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

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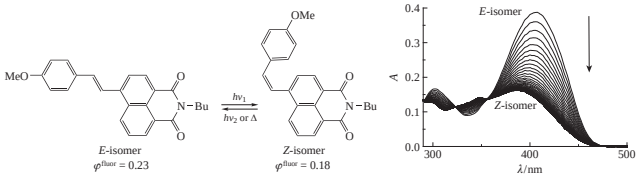
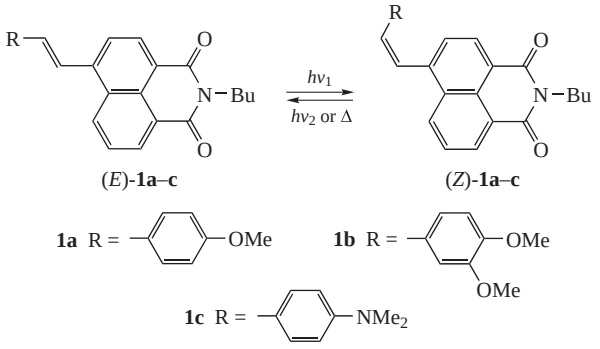
Photochromic *E*,*Z*-isomerization in 4-styryl-1,8-naphthalimides does not significantly affect their fluorescent properties and can be neglected when choosing them as navigators and biological markers.



At present, intense studies aimed at synthesis of new photoactive materials for a broad spectrum of applications in technology, medicine and biology are in progress.[1–6] Design and creation of hybrid photosensitive systems are of special interest owing to the possibility to implement reversible control of their properties.[7,8] In this work, we have studied new hybrid photoactive systems based on 1,8-naphthalimide containing a stilbene moiety as a photochromic component. Naphthalimide derivatives are efficient organic luminophores[9] and are used as dyes for natural and synthetic fibers,[10] active media for lasers based on dye solutions,[11] optical brightening agents,[12] fluorescent chemosensors,[13] fluorescent markers in biology,[14] and in creation of electroluminescent materials.[15] Considerable attention is given in literature to styryl-substituted naphthalimides since they possess unique photoluminescent and electroluminescent properties and demonstrate aggregation-induced emission in biological objects.[16–19] However, the effect of photochromic *E*,*Z*-isomerization on the fluorescent properties of the naphthalimide residue in a hybrid molecule combining two conjugated moieties, stilbene as a photochrome and naphthalimide as a fluorophore, has not been documented so far. To clarify this issue, herein we studied compounds **1a–c** (Scheme 1) with various substituents in the styryl moiety. The syntheses of these compounds were published previously.[20]

Compounds **1a–c** exhibit a long-wave absorption band whose maximum shifts bathochromically on going from methoxy-substituted styrylnaphthalimide **1a** to dimethylamino derivative **1c** and intense fluorescence in the visible region of the spectrum (Table 1).

It is known that stilbene derivatives are capable of *E*,*Z*-isomerization on exposure to light.[21] Using UV and NMR spectroscopy, we studied photochromic *E*,*Z*-isomerization styrylnaphthalimides **1a–c** (see Scheme 1) in toluene. On irradiation of solutions of compounds **1a–c** with filtered light of a mercury lamp (DRK-120, 120 W) (436 nm), formation of a photostationary state is observed. It is characterized by a lower optical density in comparison with the starting *E*-isomer, as well as a hypsochromic shift of the absorption band by 5–21 nm (Figures 1 and S1 in Online Supplementary Materials).



Scheme 1

Table 1 Spectral properties of (*E*)-styrylnaphthalimides (*E*)-**1** and their photostationary states in toluene at room temperature.

Compound	Isomer	λ_{max}^{abs}/nm	*E*/*Z*[a]	λ_{max}^{fluor} (λ_{exc})/nm	φ^{fluor}[b]	$\varphi^{E\to Z}$	$\varphi^{Z\to E}$	φ^{is}[c]	$\varphi^{is} + \varphi^{fluor}$
1a	*E*	405	1/0	495 (415)	0.23	0.33	0.44	0.59	0.82
	E+*Z*	386	0.14/0.86	498 (415)	0.18				
1b	*E*	412	1/0	510 (415)	0.35	0.22	0.40	0.37	0.72
	E+*Z*	403	0.24/0.76	512 (415)	0.28				
1c	*E*	460	1/0	585 (460)	0.33	0.22	0.53	0.47	0.80
	E+*Z*	455	0.39/0.61	585 (460)	0.32				

[a] The ratio of molar fractions of *E*- and *Z*-isomers in the photostationary state. [b] The quantum yields of fluorescence of (*E*)-**1a–c** were determined with respect to coumarin 6. The quantum yields of fluorescence of solutions in the photostationary state were determined with respect to the corresponding *E*-isomers (Figure S2, Online Supplementary Materials). The concentration of compounds in the cell was 1.2×10^{-5} mol dm^{-3}. [c] Calculated as $\varphi^{is} = \varphi^{E\to Z}/(1-\varphi^{Z\to E})$.[23–25] The value φ^{is} corresponds to the fraction of molecules of *E*-isomer in the initially formed local excited state relaxing *via* isomerization pathway.

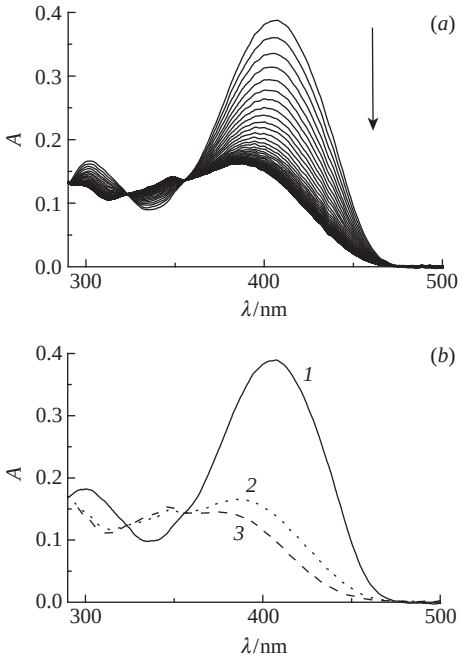


Figure 1 (*a*) Changes in the absorption spectrum of styrylnaphthalimide (*E*)-**1a** under light irradiation (10 min, 436 nm, $C = 1.7\times10^{-5}$ mol dm^{-3}) in toluene at room temperature. (*b*) Absorption spectra of (*1*) *E*-isomer, (*2*) photostationary state and (*3*) *Z*-isomer. The spectrum of the *Z*-isomer was calculated by the Fisher method.

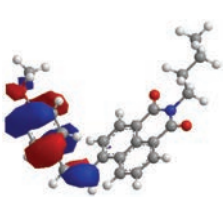
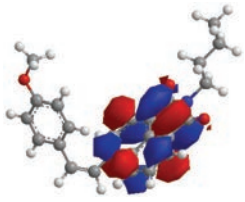
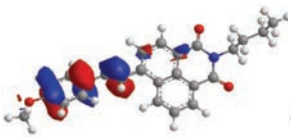
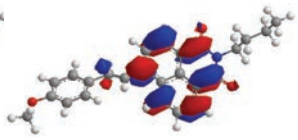
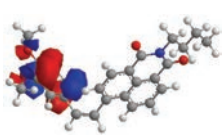
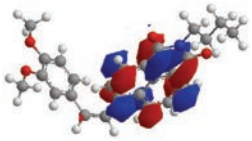
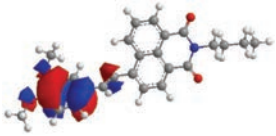
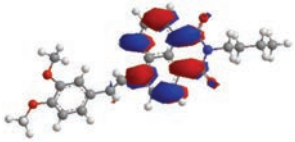
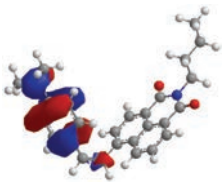
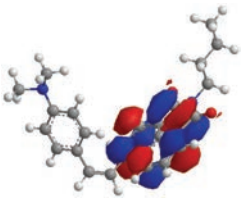
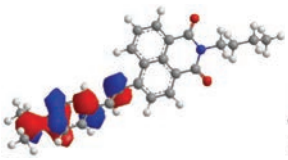
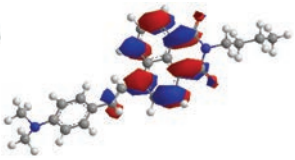
Using the Fisher method,[22,23] we determined the fraction of *Z*-isomers in the photostationary states formed (Table 1) and the shape of their absorption spectra (Figures 1 and S1).

The values given in Table 1 indicate that the photostationary mixture contains a considerable amount (60–80%) of the *Z*-isomer. However, no considerable variation of the fluorescence quantum yields is observed. In order to explain the observed effects, we carried out quantum-chemical calculations of the HOMO–LUMO transitions in compounds (*E*)-**1** and (*Z*)-**1** using the MOPAC 2009 software complex and the PM6 semiempirical method (see Online Supplementary Materials) (Table 2). As follows from the data provided, the geometry of the molecules changes noticeably on going from *E*-isomers to *Z*-isomers, but conjugation between the styryl and naphthalimide moieties remains efficient. The latter statement is supported by the fact that the orbital energies and electron density distribution in the HOMO and LUMO are rather similar for the *E*- and *Z*-isomers.

According to NMR spectroscopic data (Figures S3 and S4), irradiation of the *E*-isomers of styrylnaphthalimides **1a**–**c** gives rise to new signals of the C(12a)=C(12b) double bond at δ 6.6 ppm with coupling constants of 12.4 Hz typical of the *Z*-isomers. Moreover, the positions of the signals of nearly all protons in the compounds also change. The most considerable upfield shift is observed for the H-14′,15′ and H-17′,18′ protons in the aromatic ring of the styryl moiety. This is probably due to the anisotropic effect of the adjacent naphthalene moiety in the *Z*-isomer.

In conclusion, photoirradiation of *E*-isomers of 4-styrylnaphthalimide derivatives results in their *Z*-isomers, which is accompanied by a transition of the structure into a nonplanar state. One can expect that violation of the planar structure would result in violation of conjugation between the aryl and naphthalimide moieties and in considerable changes in the spectral characteristics of the fluorophore. However, the results of experimental studies and quantum-chemical calculations show that conjugation between the molecule parts is preserved, to a considerable extent, in the nonplanar structure of the *Z*-isomer, which explains the similarity in the optical parameters of both *E*- and *Z*-isomers. In the case of methoxy derivatives **1a**,**b**, the fluorescence quantum yields of their solutions decreased 1.2-fold under photostationary conditions in comparison with the corresponding solutions of the *E*-isomers. No changes were observed for compound **1c**. Note that incorporation of a styryl moiety into a naphthalimide molecule is a convenient means of derivatization giving compounds that have fluorescence bands in the long-wave region. The results of these studies show that *E*,*Z*-isomerization in styryl-substituted naphthalimides can be neglected when choosing them as fluorescent reagents since it does not have a significant effect on the fluorescent characteristics. The results obtained are

Table 2 Quantum-chemical calculations of HOMO–LUMO transitions in (*E*)-**1** and (*Z*)-**1**.

Compound	*Z*-isomers		*E*-isomers	
	HOMO/eV	LUMO/eV	HOMO/eV	LUMO/eV
1a	 –8.94	 –1.74	 –8.84	 –1.80
1b	 –8.75	 –1.76	 –8.70	 –1.79
1c	 –8.40	 –1.72	 –8.35	 –1.79

of interest for the quickly expanding area of development of fluorescent navigators and markers of biological molecules.[26,27]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.01.016.

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