The mechanisms of photochromic transformations of 2-indolylfulgides

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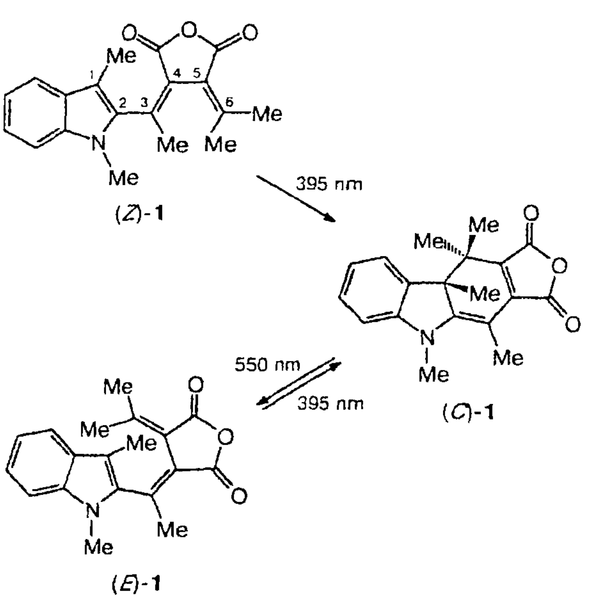
Photochromic properties of 2-indolylfulgides, namely, Z-3-[1-(1,3-dimethyl-1*H*-indol-2-yl)ethylidene]-4-isopropylidenetetrahydrofuran-2,5-dione and *E*-3-isopropylidene-4-(1-methyl-1*H*-indol-2-ylmethylidene)tetrahydrofuran-2,5-dione, were studied. The quantum yields of their photochemical isomerizations in toluene and the rate constant of the dark ring-opening in ethanol were determined. The fluorescence spectra of the open and cyclic forms of 2-indolylfulgides were measured. It was assumed that the excited-state *Z*-isomer can be transformed into a cyclic isomer without intermediacy of an *E*-isomer in the ground state.

Key words: photochromism, 2-indolylfulgides, fluorescence, quantum yields.

Fulgides are promising photochromic compounds because of the high thermal and chemical stability of their cyclic forms.[1,2] It is known that irradiation of fulgides causes reversible *E*→*Z* isomerization and gives rise to cyclic isomers (*C*).[1] Phototransformations of 2-indolylfulgides have been described in the literature[3]; they were shown to be promising photochromic systems with long service life.[3] In the present work, the mechanism of photo- and thermochromic transformations of fulgides **1** and **2** was studied.

Fulgides **1** and **2** were synthesized in the form of *Z*- and *E*-isomers, respectively (^{1}H NMR data). Irradiation of (*Z*)-**1** (λ_{max} = 399 nm, ε_{PhMe} = 6900 L mol cm^{-1}) with the light of a xenon lamp through an F1 filter (λ_{max} = 395 nm, half-width 30 nm) yields a cyclic form (*C*)-**1**, which absorbs in the long-wavelength spectral region (λ_{max} = 531 nm, ε_{PhMe} = 12200 L mol cm^{-1}). The absorption spectra exhibit an isosbestic point at 451 nm (Fig. 1, *a*), suggesting that the solution contains two isomers, *viz*., (*Z*)-**1** and (*C*)-**1**. When irradiated with the light of a xenon lamp through an F2 filter (λ_{max} = 550 nm, half-width 30 nm), the tetracyclic isomer (*C*)-**1** is converted into an *E*-isomer (*E*)-**1** (λ_{max} = 395 nm, ε_{PhMe} = 9060 L mol cm^{-1}). The absorption spectra contain an isosbestic point at 444 nm (Fig. 1, *b*), which indicates the lack of absorption due to the *Z*-isomer. The quantum yield of the (*C*)-**1** → (*E*)-**1** conversion (Φ_{CE}) is equal to 0.17. Irradiation of the *E*-isomer with the light of a xenon lamp through an F1 filter results in its complete isomerization into (*C*)-**1** (the quantum yield of the (*E*)-**1** → (*C*)-**1** conversion (Φ_{EC}) equals 0.24). The changes in the absorption spectra upon (*C*)-**1** → (*E*)-**1** and (*E*)-**1** → (*C*)-**1** photoreactions are the same (see Fig. 1, *b*). The photochromic transformations of fulgide **1** are illustrated in Scheme 1.

Scheme 1



The presence of isosbestic points in all the transformations suggests that each solution subjected to irradiation contains only two isomers, namely, (*Z*)-**1** and (*C*)-**1** or (*C*)-**1** and (*E*)-**1**. We assume that (*Z*)-**1** → (*C*)-**1** photoisomerization occurs without intermediacy of the *E*-isomer in the ground state. This means that a rotation about the C(3)—C(4) bond, necessary for cyclization to occur, takes place in the excited state of the *Z*-isomer, which is accompanied by the formation of a new C(1)—C(6) bond (cyclization). No *E*→*Z* isomerization

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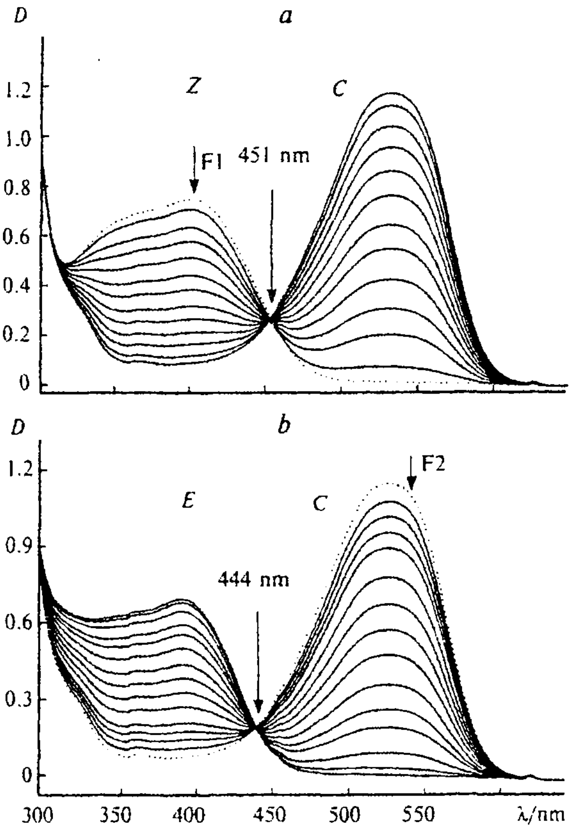


Fig. 1. Spectral changes upon irradiation of (*a*) a solution of (*Z*)-**1** in toluene with the light of a xenon lamp through an F1 filter and (*b*) a solution of (*C*)-**1** in toluene with the light of a xenon lamp through an F2 filter. The dotted lines refer to the absorption spectra of the initial isomers (*a*) (*Z*)-**1** and (*b*) (*C*)-**1**.

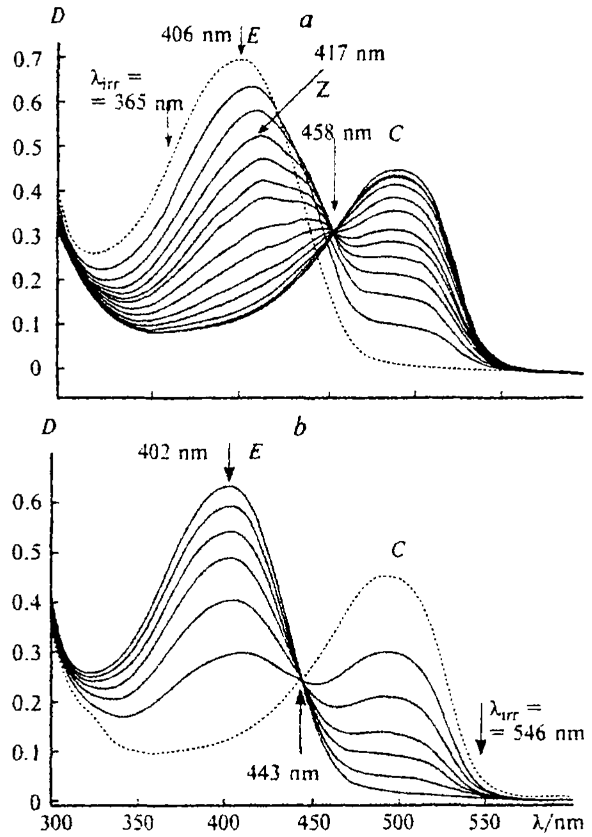


Fig. 2. Spectral changes upon irradiation of (*a*) a solution of (*E*)-**2** in toluene with the light of a mercury lamp (filter 365 nm) and (*b*) a solution of (*C*)-**2** in toluene with the light of a mercury lamp (546 nm). The dotted lines refer to the absorption spectra of the initial isomers (*a*) (*E*)-**2** and (*b*) (*C*)-**2**.

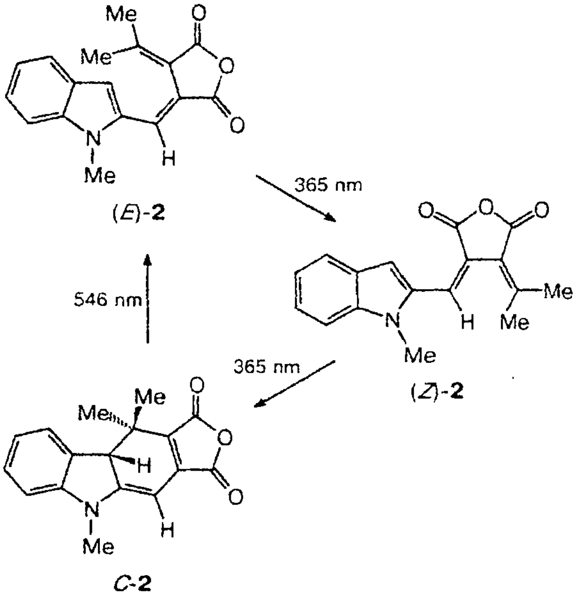
is observed upon irradiation of (*E*)-**1**, probably, because of a higher activation energy of this process, as compared to the (*E*)-**1** → (*C*)-**1** cyclization. Hence, the photochromic cycle includes interconversions of (*E*)-**1** and (*C*)-**1**.

An assumption that the *Z*-isomer is transformed into a tetracyclic *C*-isomer without intermediacy of the *E*-isomer in the ground-state was supported by the results of the photochromic transformations of fulgide **2**. The absorption spectrum of a toluene solution of (*E*)-**2** contaminated with an admixture of (*Z*)-**2** exhibits a maximum at 406 nm (Fig. 2, *a*). Irradiation of this solution with the light of a mercury lamp with a wavelength of 365 nm diminishes its optical density at λ = 406 nm and causes a bathochromic shift of λ_{max} from 406 to 417 nm, thus suggesting *E*→*Z* isomerization. In addition, the absorption spectrum exhibits a new band at 494 nm, which corresponds to the photocyclization into compound (*C*)-**2**. The ^{1}H NMR spectra of the irradiated solutions contain signals for (*E*)-**2** and (*Z*)-**2**. Following irradiation for 40 s, the absorption maximum is not shifted any more and remains at λ_{max} = 417 nm. Then an isosbestic point appears at 458 nm, indicating the presence of compounds (*Z*)-**2** and (*C*)-**2** in the solution. Hence, *Z*→*C* isomerization is the main process upon irradiation of the *Z*-isomer. Further irradiation with the same wavelength results in disappearance of a band with λ_{max} = 417 nm and appearance of a distinct band with λ_{max} = 494 nm characteristic of (*C*)-**2**.

Similar results were obtained in a more polar solvent, namely, ethyl acetate. An increase in the solvent polarity results in a hypsochromic shift of the absorption maximum for (*E*)-**2** by 10 nm and in a bathochromic shift of the absorption maximum for (*C*)-**2** by 4 nm. Irradiation of a solution of (*Z*)-**2** yields (*C*)-**2**, and an isosbestic point at 453 nm is observed in the absorption spectra. The isosbestic point appears after completion of the *E*→*Z* isomerization and suggests that the solution contains only *Z*- and *C*-isomers of **2**.

When a toluene solution of the tetracyclic isomer (*C*)-**2** is irradiated with light with λ = 546 nm (Hg line), (*C*)-**2** is completely converted into (*E*)-**2** (Fig. 2, *b*). The absorption spectra contain an isosbestic point at 443 nm, indicating the absence of the *Z*-isomer in the solution irradiated. The quantum yield of the (*C*)-**2** → (*E*)-**2** conversion (Φ_{CE}) is equal to 0.16. A difference in the absorption maxima for (*E*)-2 (see Figs. 2, *a* and 2, *b*) is due to absorption by a minor admixture of (*Z*)-2 in the initial solution (see Fig. 2, *a*). When the *E*-isomer is irradiated once again with light with 365 nm (Hg line), the absorption spectral pattern changes in the same way as shown in Fig. 2*a*, with retention of the isosbestic point at 458 nm. The photochromic transformations of fulgide **2** are presented in Scheme 2.

Scheme 2



In ethanol, (*C*)-**2** undergoes dark thermal ring-opening to give (*E*)-**2**. A decrease in the optical density of an ethanolic solution of (*C*)-**2** at λ = 500 nm with time follows an exponential law, *i.e.*, the dark conversion is a monomolecular reaction for which the optical density D_t at moment t is related to the initial optical density D_0 by equation (1)

$$D_t = D_0 \cdot \exp(-kt). \qquad (1)$$

The reaction rate constant (k) is equal to $1.46 \cdot 10^{-3}$ s^{-1}.

The fluorescence of components of a photochromic system is very important when photochromic compounds are used in optical memory elements. It is believed that reading of information from the fluorescence of a colored form largely prevents the information from being erased (in our case, *C*→*E* ring opening) and allows one to create three-dimensional recording. We detected the fluorescence of solutions of the *E*- and *C*-isomers of fulgide **1** in acetonitrile[8] and of fulgide **2** in toluene. The *Z*-isomers of fulgides **1** and **2** do not fluoresce. The quantum yield of the fluorescence of (*C*)-**2** is higher than that for (*E*)-**2** by an order of magnitude, and Φ_{fl} equals 0.03.

We believe that steric factors, *viz.*, the presence of the methyl group at the side double bond of compound **1**, is responsible for the difference in the mechanisms of photocyclization of fulgides **1** and **2**. Literature data on the *Z*→*C* photoisomerization of 2-indolylfulgides are lacking. Thus, we observed for the first time the *Z*→*C* photocyclization and the fluorescence of the open and cyclic forms of 2-indolylfulgides. The quantum yields of photochemical isomerization reactions and the rate constant of the dark ring-opening of (*C*)-**2** were determined.

Experimental

Synthesis of fulgides 1 and 2. Compounds **1** and **2** were synthesized according to the known procedures.[3,4] **(*Z*)-3-[1-(1,3-Dimethyl-1*H*-indol-2-yl)ethylidene]-4-isopropylidenetetrahydrofuran-2,5-dione (*Z*)-1.** ^{1}H NMR (CDCl$_3$), δ: 7.07—7.70 (m, 4 H, C_6H_4); 3.61 (s, 3 H, N—Me); 2.51 (s, 3 H, *cis*-Me); 2.27 (s, 3 H, =C(Me)—); 2.23 (s, 3 H, β-CH$_3$, indole); 2.13 (s, 3 H, *trans*-Me). ***E*-3-Isopropylidene-4-(1-methyl-1*H*-indol-2-ylmethylidene)tetrahydrofuran-2,5-dione (*E*)-2.** ^{1}H NMR (CDCl$_3$), δ: 7.70—7.10 (m, 4 H, C_6H_4); 7.71 (s, 1 H, —CH=); 6.51 (s, 1 H, H(3)); 3.86 (s, 3 H, N—Me); 2.52 (s, 3 H, *cis*-Me); 1.77 (s, 3 H, *trans*-Me).

Solutions of **1** in toluene were irradiated with the light of a DKSSh-150 xenon lamp, and solutions of **2** in toluene and ethyl acetate were irradiated with the light of a DRSh-500 mercury lamp through glass filters with wavelengths of 365, 405, and 546 nm. The radiation intensities of the xenon and mercury lamps were determined on a ferrioxalate actinometer[6] (for 365 and 405 nm) and with the use of Reinecke salt[7] (for 546 nm). The light intensities of the mercury lamp through light filters with 365, 405, and 546 nm are equal to $3.54 \cdot 10^{-8}$, $5.08 \cdot 10^{-9}$, and $5.82 \cdot 10^{-8}$ Einstein s^{-1}, respectively. Absorption spectra were recorded on Shimadzu UV-3100 and Shimadzu UV-2101 PC spectrophotometers. Fluorescence spectra were obtained with Elumin-2M and Perkin—Elmer LS50 spectrofluorimeters. ^{1}H NMR spectra were recorded on a Bruker 200 instrument with Me$_4$Si as the internal standard. All experiments were carried out at ~20 °C.

Quantum yield determination. To determine the quantum yields of forward and reverse reactions, a solution of compound **1** was placed in a quartz tube (10×10 mm, volume 3 mL) and irradiated with the light of a xenon lamp through a filter with the maximum at 395 nm and half-width of 30 nm. A solution of compound **2** was irradiated with the light of a mercury lamp through a filter with a wavelength of 365 nm. To determine the

Table 1. Absorption (λ_a) and fluorescence (λ_f) maxima for isomers **1** and **2** and the quantum yields Φ of the photoreactions

Fulgide	λ_a/nm			λ_f/nm		Conversions	Φ
	Z	*E*	*C*	*E*	*C*		
1	399[a]	395[a]	531[a]			*Z*→*C* [a,b]	0.043[a]
	388[b]	388[b]	540[b]	497[b]	678[b]	*C*→*E* [a,b]	0.17[a]
						E→*C* [a,b]	0.24[a]
2	417[a]	402[a]	494[a]	470[a]	572[a]	*E*→*C* [a,b]	—
	432[c]	396[c]	510[c]			*Z*→*C* [a,b]	0.034,[a] 0.014[c]
						C→*E* [a,b]	0.16[a]

[a] Toluene.
[b] Acetonitrile.
[c] Ethyl acetate.

quantum yields of the reverse reactions, a solution of compound **1** was irradiated with the light of a xenon lamp through a filter with the maximum at 550 nm and half-width of 30 nm, while a solution of compound **2** was irradiated with the light of a mercury lamp through a filter with a wavelength of 546 nm. Exposure time for samples was gradually extended from 5 to 120 s. After each exposure, an absorption spectrum of the solution irradiated was recorded.

The quantum yield of a photochemical reaction A → B was calculated by equation (2)[5]

$$\Phi = V \cdot \Delta D^{B}(t)/(\varepsilon^{B} \cdot L \cdot \int I_{abs}(t)), \qquad (2)$$

where V/L is the volume of a solution subjected to irradiation; $\Delta D^{B}(t)$ is the change in the optical density of the solution at the maximum of the absorption spectrum of compound B over the irradiation time t; ε^{B}/L mol^{-1} cm^{-1} is the extinction coefficient for compound B; L/cm is the optical pathway length; $\int I_{abs}(t)$ is the amount of light absorbed (Einstein (L s)$^{-1}$) over time t. The quantum yields are presented in Table 1.

Determination of extinction coefficients. The extinction coefficient $\varepsilon(Z_1)$ for (*Z*)-**1** at the absorption maximum (399 nm) is equal to 6900 L mol^{-1} cm^{-1}. The extinction coefficient of the tetracyclic isomer (*C*)-**1** was determined from the changes in the absorption spectra during a conversion of (*Z*)-**1** into (*C*)-**1**. It was taken that the amount of the consumed *Z*-isomer is equal to that of the resulting (*C*)-**1**, and hence the ratio of the optical densities at the absorption maximum is equal to the ratio of the extinction coefficients. The extinction coefficient for (*C*)-**1**, $\varepsilon(C_1)$, equals 12200 L mol^{-1} cm^{-1} at λ = 531 nm. In a similar way, $\varepsilon(E_1)$ = 9060 L mol^{-1} cm^{-1} at λ = 394 nm for (*E*)-**1**. The extinction coefficients for (*Z*)-**2** and (*C*)-**2** were determined analogously.

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