Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 53–55

Relationship between photochromic and fluorescent properties of 4-styryl derivatives of *N*-butyl-1,8-naphthalimide

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Absorption spectra

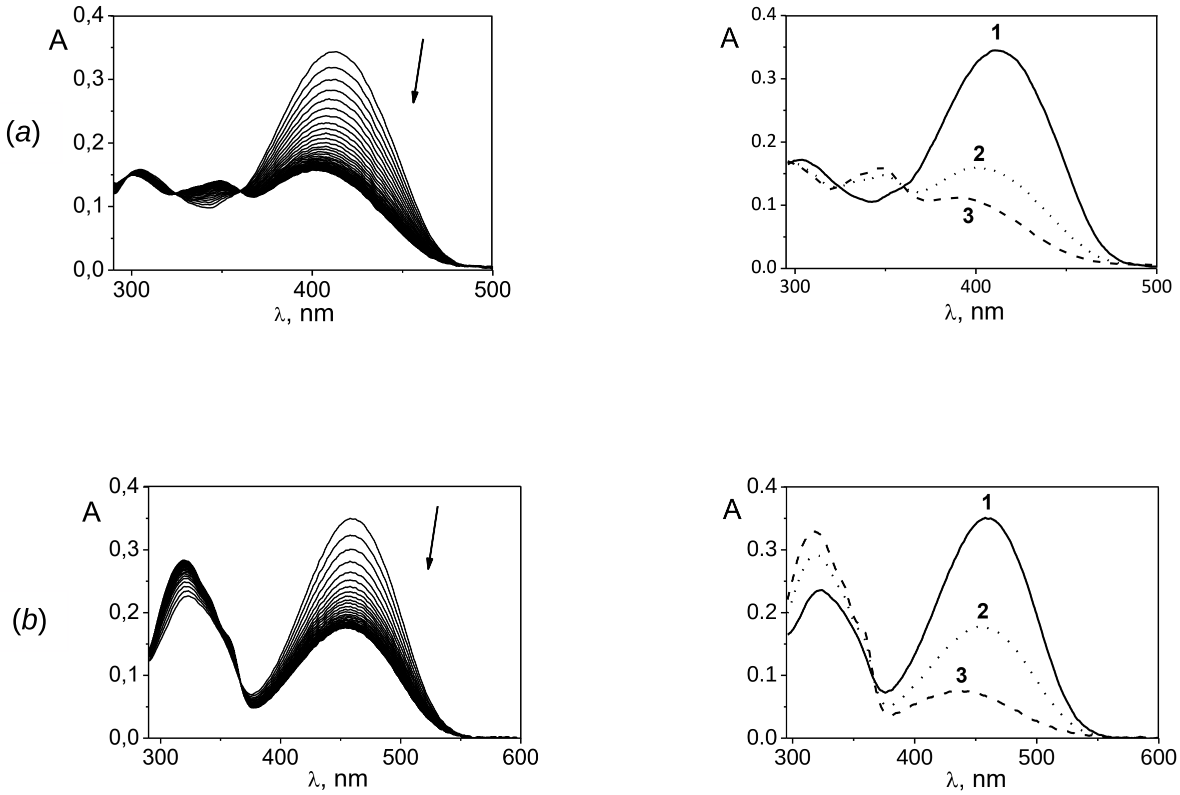
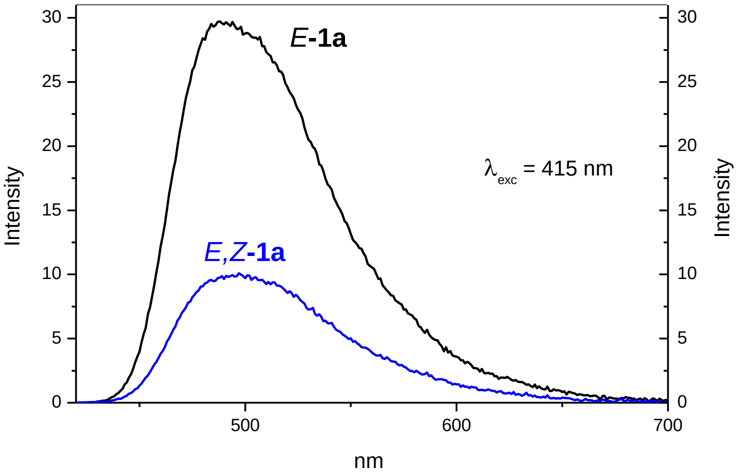
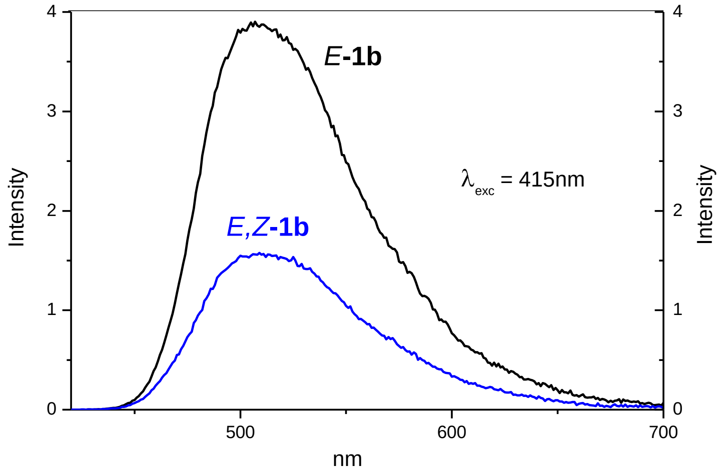


Figure S1 Changes in the absorption spectra of styrylnaphthalimides *E*-**1b** (*a*) and *E*-**1c** (*b*) upon light irradiation (436 nm, C = $1.2 \cdot 10^{-5}$ mol/l) in toluene at room temperature: 1 – *E*-isomer; 2 – photostationary state; 3 – *Z*-isomer. The spectra of the *Z*-isomers were calculated by the Fischer method.

Fluorescence spectra





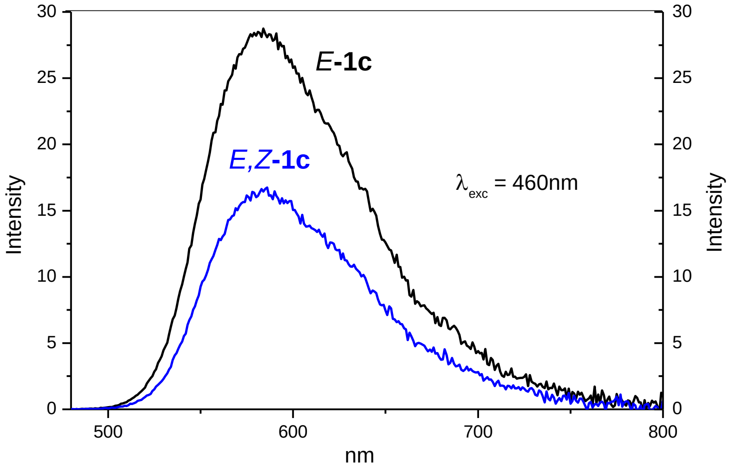


Figure S2 Fluorescence spectra of styrylnaphthalimides *E*-**1a**, *E*-**1b**, *E*-**1c** before and after light irradiation (436 nm, C = $1.2 \cdot 10^{-5}$ mol/l) in toluene at room temperature.

NMR spectra

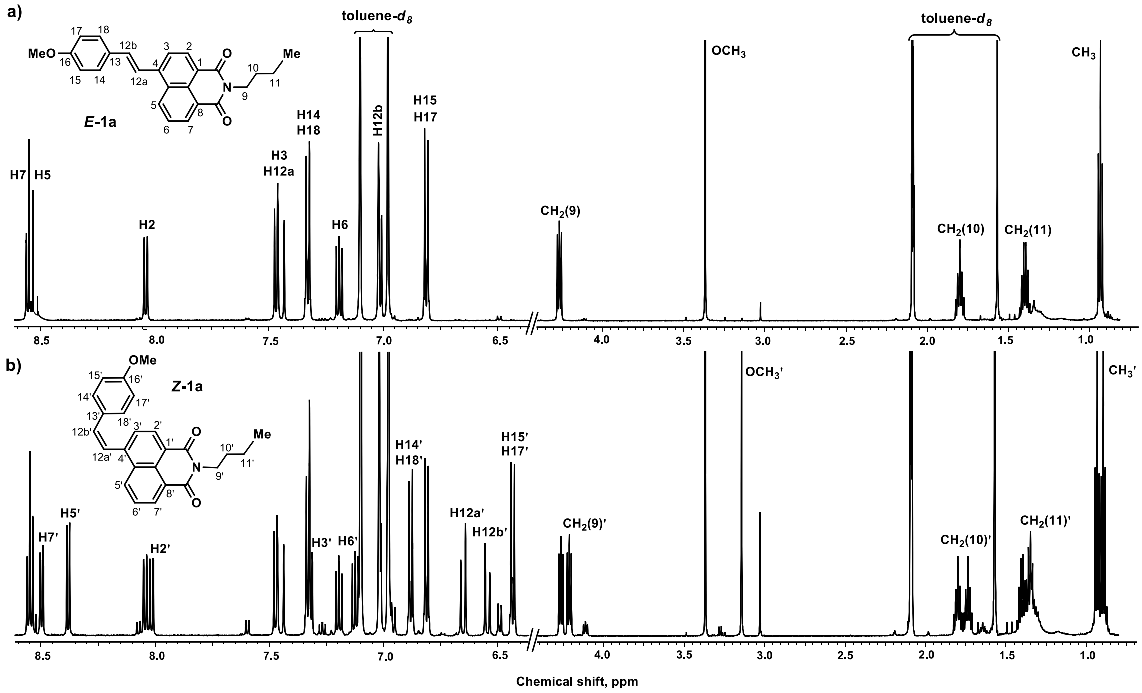
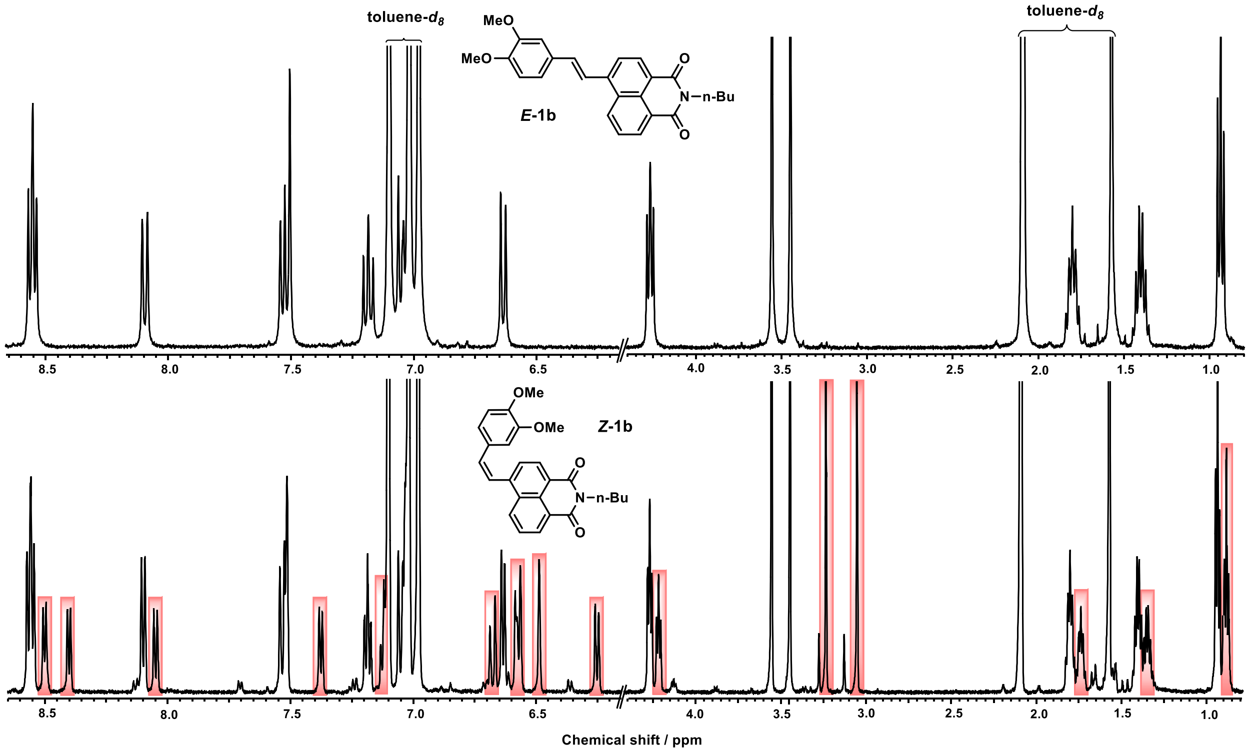


Figure S3 Study of the photoisomerization of styrylnaphthalimide **1a** by NMR spectroscopy in toluene-d_8 at room temperature (Bruker Avance 600, 600 MHz). Bottom spectrum (*b*) corresponds to a photostationary mixture.



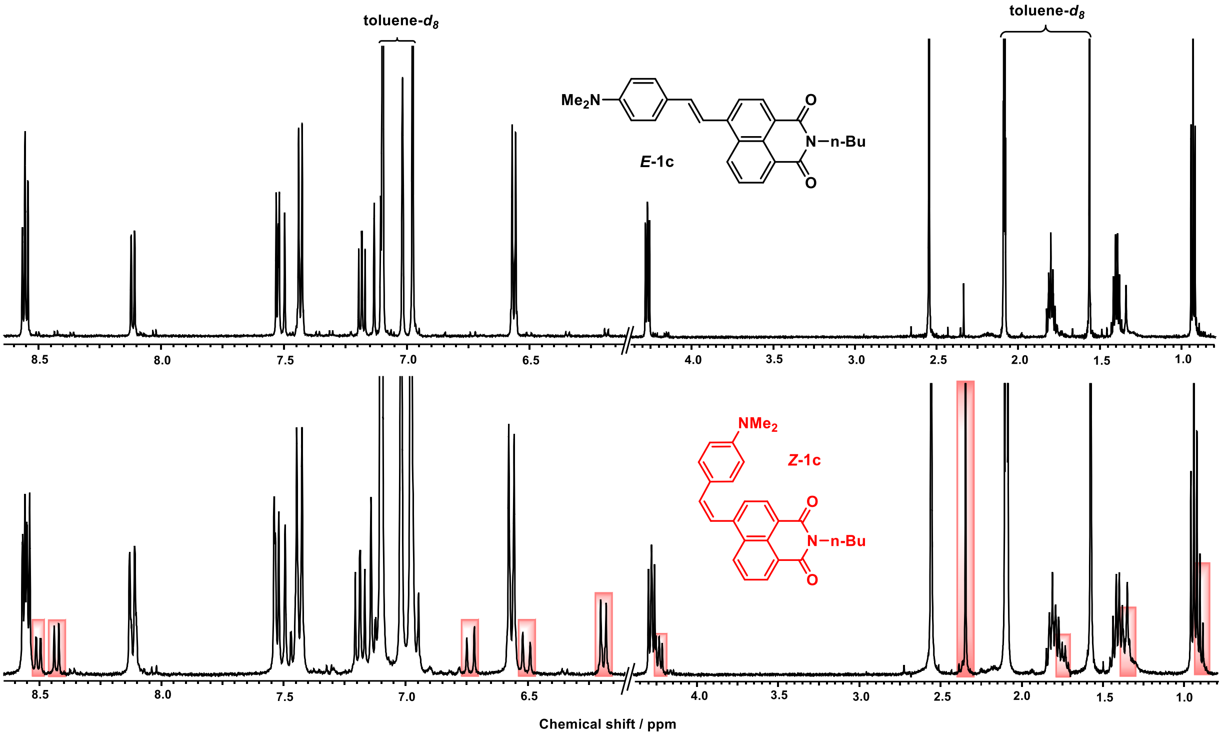
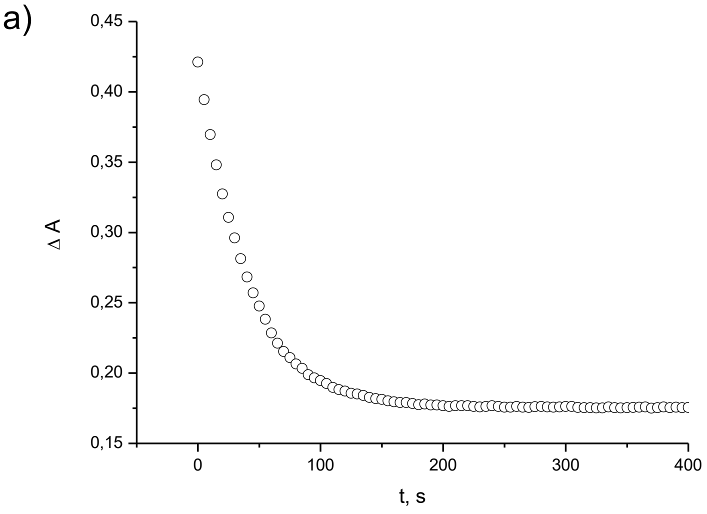


Figure S4 Study of the photoisomerization of styrylnaphthalimides **1b,c** by NMR spectroscopy in toluene-d8 at room temperature (λ = 436 nm, 20 min, C = $2\cdot10^{-2}$ M, Avance Bruker 600). Bottom spectrum corresponds to a photostationary mix.

Kinetic curves



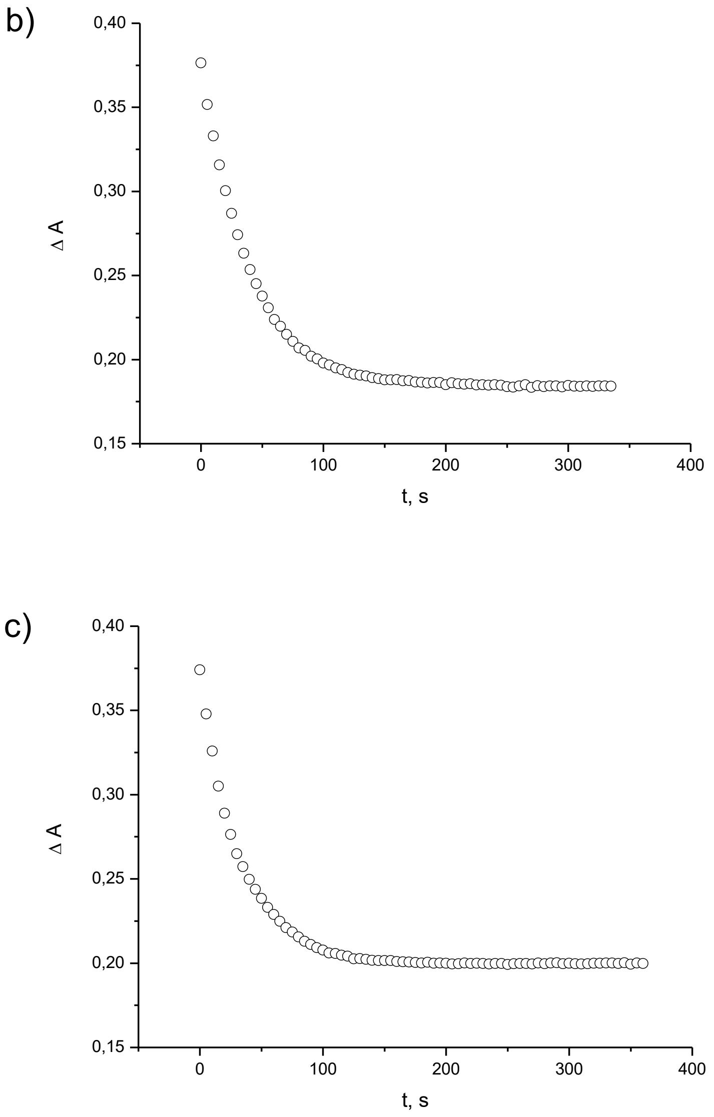


Figure S5 The formation kinetics of photostationary mix of styrylnaphthalimides *E*-**1a** (*a*, 405 nm), *E*-**1b** (*b*, 412 nm), *E*-**1c** (*c*, 460 nm) upon irradiation (436 nm, C = $1.2 \cdot 10^{-5}$ mol/l) in toluene at room temperature.

Calculation of the absorption spectra of *Z*-isomers of 4-styryl-*N*-butylnapthalimide derivatives

The Fisher method [22,23] is used to calculate the absorption spectra of *Z*-isomers. First, we recorded the absorption spectrum of a solution of a dye's *E*-isomer with a known concentration C_L and the spectra of this solution in *E,Z*-photostationary states obtained by irradiation with light at two wavelengths λ = 365 and 436 nm. Using the assumption that the φ_Z/φ_E ratio (the quantum yields of the *Z*- and *E*-isomers, respectively) does not depend on the irradiation wavelength, the fraction of the *Z*-isomer in the photostationary state created by light with λ = 436 nm was calculated from these spectra using the formula:

$$\alpha_{436} = \frac{\Delta_{365}/D_{365} - \Delta_{436}/D_{436}}{1 + \Delta_{365}/D_{365} - n \times \left(1 + \Delta_{436}/D_{436}\right)}$$

where Δ_{365} (Δ_{436}) is the difference between the optical density of the solution in the photostationary state created by light with λ = 365 nm (436 nm) at a wavelength of 365 nm (436 nm) and the optical density of the starting solution of the *E*-isomer at λ = 365 nm (436 nm); $n = \left(D_{436}^{365} - D_{436}^{E}\right)/\left(D_{436}^{436} - D_{436}^{E}\right)$, where D_{436}^{365} and D_{436}^{436} are the optical densities of the solution at the wavelength with the maximum optical density change (λ = 436 nm) in the photostationary states created by light with λ = 365 and 436 nm, respectively; D_{436}^{E} is the optical density of the solution of the starting *E*-isomer at the wavelength with the maximum changes in the optical parameters.

Once α_{436} was determined, the optical density of the pure *Z*-isomer was calculated:

$$D_Z(\lambda) = \frac{D^{436}(\lambda) - (1 - \alpha_{436}) \times D_E(\lambda)}{\alpha_{436}}$$

where $D_E(\lambda)$ is the spectrum of the starting solution of the *E*-isomer; $D^{436}(\lambda)$ is the spectrum of the solution in the photostationary state created by light with λ = 436 nm.

After that, the ratio of the quantum yields of the direct and reverse photoisomerization reactions was calculated:

$$\varphi_Z / \varphi_E = \frac{(1 - \alpha_{436}) \cdot \varepsilon_E^{436}}{\alpha_{436} \cdot \varepsilon_Z^{436}}$$

where ε_E^{436} and ε_Z^{436} are the molar absorption coefficients for the *E*- and *Z*-isomer, respectively, at λ = 436 nm; *d* is the optical path length that equals 1 cm. In the calculation of the theoretical spectrum of the *Z*-isomer we assume that the C_L values for the isomers are equal since the entire *E*-isomer is converted to the *Z*-isomer.

Light intensity measurement

The absolute light intensity was measured using a chemical ferrioxalate actinometer. With a chemical actinometer, the number of light quanta is determined from the amount of the photochemical reaction product with a quantum yield known in advance:

$$I = \frac{N}{\Phi \cdot t \cdot (1-10^{-D})} \approx \frac{N}{\Phi \cdot t}$$

where N is the number of moles of the product formed; Φ is the quantum yield of product formation; t is the irradiation time; $(1\text{-}10^{-D})$ is the coefficient representing the fraction of absorbed light (it usually equals 1, since the concentration of the actinometer is most commonly chosen to ensure complete light absorption).

A ferrioxalate actinometer is a solution of the $K_3Fe(C_2O_4)_3]\cdot 3H_2O$ complex salt in 0.1 N sulfuric acid. Under exposure to light, it undergoes the following reaction:

$$2[Fe(C_2O_4)_3]^{3-} \rightarrow 2Fe^{2+} + 5C_2O_4^{2-} + 2CO_2$$

The quantum yield of ferrioxalate decomposition depends on the wavelength. Ferrous iron that is formed upon photolysis gives a colored complex with 1,10-phenanthroline. The complex of 1,10-phenanthroline with Fe^{2+} ions is formed relatively slowly at pH = 2.5 and considerably more quickly at pH 3.5 - 4.2. In this pH range, the resulting complex is stable to UV and visible light, and its absorption at 510 nm changes linearly with variation in the concentration of Fe^{2+} ions.

By measuring the color intensity of this complex, one can determine the amount of Fe^{2+} ions formed and hence the intensity of the light source. To measure the light intensity by the ferrioxalate method, a solution of potassium ferrioxalate is used with a concentration that, as a rule, ensures complete light absorption at the irradiation wavelength.

The following solutions are required to perform the measurements: A) a solution of potassium ferrioxalate in 0.1 N sulfuric acid, where the required concentration of potassium ferrioxalate is selected depending on the irradiation wavelength; B) 0.1% aqueous solution of 1,10-phenanthroline; C) buffer solution: 600 ml of 1 N sodium acetate + 360 ml of 1 N sulfuric acid + water to 1000 ml.

The light intensity is determined as follows. A preset volume (2 ml) of actinometer solution “A” is irradiated with stirring for such a time period t that the optical density changes by 0.1 − 0.6 (*e.g.*, t = 0, 60, 120, 240, 480 s). After that, V_2 (*e.g.*, 1.5 ml) of the irradiated solution is transferred into a measuring flask of volume V_3 **(***e.g.*, 20 ml), then $(8-V_2)$ ml of 0.1 N sulfuric acid, 1.6 ml of solution “B” and 4 ml of solution “C” are added into the flask. The solution volume in the flask is brought to the mark with water, stirred and kept in the dark for 30 min in order to fully complete the complexation reaction. Then, the optical density of the solution of the resulting complex of ferrous iron with 1,10-phenanthroline is measured at 510 nm. The same operations are carried out with V_1 of the non-irradiated actinometer solution used in the reference cell.

The number of moles of ferrous ions formed during photolysis, $N_{Fe^{2+}}$, is determined by the formula:

$$N_{Fe^{2+}} = 10^{-3} \frac{V_1 \cdot V_3 \cdot D}{V_1 \cdot l \cdot \varepsilon}$$

where V_1 is the volume of the irradiated actinometer solution, ml; V_2 is the volume of the irradiated actinometer taken for the analysis, ml; V_3 is the final volume to which the V_2 solution was diluted, ml; D is the solution optical density at 510 nm; l is the optical path length, cm; and ε is the extinction coefficient of the 1,10-phenanthroline–Fe^{2+} complex at 510 nm that equals $1.11 \cdot 10^4$ $M^{-1} \cdot cm^{-1}$.

If $N_{Fe^{2+}}$, the $\Phi_{Fe^{2+}}$ value at a certain irradiation wavelength and the irradiation time t are known, the intensity of incident light can be calculated as:

$$I = \frac{N_{Fe^{2+}}}{\Phi \cdot t}, \text{ [Einstein/s]}$$

Calculation of the quantum yields of *E*,*Z*-photoisomerization of 4-styryl-*N*-butylnaphthalimide derivatives

The quantum yields of *E*,*Z*-photoisomerization were calculated by the method developed in our laboratory [24,25] based on the experimental plot of the solution optical density at the irradiation wavelength *vs*. irradiation time. This method takes both direct and reverse isomerization into account and is based on a numerical solution of the corresponding differential equations. The calculation also uses the ratio of the quantum yields of reverse and direct isomerization obtained in the calculation of the *Z*-isomer’s spectrum by the Fisher method. The equations for the formation of compounds A and B in a reversible photochemical reaction $A \Leftrightarrow B$ can be written as follows:

$$\frac{d[A]}{dt} = -\phi_{A\to B} \cdot I_{abs}^{A} + \phi_{B\to A} \cdot I_{abs}^{B}$$
$$\frac{d[B]}{dt} = +\phi_{A\to B} \cdot I_{abs}^{A} - \phi_{B\to A} \cdot I_{abs}^{B}$$

where I_{abs}^{A} and I_{abs}^{B} are the numbers of irradiation quanta absorbed by the corresponding compound A and B in time dt; $\phi_{A\to B}$ and $\phi_{B\to A}$ are the quantum yields of the direct and reverse reactions, respectively; $[A]$ and $[B]$ are the numbers of molecules of the corresponding compounds.

The number of light quanta absorbed by each of the compounds can be determined from the following equations:

$$I_{abs}^{\Sigma} = I_0 \cdot (1-10^{-D_{\Sigma}}),$$

$$D_A = \varepsilon_A \cdot [A] \cdot l, \qquad D_B = \varepsilon_B \cdot [B] \cdot l, \qquad D_{\Sigma} = \sum D_i$$

$$I_{abs}^{A} = I_{abs}^{\Sigma} \frac{D_A}{D_{\Sigma}}, \qquad I_{abs}^{B} = I_{abs}^{\Sigma} \frac{D_B}{D_{\Sigma}}$$

where D_{Σ} is the total absorption of all the components; D_A and D_B designate absorption by the corresponding compound; I_{abs}^{Σ} is the total number of radiation quanta absorbed per second of dt; ε_A and ε_B are the absorption coefficients of compounds A and B; and l is the optical path length, cm.

$$\varepsilon_A = \frac{D_A}{N_A}, \quad N_A = C_A \cdot V \cdot N_{Av}$$

$$\varepsilon_B = \frac{D_B}{N_B}, \quad N_B = C_B \cdot V \cdot N_{Av}$$

where N_A and N_B are the numbers of molecules of compounds A and B, respectively; N_{Av} is the Avogadro number; C_A and C_B are the molar concentrations of the corresponding compounds, mol/l; and V is the solution volume, liters.

The $\phi_{A\to B}$ and $\phi_{B\to A}$ values were calculated by an iterative method using a program written in Visual Basic built into Microsoft Excel 2000; an arbitrary initial $\phi_{A\to B}$ value was set.

Computational details

The quantum-chemical calculations were carried out in MOPAC 2009 software complex using the PM6 semiempirical method. The configurational coupling involved 8 highest occupied and 8 lowest unoccupied molecular orbitals. The iterative procedure was continued until the difference in the molecule energy for two consecutive iterations became smaller than 0.01 kcal / mol. The effect of the solvent nature was taken into account in accordance with the COSMO model (Conductor-like Screening Model) built into MOPAC 2009. It was assumed in the calculations that the dielectric constant of the solvent is $\varepsilon = 40$ and its refraction index n is such that $n^2 = 2$.