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Novel photochromic 3-(3-coumarinyl)-4-(3-thienyl)maleic acid cyclic derivatives

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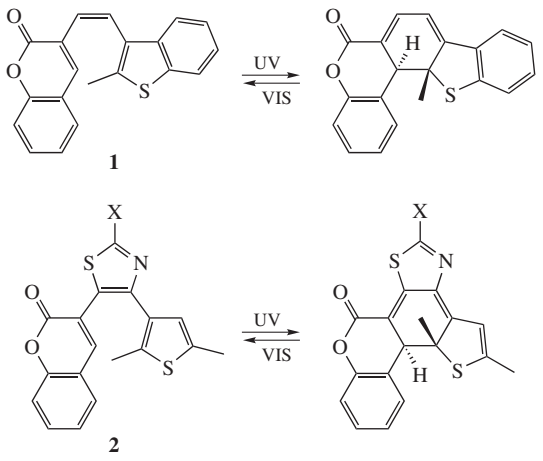
Novel unsymmetrical photosensitive derivatives of maleic acid, anhydride and *N*-alkylimide, including coumarin and thiophene moieties, have been designed and synthesized; their photochromism study and fatigue resistance estimation are reported.

Dihetaryl derivatives of maleic anhydride and maleimide are known as thermally irreversible and fatigue resistant photochromic systems.[1] The variety of such heterocyclic systems yet studied as photochromic molecules include symmetric thiophene,[2] benzo[*b*]thiophene,[3] selenothiophene,[4] indole,[4] thieno[3,2-*b*]pyrrole[5] and a number of non-symmetric[6] derivatives.



Scheme 1 Previously studied coumarinyl(thienyl)ethenes.

We have recently studied photochromic dihetarylethenes bearing coumarin moiety as a part of photosensitive hexatriene system, including non-annelated[7] and thiazole-annelated[8] dihetarylethenes (Scheme 1). Compounds **1** and **2** along with photochromic transformations show fluorescence switching upon UV/Vis irradiation, open forms being fluorescent and closed forms, non-fluorescent. Looking for coumarinyl(thienyl)ethenes, which would have better fatigue resistant properties, we decided to replace thiazole ring in the photochromic system with a maleic anhydride (or maleimide) bridge.

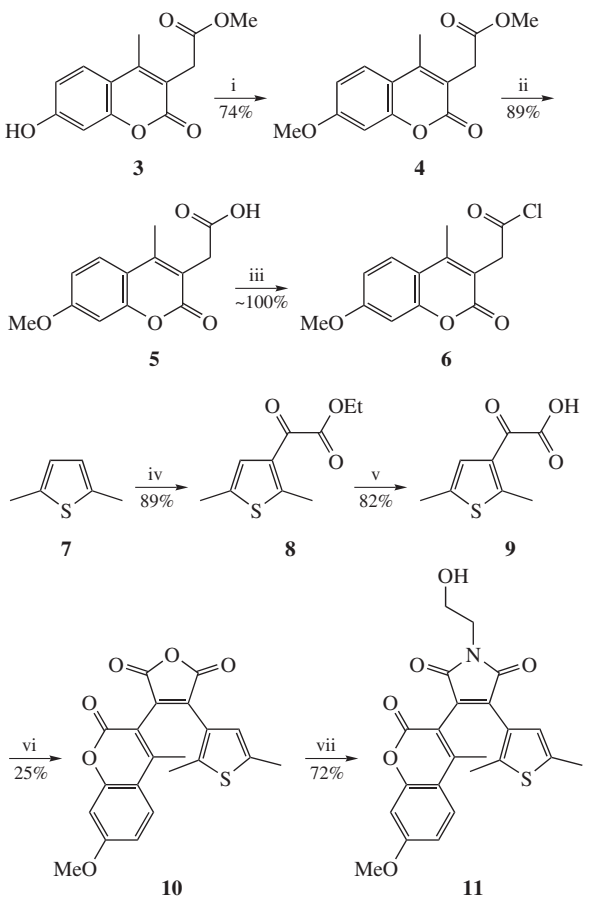
Here, we present the synthesis, the study of the photochromic properties and the estimation of the photoreversibility of coumarinyl(thienyl)maleic anhydride and maleimide.†

The synthesis of coumarinyl(thienyl)maleic anhydride **10** has been performed as shown in Scheme 2. Methyl ester of (7-hydroxy-4-methylcoumarin-3-yl)acetic acid **3** was prepared *via* Pechmann condensation of dimethyl acetyl succinate[9] and resorcinol in concentrated H_2SO_4.‡ Further methylation with dimethyl sulfate and alkaline hydrolysis according to reported procedures[10] gave acid **5**.§ Acylation of 2,5-dimethylthiophene with ethyl oxalylchloride gave thienylglyoxalic ester[11] **8**, which was hydrolyzed to acid **9**. Coumarinylacetic acid **5** was converted to corresponding acid chloride **6** by a standard procedure using thionyl chloride. Furandione **10** was obtained upon slow addition of triethylamine to a cooled solution of acid **9** and acid chloride **6** in dichloromethane. Furandione **10** gave functionalized maleimide **11**, upon reflux with ethanolamine in methanol.[12]

† All commercial reagents were used as received. Column chromatography was carried out using Merck Kieselgel 60 H silica gel. TLC was performed with aluminium-backed plates coated with Merck Kieselgel 60 F_{254}, which were visualized under UV light (at 254 or 363 nm). NMR spectra were measured in $CDCl_3$ solutions on Bruker AC-200 (^{1}H, 200 MHz) and Bruker Avance II 300 (^{13}C, 75 MHz) spectrometers using TMS as an internal standard. Mass spectra (EI) were recorded on a Kratos MS-30 instrument. Absorption spectrometry was performed on a CARY UV 50 (Varian) spectrophotometer. Fluorescence measurements were conducted using a CARY ECLIPSE (Varian) spectrofluorimeter. Absorption and fluorescence spectra were recorded in toluene solutions (4×10^{-5} M) in 1-cm quartz cuvette. Irradiation of solutions during photochemical studies was performed using a Hamamatsu LC-4 mercury-xenon lamp (Hamamatsu photonics), equipped with composite glass light filters. Toluene used for spectroscopy experiments was of spectrophotometric grade.

‡ *Methyl 2-(7-hydroxy-4-methyl-2-oxo-2*H*-chromen-3-yl)acetate* **3**. A suspension of resorcinol (36 mmol, 4.0 g) in dimethyl acetylsuccinate (37 mmol, 8.0 g) was added in few portions to concentrated H_2SO_4 (20 ml) with stirring and after complete addition placed in refrigerator for 18 h. The reaction mixture was poured into crushed ice and precipitate formed was filtered off, dried in a vacuum and recrystallized from ethanol–water (1:1 v/v). Yield 3.9 g (43%), white crystals, mp 202–203 °C (lit.,[10] 203–205 °C). ^{1}H NMR, δ: 2.37 (s, 3H), 3.74 (s, 2H), 3.80 (s, 3H), 6.70 (d, 1H, *J* 2.4 Hz), 6.75 (d, 1H, *J* 2.4 Hz), 7.38 (d, 1H, *J* 8.5 Hz).

*Methyl 2-(7-methoxy-4-methyl-2-oxo-2*H*-chromen-3-yl)acetate* **4**. K_2CO_3 (32 mmol, 4.7 g) and dimethyl sulfate (24 mmol, 3.0 g) were added to a solution of 7-hydroxycoumarin **3** (16 mmol, 4.0 g) in DMF (50 ml) and resulting suspension was vigorously stirred for 4 h at 60 °C. The reaction mixture was cooled and poured into water. Precipitate formed was filtered off, dried and recrystallized from ethanol. Yield 3.1 g (74%), white crystals, mp 135–136 °C (lit.,[10] 136–137 °C). ^{1}H NMR, δ: 2.39 (s, 3H), 3.72 (s, 5H), 3.88 (s, 3H), 6.82–6.89 (m, 2H), 7.54 (d, 1H, *J* 8.8 Hz).



Scheme 2 *Reagents and conditions*: i, Me_2SO_4, K_2CO_3, DMF; ii, KOH, MeOH/H_2O; iii, $SOCl_2$, CH_2Cl_2; iv, ClCOCOOEt, $AlCl_3$, $MeNO_2$; v, KOH, EtOH; vi, **6**, NEt_3, CH_2Cl_2; vii, $HOCH_2CH_2NH_2$, MeOH.

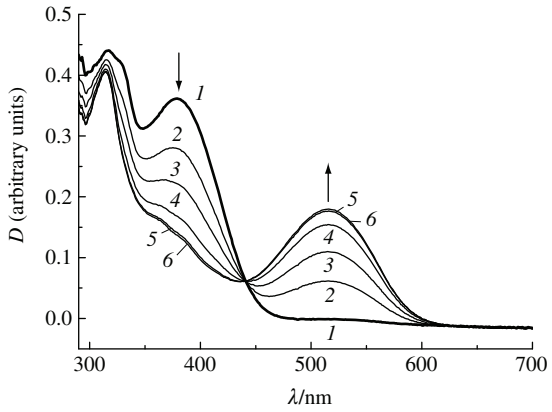


Figure 1 UV/VIS absorption spectra of compound **10** (4×10^{-5} M, toluene, 25 °C) before (*1*) and after irradiation at λ = 365 nm for (*2*) 2, (*3*) 4, (*4*) 8, (*5*) 16 and (*6*) 32 s.

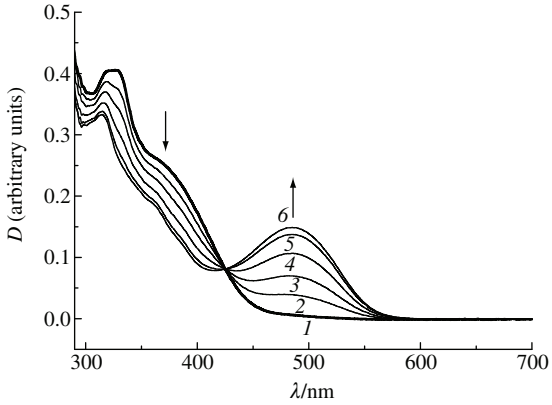


Figure 2 UV/VIS absorption spectra of compound **11** (4×10^{-5} M, toluene, 25 °C) before (*1*) and after irradiation at λ = 365 nm for (*2*) 2, (*3*) 4, (*4*) 8, (*5*) 16 and (*6*) 32 s.

The free hydroxyl group of maleimide **11** may be used for covalent binding of photochrome to polymers.

Structures of compounds **10** and **11** were confirmed by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.¶

The photochromic properties of **10** and **11** were studied in toluene solution. The UV/VIS absorption spectra of **10** and **11** and their changes upon UV irradiation are shown in Figures 1 and 2.

Upon irradiation with UV light (365 nm), the absorption band intensity at 350–400 nm decreases and simultaneous rise of optical density at visible range (516 nm maxima for **10** and 485 nm maxima for **11**) is observed due to photocyclization. Note that maleimide derivative **11** shows a definite hypsochromic shift relative to **10**.

The cyclic forms of **10** and **11** return to initial state upon irradiation with visible light (>450 nm). The photochromic cycle may be performed for many times without significant decrease of optical density. In opposite to photochrome **2**, bearing thiazole bridge, novel photochromes, maleic acid cyclic derivatives, seem to be much more fatigue resistant. Moreover, maleimide **11** is more fatigue resistant than maleic anhydride **10**: after 50 cycles of photochromic transformation (in the presence of air), its photostationary optical density makes up 94% from initial value (Figure 4). Maleic anhydride **10** shows 83% of initial optical density after 50 cycles and previously studied

§ *2-(7-Methoxy-4-methyl-2-oxo-2*H*-chromen-3-yl)acetic acid* **5**. A suspension of ester **4** (11.5 mmol, 3.01 g) in 10% aqueous NaOH (30 ml) was stirred for 3 h at 50 °C until clear solution formed. The reaction mixture was filtered, cooled and crushed ice was added, followed by concentrated HCl. The precipitate formed upon acidification was filtered off, washed with cold water and dried. Yield 2.53 g (89%), white crystals, mp 266–267 °C (lit.,[10] 268–269 °C; lit.,[13] 265–268 °C). ^{1}H NMR, δ: 2.43 (s, 3H), 3.77 (s, 2H), 3.89 (s, 3H), 6.85–6.92 (m, 2H), 7.57 (d, 1H, *J* 8.9 Hz).

¶ *3-(2,5-Dimethylthiophen-3-yl)-4-(7-methoxy-4-methyl-2-oxo-2*H*-chromen-3-yl)furan-2,5-dione* **10**. Acid **5** (1 mmol, 248 mg) was dissolved in anhydrous dichloromethane (10 ml) and thionyl chloride excess (0.4 ml) was added, followed by one drop of DMF and left overnight. The volatiles were removed *in vacuo* and the residue acid chloride was dissolved in anhydrous dichloromethane (20 ml) and thienyl glyoxylic acid (1 mmol, 184 mg) was added. To a stirred solution, triethylamine (2.1 mmol, 212 mg) dissolved in dichloromethane (5 ml) was slowly added dropwise at 0 °C. The stirring was continued for 3 h, the solvent was removed *in vacuo* and the residue chromatographed on a silica gel column (EtOAc–hexane, 1:3 v/v). Yield 100 mg (25%), yellow crystals, mp 159–160 °C. ^{1}H NMR, δ: 2.17 (s, 3H), 2.22 (s, 3H), 2.40 (s, 3H), 3.92 (s, 3H), 6.71 (s, 1H), 6.86–6.96 (m, 2H), 7.59 (d, 1H, *J* 8.8 Hz). ^{13}C NMR, δ: 16.2, 16.8, 29.8, 56.0, 100.9, 101.9, 112.1, 112.7, 113.4, 124.9, 125.4, 126.8, 134.4, 138.3, 141.1, 142.1, 153.0, 155.3, 158.4, 163.6, 164.0. MS, *m*/*z*: 396 (100) $[M]^+$, 378 (40), 363 (13), 351 (32), 324 (42). UV [λ_{max}/nm (lg ε)]: 316 (4.05), 378 (3.96). Found (%): C, 63.99; H, 4.18. Calc. for $C_{21}H_{16}O_6S$ (%): C, 63.63; H, 4.07.

*3-(2,5-Dimethylthiophen-3-yl)-1-(2-hydroxyethyl)-4-(7-methoxy-4-methyl-2-oxo-2*H*-chromen-3-yl)-1*H*-pyrrole-2,5-dione* **11**. The solution of **10** (0.2 mmol, 80 mg), ethanolamine (0.25 mmol, 15 mg) and catalytic amount of *p*-toluenesulfonic acid in methanol (10 ml) was refluxed for 3 h. The solvent was removed *in vacuo* and the residue chromatographed on a silica gel column (EtOAc–hexane, 1:3 v/v). Yield 63 mg (72%), yellow crystals, mp 171–172 °C. ^{1}H NMR, δ: 2.17 (s, 3H), 2.22 (s, 3H), 2.40 (s, 3H), 3.92 (s, 3H), 6.71 (s, 1H), 6.86–6.96 (m, 2H), 7.59 (d, 1H, *J* 8.8 Hz). ^{13}C NMR, δ: 16.1, 16.6, 29.7, 39.4, 56.0, 58.6, 100.7, 110.8, 111.4, 122.2, 122.9, 123.5, 127.0, 129.9, 131.8, 141.2, 155.1, 157.7, 160.4, 161.1, 163.6, 168.8, 170.7. MS, *m*/*z*: 439 (100) $[M]^+$, 378 (40), 363 (13), 351 (32), 324 (42). UV [λ_{max}/nm (lg ε)]: 326 (4.01), 373 (3.79). Found (%): C, 63.02; H, 4.97. Calc. for $C_{23}H_{21}NO_6S$ (%): C, 62.86; H, 4.82.

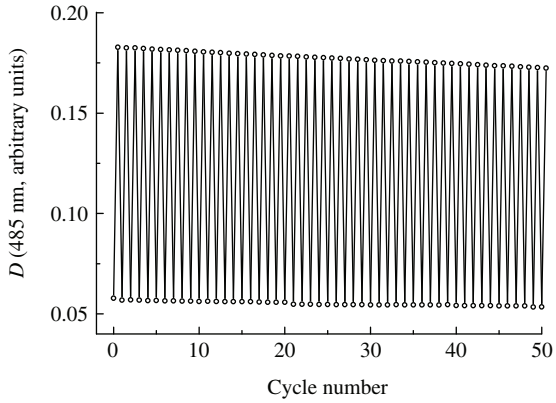


Figure 3 Reversibility of photochromic transformations of compound **11** in toluene solution.

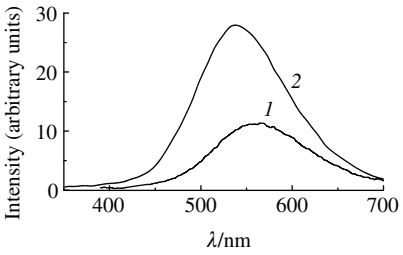


Figure 4 Fluorescence spectra of open forms of (*1*) compound **10** and (*2*) compound **11**.

coumarinyl(thienyl)thiazoles **2** did not reach even 50% of initial optical density after 5–10 cycles.

To the best of our knowledge, no direct comparison of fatigue resistance properties of maleic anhydride- and maleimide-bridged dihetarylethenes (for same structures, distinguished only by bridging fragment) was performed earlier. Thus, we can assume that conversion of maleic anhydride function to the *N*-alkylmaleimide one improves fatigue resistance of dihetarylethenes.

Coumarinyl(thienyl)maleic anhydride **10** and maleimide **11** show low intense fluorescence in toluene solution in an open form (at 565 and 540 nm, respectively) (Figure 4), which slightly decreases upon photocyclization.

The cyclic forms of **10** and **11** are stable in the dark: irradiated to reach photostationary state solutions were stored for 8 days in the absence of light with only 7% decrease of optical density in cyclic form absorption maxima. Thiazole-bridged coumarinyl-(thienyl)ethenes **2** showed 27–100% decolouration in the dark depending on the substituent at the 2-position in thiazole ring during the same period of time.[8]

In summary, novel coumarinyl(thienyl)maleic acid cyclic derivatives, anhydride and maleimide, show photochromism in toluene solution. In comparison with coumarinyl(thienyl)thiazoles,[8] they show much better fatigue resistance and dark stability of cyclic forms.

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