (I_{rel} (%)): 320 $[M]^+$ (100), 305 (6), 292 (14), 278 (10), 205 (10), 221 (13), 189 (13).

3-(4-Phenyl-2-phenylamino-1,3-thiazol-5-yl)-2*H*-chromen-2-one (8e). The yield was 94%, orange crystals, m.p. 205—206 °C. Found (%): C, 72.62; H, 4.13; N, 7.01; S, 7.99. $C_{24}H_{16}N_2O_2S$. Calculated (%): C, 72.71; H, 4.07; N, 7.07; S, 8.09. ^{1}H NMR ($CDCl_3$), δ: 7.07—7.63 (m, 15 H arom.); 7.77 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 396 $[M]^+$ (100), 293 (12), 278 (9), 265 (8), 251 (9), 237 (9), 221 (10).

3-[4-(2,5-Dimethyl-3-thienyl)-2-methyl-1,3-thiazol-5-yl]-2*H*-chromen-2-one (9a). The yield was 64%, white crystals, m.p. 150—151 °C. Found (%): C, 64.63; H, 4.11; N, 4.02; S, 9.21. $C_{19}H_{15}NO_2S_2$. Calculated (%): C, 64.56; H, 4.28; N, 3.96; S, 9.05. ^{1}H NMR ($CDCl_3$), δ: 2.35 (s, 3 H, Me(5) thiophene); 2.53 (s, 3 H, Me(2) thiophene); 3.27 (s, 3 H, Me(2) thiazole); 6.81 (s, 1 H, H(4) thiophene); 7.33—7.66 (m, 5 H, H(4)—H(8) coumarin). MS, *m/z* (I_{rel} (%)): 353 $[M]^+$ (100), 338 $[M - Me]^+$ (21), 325 (12), 311 (7), 294 (6), 279 (18), 251 (14), 219 (39), 208 (13), 189 (7), 139 (48).

3-[4-(2,5-Dimethyl-3-thienyl)-2-phenyl-1,3-thiazol-5-yl]-2*H*-chromen-2-one (9b). The yield was 76%, yellow crystals, m.p. 170—171 °C. Found (%): C, 69.46; H, 4.00; N, 3.45; S, 15.32. $C_{24}H_{17}NO_2S_2$. Calculated (%): C, 69.37; H, 4.12; N, 3.37; S, 15.43. ^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 3 H, Me(5) thiophene); 2.48 (s, 3 H, Me(2) thiophene); 6.78 (s, 1 H, H(4) coumarin); 7.33—7.65 (m, 4 H, H(5)—H(8) coumarin). MS, *m/z* (I_{rel} (%)): 415 $[M]^+$ (100).

3-[4-(2,5-Dimethyl-3-thienyl)-2-(4-methoxyphenyl)-1,3-thiazol-5-yl]-2*H*-chromen-2-one (9c). The yield was 61%, yellow crystals, m.p. 142—143 °C. Found (%): C, 67.53; H, 4.44; N, 3.02; S, 14.23. $C_{25}H_{19}NO_3S_2$. Calculated (%): C, 67.39; H, 4.30; N, 3.14; S, 14.39. ^{1}H NMR ($CDCl_3$), δ: 2.33 (s, 3 H, Me(5) thiophene); 2.47 (s, 3 H, Me(2) thiophene); 3.90 (s, 3 H, OMe); 6.78 (s, 1 H, H(4) thiophene); 7.02 (d, 2 H, J = 8.4 Hz); 7.28—7.60 (m, 5 H, H(4)—H(8) coumarin); 8.22 (d, 2 H, J = 8.4 Hz). MS, *m/z* (I_{rel} (%)): 445 $[M]^+$ (100).

3-[2-Amino-4-(2,5-dimethyl-3-thienyl)-1,3-thiazol-5-yl]-2*H*-chromen-2-one (9d). The yield was 80%, yellow crystals, m.p. 160—165 °C (decomp.). Found (%): C, 60.88; H, 3.81; N, 7.97; S, 18.01. $C_{18}H_{14}N_2O_2S_2$. Calculated (%): C, 61.00; H, 3.98; N, 7.90; S, 18.09. ^{1}H NMR ($CDCl_3$), δ: 2.21 (s, 3 H, Me(5) thiophene); 2.43 (s, 3 H, Me(2) thiophene); 5.16 (br.s, 2 H, NH_2); 6.68 (s, 1 H, H(4) thiophene); 7.22—7.52 (m, 5 H, H(4)—H(8) coumarin). MS, *m/z* (I_{rel} (%)): 354 $[M]^+$ (100).

3-[4-(2,5-Dimethyl-3-thienyl)-2-(phenylamino)-1,3-thiazol-5-yl]-2*H*-chromen-2-one (9e). The yield was 89%, yellow crystals, m.p. 172 °C (decomp.). Found (%): C, 67.03; H, 4.30; N, 6.38; S, 14.74. $C_{24}H_{18}N_2O_2S_2$. Calculated (%): C, 66.95; H, 4.21; N, 6.51; S, 14.89. ^{1}H NMR ($CDCl_3$), δ: 2.26 (s, 3 H, Me(5) thiophene); 2.40 (s, 3 H, Me(2) thiophene); 6.69 (s, 1 H, H(4) thiophene); 7.05—7.53 (m, 10 H arom.); 8.50 (br.s, 1 H, NH). MS, *m/z* (I_{rel} (%)): 430 $[M]^+$ (100).

3-[2-Methyl-4-(2-methylbenzo[*b*]thiophen-3-yl)-1,3-thiazol-5-yl]-2*H*-chromen-2-one (10a). The yield was 68%, white crystals, m.p. 135—136 °C. Found (%): C, 67.68; H, 3.98; N, 3.49; S, 16.60. $C_{22}H_{15}NO_2S_2$. Calculated (%): C, 67.84; H, 3.88; N, 3.60; S, 16.46. ^{1}H NMR ($CDCl_3$), δ: 2.56, 2.82 (both s, 3 H each, Me); 6.80—7.80 (m, 9 H arom.). MS, *m/z* (I_{rel} (%)): 389 $[M]^+$ (100), 374 $[M - Me]^+$ (35).

3-[4-(2-Methylbenzo[*b*]thiophen-3-yl)-2-phenyl-1,3-thiazol-5-yl]-2*H*-chromen-2-one (10b). The yield was 54%, yellow crystals, m.p. 139—140 °C. Found (%): C, 72.01; H, 3.89; N, 3.01; S, 14.33. $C_{27}H_{17}NO_2S_2$. Calculated (%): C, 71.82; H, 3.79; N, 3.10; S, 14.20. ^{1}H NMR ($CDCl_3$), δ: 2.59 (s, 3 H, Me); 7.23—7.69 (m, 14 H arom.). MS, *m/z* (I_{rel} (%)): 451 $[M]^+$ (100).

2-(4-Methoxyphenyl)-3-[4-(2-methylbenzo[*b*]thiophen-3-yl)-1,3-thiazol-5-yl]-2*H*-chromen-2-one (10c). The yield was 73%, yellow crystals, m.p. 158—159 °C. Found (%): C, 69.73; H, 3.87; N, 2.99; S, 13.30. $C_{28}H_{19}NO_3S_2$. Calculated (%): C, 69.83; H, 3.98; N, 2.91; S, 13.32. ^{1}H NMR ($CDCl_3$), δ: 2.58, 3.89 (both s, 3 H each, OMe); 6.98—8.20 (m, 13 H arom.). MS, *m/z* (I_{rel} (%)): 481 $[M]^+$ (100), 454 (12), 348 (11), 315 (11), 287 (10), 258 (11), 253 (37).

3-[2-Amino-4-(2-methylbenzo[*b*]thiophen-3-yl)-1,3-thiazol-5-yl]-2*H*-chromen-2-one (10d). The yield was 65%, yellow crystals, m.p. 172—176 °C (decomp.). Found (%): C, 64.63; H, 3.65; N, 7.07; S, 16.48. $C_{21}H_{14}N_2O_2S_2$. Calculated (%): C, 64.59; H, 3.61; N, 7.17; S, 16.42. ^{1}H NMR ($CDCl_3$), δ: 2.56 (s, 3 H, Me); 5.28 (br.s, 2 H, NH_2); 6.98—7.82 (m, 8 H arom.); 8.03 (s, 1 H, H(4) coumarin). MS, *m/z* (I_{rel} (%)): 390 $[M]^+$ (100), 375 (17), 362 (14), 348 (20), 332 (26).

3-[4-(2-Methylbenzo[*b*]thiophen-3-yl)-2-(phenylamino)-1,3-thiazol-5-yl]-2*H*-chromen-2-one (10e). The yield was 82%, yellow crystals, m.p. 185 °C (decomp.). Found (%): C, 69.42; H, 3.80; N, 6.07; S, 13.83. $C_{27}H_{18}N_2O_2S_2$. Calculated (%):

C, 69.51; H, 3.89; N, 6.00; S, 13.74. ^{1}H NMR ($CDCl_3$), δ: 2.44 (s, 3 H, Me); 6.92—7.80 (m, 14 H arom.); 8.29 (br.s, 1 H, NH). MS, m/z (I_{rel} (%)): 466 $[M]^+$ (100), 451 (11), 438 (10), 348 (9), 331 (27).

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