

Photochromic 1-benzofurylfulgides with modulated fluorescence

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Abstract

Spectral luminescent and photochromic properties of 5-alkoxy-2-methyl-1-benzofuran-3-yl fulgides with increasing alkyl chain length were investigated. All compounds exist in the form of ring-opened *Z*-isomers (λ_{max} 344-346 nm). Under UV-irradiation they rearrange into thermally stable colored ring-closed isomers ($\lambda_{\text{max}} \sim 500$ nm) exhibiting fluorescence emission (λ_{max} 603-608 nm). Fluorescence in ring-closed form *C* is modulated by light, irradiation with visible light (546 nm) results in formation of the initial opened form *O* and complete quenching of the emission. The quantum efficiency of photodecoloration is by 3.47-4.25 times higher than that of the photocoloration. 5-Alkoxy-2-methyl-1-benzofuran-3-yl fulgides demonstrate high fatigue resistance and are characterized by excellent thermal stability of the photoinduced cyclic form.

Keywords: Fulgides, 1-benzofuran, photochromism, fluorescence

Introduction

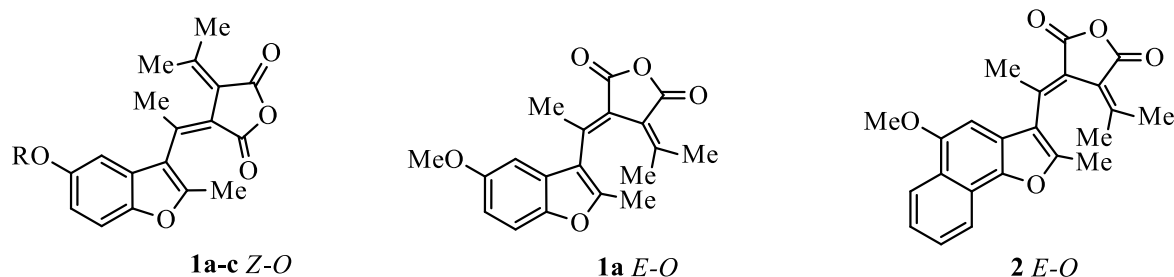
Photochromic compounds have already found an important place in the design of novel polyfunctional materials for molecular electronics, molecular logic devices, molecular switches and motors, rewritable optical memory, photodynamic chemo- and biosensors.¹⁻⁷ The light-induced rearrangement between two metastable isomeric forms of photochromic compounds results in significant changes in various physical properties of the system, such as electronic absorption spectra, fluorescence, dipole moment and nonlinear optic parameters. The most thoroughly studied classes of organic photochromic compounds are represented by spiropyrans and spirooxazines,^{8,9} azobenzenes,¹⁰ dihetarylethenes,¹¹ fulgides and fulgimides.^{12,13} Fulgides, the compounds with the structural skeleton of bismethylenesuccinic anhydride and an aromatic

or heterocyclic substituent linked to a methylene group, are susceptible to the light-induced hexatriene-cyclohexadiene rearrangement of their ground state colourless ring-opened forms to give coloured ring-closed isomers possessing high fatigue resistance, thermal and photostability capable to display fluorescent, chemosensor and complexing properties.¹⁴⁻¹⁶ These isomeric forms do not interconvert in dark and have markedly different physical chemical characteristics, which makes fulgides to be promising candidates for the use in high capacity three-dimensional multilayer optical memory devices.¹⁷⁻²¹ The most studied groups of the heterocyclic fulgides are currently represented by furyl-, thienyl-, oxazolyl-, pyrrol-, and indolylfulgides; reports on the synthesis and properties of fulgides with benzofuryl and naphthofuryl groups are relatively scarce.²²⁻²⁴

Therefore, the main goal of this work was the investigation into the spectral luminescent and photochromic properties (kinetics of photodecoloration and photocoloration processes, quantum efficiency of photorearrangements, quantum yields of fluorescence) of 5-alkoxy-2-methyl-1-benzofuran-3-yl fulgides **1** bearing long alkyl groups allowing application of these photochromic compounds in Langmuir-Blodgett films, which are widely used in the developing of multifunctional materials possessing advanced properties.²⁵ A preliminary information on the synthesis of compounds **1** was reported earlier.²⁶

Results and Discussion

According to ¹H NMR data²⁶ fulgides **1a-c** have the structure of ring-opened *Z*-isomers, whereas previously synthesized 5-methoxy-2-methyl-1-benzofuran-3-yl (**1a**)²³ and 5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl (**2**) fulgides²² existed in the form of *E*-isomers (Scheme 1).



Scheme 1. Structures of **1a-c** and **2**.

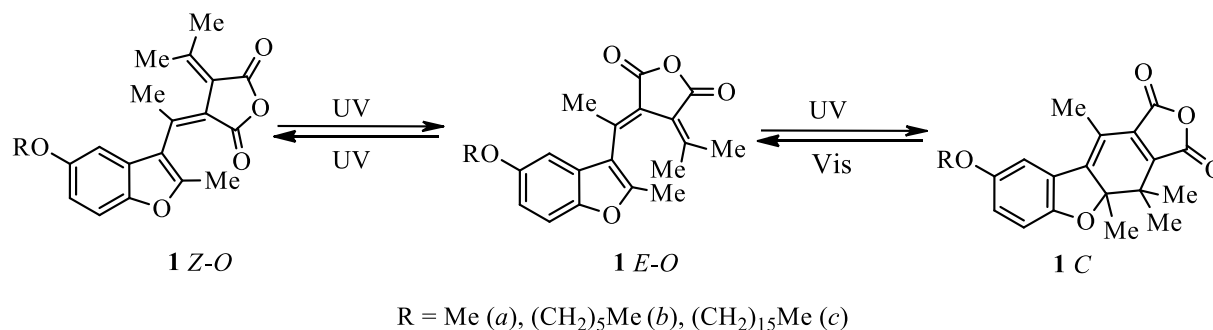
The three-proton singlet signals of isopropylidene methyl groups are found, indeed, in the region of 2.04-2.46 ppm, while for the *E*-structures the characteristic signal appears at 1.12 ppm.²³ The *E*-configuration of **2** was unequivocally confirmed by the X-ray structural determination.²² Spectral and photochromic properties of **1a-c** were studied in toluene solutions

at ambient temperature. Electronic absorption spectra of fulgides **1a-c** are characterized by long-wave absorption bands with the maxima in the region 344-346 nm and the molar extinction coefficients 9150-9300 L mol⁻¹ cm⁻¹ (Table 1).

Table 1. Spectral absorption and spectral fluorescent characteristics of isomeric forms of **1a-c** and **2**²² in toluene at $T = 293$ K

Compound	Isomeric form	Absorption		Fluorescence excitation, λ_{exc} (nm)	Fluorescence, λ_{max} (nm), (quantum yield)
		λ_{max} (nm)	ϵ_{max} (L mol ⁻¹ cm ⁻¹)		
1a	<i>Z</i>	344	9300		
	<i>C</i>	500		370 (S ₀ →S ₂) 500 (S ₀ →S ₁)	603 (0.003)
1b	<i>Z</i>	346	9200		
	<i>C</i>	500		370 (S ₀ →S ₂) 500 (S ₀ →S ₁)	608 (0.004)
1c	<i>Z</i>	346	9150		
	<i>C</i>	500		370 (S ₀ →S ₂) 500 (S ₀ →S ₁)	608 (0.005)
2	<i>E</i>	344	10100		
	<i>C</i>	546		340 (S ₀ →S ₂) 542 (S ₀ →S ₁)	648 (0.002)

The intensity and the position of the absorption maxima of ring-opened *Z*-isomers of the fulgides **1a-c** do not practically depend on the length of the alkyl chain. The observed bathochromic shift of a long-wavelength band absorption maximum in the sequence of compounds R = Me (**1a**), (CH₂)₅Me (**1b**) and (CH₂)₁₅Me (**1c**) changes by not more than 2 nm. Ring-opened *Z*-isomers **1a-c** do not exhibit fluorescent properties in toluene at ambient temperature. Irradiation of toluene solutions of colorless ring-opened isomers **1a-c** with light of 365 nm wavelength leads to their rose red photocoloration due to the appearance of a new absorption band with a maximum at 500 nm, the intensity of which increases upon irradiation while the intensity of the initial long wavelength absorption band decreases (Fig. 1). These spectral changes are indicative of the occurrence of the electrocyclic rearrangement of hexatriene ring-opened isomer *O* into 1,3-cyclohexadiene ring-closed form *C* that involves a prior step of *Z/E*-isomerization (Table 1, Scheme 2). Ring-closed form *C* of 5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl fulgide **2** absorbs in a longer wavelength region ($\lambda_{\text{max}} = 546$ nm, $\Delta\lambda = 46$ nm)²² due to the additional stabilization of aromatic heterocyclic system caused by benzoannulation.



Scheme 2. Photoisomerization of fulgides **1a-c**.

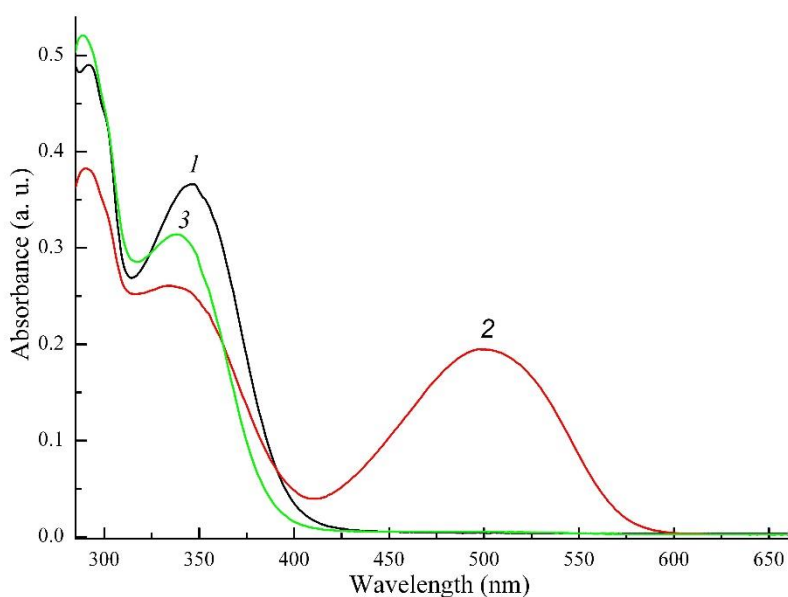


Figure 1. Absorption spectra of fulgide **1c** Z-*O* in toluene ($4 \cdot 10^{-5}$ mol L⁻¹, $T = 293$ K) corresponding to the initial state (*1*), to the photostationary state established after irradiation for 12 min with light of 365 nm wavelength (*2*) and to the Z/*E-O* mixture obtained upon subsequent irradiation for 13 min with light of 546 nm wavelength (*3*).

The prolonged UV-irradiation does not lead to the full conversion of **1a-c** into colored ring-closed form *C* due to the establishment of the photostationary state including all isomeric forms, Z-*O*, *E-O* and *C*, of the photochromic fulgides (Fig. 1, curve 2). Its formation is caused by the substantial overlap of the absorption bands related to the S₀→S₁ transition of the initial ring-opened form *O* and the S₀→S₂ transition of the photoinduced isomer *C* (Table 1).¹²⁻¹⁵ The subsequent irradiation of colored solutions of **1a-c** with visible light ($\lambda_{\text{irr}} = 546$ nm) leads to their photodecoloration due to the reverse ring-opening photoreaction $C \rightarrow E/Z-O$ (Fig.1, curve 3).^{12,15}

Therefore, no complete restoration of the initial (observed before irradiation) absorption spectra occurs. The recurrence of the initial spectral characteristics can, however, be achieved under a series of repeated cycles of photocoloration-photodecoloration. No spectral changes for the solutions of *C* forms of **1a-c** were found at room temperature after seven days in dark conditions, which indicates the absence of backward thermal processes and high thermal stability of the ring-closed isomers of the studied fulgides.

Ring-closed *C* forms of fulgides **1a-c** exhibit fluorescence of the toluene solutions (Table 1, Fig. 2). Their fluorescence bands maxima are located in the region at 603-608 nm, while the maxima of the fluorescence band of *C* isomer of 5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl fulgide **2** was found in the longer wavelength region ($\lambda_{\text{max}} = 648 \text{ nm}$).²² Elongation of the alkyl chain in **1b** and **1c** leads to a rather small ($\Delta\lambda = 5 \text{ nm}$) bathochromic shift of the fluorescence bands as compared with the methoxy substituted fulgide **1a**.

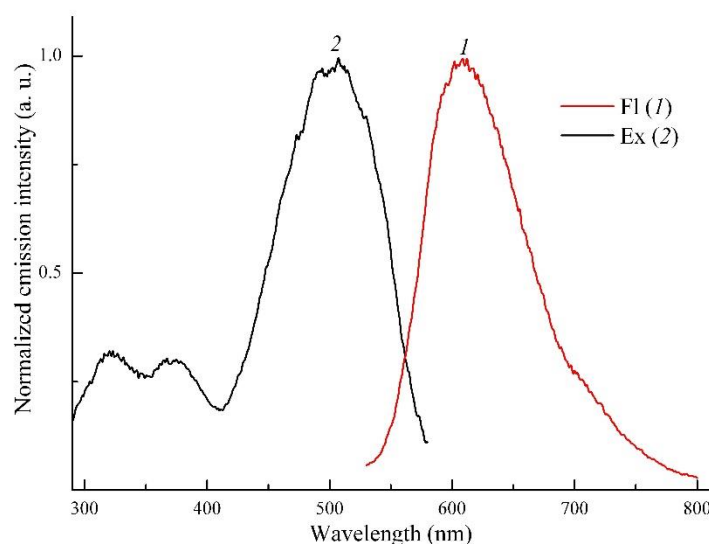


Figure 2. Spectra of fluorescence (*I*) ($\lambda_{\text{exc}} = 500 \text{ nm}$) and fluorescence excitation (*2*) ($\lambda_{\text{obs}} = 600 \text{ nm}$) of photoisomer *C* in toluene obtained after irradiation of **1c** for 12 min with light of 365 nm wavelength ($4 \cdot 10^{-5} \text{ mol L}^{-1}$, $T = 293 \text{ K}$).

Quantum yields of fluorescence of fulgides **1a-c** tend to increase with increasing the length of the 5-alkoxy chain: from 0.003 (**a**, $R = \text{Me}$) to 0.004 (**b**, $R = (\text{CH}_2)_5\text{Me}$) and up to 0.005 (**c**, $R = (\text{CH}_2)_{15}\text{Me}$). For comparison, we determined the quantum yield of fluorescence of **2** and found that it is only 0.002 (Table 1). The fluorescence excitation spectra are in good agreement with the long-wavelength absorption of *C* isomers, which confirms the conclusion that only ring-closed isomers of fulgides **1a-c** are responsible for the observed emission properties. In addition, these spectra demonstrate that in the spectral region from 300 to 400 nm there are two additional bands

with the maxima at 320 and 370 nm corresponding to the $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_2$ transitions of the ring-closed isomers of **1a-c** (Table 1, Fig. 2). After irradiation of colored solutions of **1a-c** with visible light ($\lambda_{\text{irr}} = 546 \text{ nm}$) the intensity of fluorescence decreases to zero. Consequently, fulgides **1a-c** are capable of efficient modulation of the emission by UV/visible light (at least for 10 cycles) while for previously known 1-benzofuryl fulgides little modulation of the fluorescence was achieved²³ and their resistance to photodegradation was insufficient (two switching cycles).

Fulgides **1a-c** manifest high resistance to photodegradation. As shown in Fig. 3 by an example of **1c**, the optical density in the maximum of absorption band of *C* form (in the photostationary state) remained practically unchanged within 10 photocoloration-photodecoloration cycles. Accordingly, no changes in fluorescence intensity of *C* form (in the photostationary state) were detected.

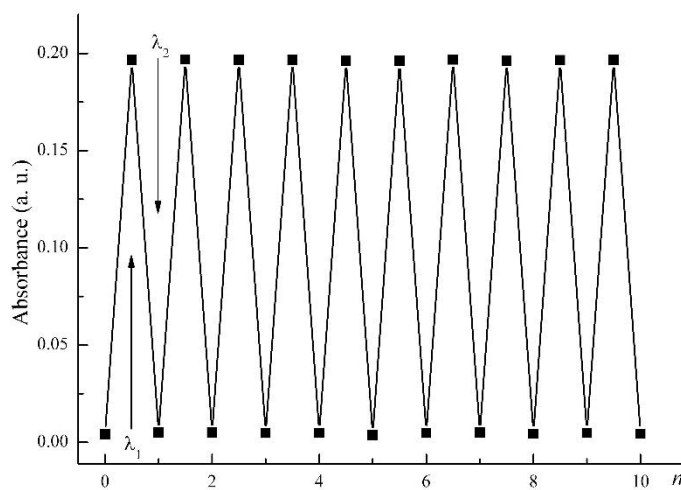


Figure 3. Optical density dynamics of fulgide **1c** in toluene at $\lambda_{\text{obs}} = 500 \text{ nm}$ (the absorbance band maximum of the ring-closed *C* isomer) under photocoloration ($\lambda_1 = 365 \text{ nm}$, $\tau = 12 \text{ min}$)-photodecoloration ($\lambda_2 = 546 \text{ nm}$, $\tau = 13 \text{ min}$) cycling; n is the number of cycles.

As a convenient integral parameter for the evaluation of efficiency of the photocoloration and photodecoloration processes, we used colorability, which is defined as the product of quantum yield of photocoloration (photodecoloration) and molar absorption coefficient of the photoinduced form:²⁷ $\Phi_{Z(E)} \cdot \epsilon_{\text{max}}^C$ (for the overall process $Z \rightarrow E \rightarrow C$, including two sequential photoinduced reactions – *Z/E*-photoisomerization and subsequent $E \rightarrow C$ photocyclization) and $\Phi_{CE} \cdot \epsilon_{\text{max}}^C$ (for the photodecoloration reaction $C \rightarrow E$).

Table 2. The values of colorabilities of fulgides **1a-c** in toluene at $T = 293$ K: (photocoloration - $\Phi_{Z(E)C} \cdot \epsilon_{\max}^C$ and photodecoloration - $\Phi_{CE} \cdot \epsilon_{\max}^C$)^a

Compound	$\Phi_{Z(E)C} \cdot \epsilon_{\max}^C$	$\Phi_{CE} \cdot \epsilon_{\max}^C$	$\Phi_{Z(E)C} / \Phi_{CE}$
	$M^{-1} \text{ cm}^{-1}$		
1a	337	1170	0.29
1b	273	1160	0.24
1c	277	1074	0.26

^a $\Phi_{Z(E)C}$ and Φ_{CE} – quantum yields of photocoloration (cyclization) and photodecoloration (opening of the ring) reactions, correspondingly; ϵ_{\max}^C – the value of a molar extinction coefficient at the absorption band maximum of the photoinduced ring-closed form *C*.

The determined values of the efficiencies of the photocoloration reactions $Z \rightarrow E \rightarrow C$ of fulgides **1a-c** show a slight dependence on the substituents (277-337 $M^{-1} \text{ cm}^{-1}$). The efficiencies of the photodecoloration reactions $C \rightarrow E$ are at 3.47-4.25 times higher than the corresponding parameters of the photocoloration (Table 2). The ratio of the quantum yields of the photocoloration to the quantum yields of the photodecoloration ($\Phi_{Z(E)C} / \Phi_{CE}$) obtained for **1a-c** on the basis of these data are 0.24-0.29 that indicates significantly higher efficiency of the photoinduced reaction of the cycle opening ($C \rightarrow E$) (Table 2).

Conclusions

Thus, 5-alkoxy-2-methyl-1-benzofuran-3-yl fulgides **1b,c**, possessing long alkyl substituents, represent novel photochromic compounds with modulated fluorescence. UV-irradiation of their ring-opened isomers *O* results in the rearrangement into thermally stable pink-colored ring-closed forms *C* exhibiting fluorescence properties in contrast to the initial *O* structures. The irradiation of ring-closed isomeric forms with visible light leads to their re-opening and complete fluorescence quenching.

Experimental Section

General. 3-[1-(5-Methoxy- (**1a**), 3-[1-(5-hexyloxy- (**1b**) and 3-[1-(5-hexadecyloxy-2-methyl-1-benzofuran-3-yl)ethylidene]-4-(1-methylethylidene)dihydro-2,5-furandione (**1c**) were synthesized earlier following the principles of the Stobbe condensation.²⁶ Their purity (> 98%) was confirmed by thin layer chromatography and by ¹H NMR spectroscopy.

The electronic absorption spectra were recorded on a Varian Cary 100 spectrophotometer, the emission spectra - on a Varian Cary Eclipse spectrofluorimeter. Toluene of the spectroscopic

grade (Aldrich) was used to prepare solutions. The fluorescence quantum yields were determined by the Parker-Rice method²⁸ using methylene blue in water ($\varphi = 0.02$, $\lambda_{\text{irr}} = 540$ nm) as a standard luminophore.²⁹ The solutions were irradiated in a quartz cell ($l = 1$ cm) with a DRSh-250 mercury lamp using a set of interferential light filters to allocate mercury spectral lines (365 and 546 nm). The kinetic photocoloration curves of fulgide solutions were recorded directly during irradiation on a Cary 50 spectrophotometer equipped with the temperature-controlled cell. A xenon lamp with a monochromator for allocation of narrow spectral lines (Newport) was used as a radiation source. The intensity of light source was determined using a Newport 2935 power meter for optical radiation. The irradiation light intensity at 365 and 546 nm was determined as $3.83 \cdot 10^{15}$ and $5.68 \cdot 10^{15}$ photon \cdot s⁻¹, correspondingly. Colorability parameters $\Phi_{Z(E)C} \cdot \epsilon_{\text{max}}^C$ and $\Phi_{CE} \cdot \epsilon_{\text{max}}^C$ were calculated on the basis of kinetic photocoloration and photodecoloration curves using the procedure.²⁷

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