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Synthesis and absorption properties of new yellow-green emitting benzo[*de*]isoquinoline-1,3-diones containing hindered amine and 2-hydroxyphenylbenzotriazole fragments

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Abstract

Two novel benzo[*de*]isoquinoline-1,3-dione yellow-green emitting fluorophores, containing both 2,2,6,6-tetramethylpiperidine and 2-(2-hydroxyphenyl)-benzotriazole stabilizer fragments have been synthesized for the first time by combination of benzotriazole UV absorber and HALS units in one fluorescent molecule. Their basic photophysical properties in solution have been determined and discussed. Photodegradation of the new fluorophores has been studied and compared to other similar fluorescent dyes, not containing either UV absorber or hindered amine fragment in their molecules as well as not containing both of them. Novel fluorophores showed the best photostability in solution, which might be caused by a possible "synergism" of two stabilizer fragments combined in one molecule, differing in their action.

Keywords: Benzo[*de*]isoquinoline-1,3-dione (1,8-naphthalimide); HALS; 2-(2-Hydroxyphenyl)-benzotriazole; Synergism; Photostability

1. Introduction

Benzo[*de*]isoquinoline-1,3-dione (1,8-naphthalimide) derivatives with amino or alkoxy groups at position C-6 usually exhibit fluorescent emission on irradiation [1–11]. The derivatives with amino groups are of excellent yellow color enhanced by fluorescence, while those with alkoxy groups are colorless and have a blue emission. Due to their good spectral properties yellow-green fluorescent benzo[*de*]isoquinoline-1,3-diones have found application in a number of areas including coloration of polymers [1], laser active media [2], potential photosensitive biological units [3], fluorescent markers in biology [4], analgesics in medicine [5], light emitting diodes [6], photo-induced electron sensors [7], fluorescence switchers [8], electroluminescent materials [9], liquid crystal displays [10] and ion probes [11].

The requirements on the properties and environmental behavior of the polymeric materials are increasing together with their production and application. It is well known that all commonly used plastics degrade under the influence of sunlight. That is why the problem of their stabilization is of eminent importance. To solve the problem of polymer stabilization, a number of different stabilizers have successfully been applied [12]. Among them, both 2-hydroxyphenylbenzotriazoles and 2,2,6,6-tetramethylpiperidines are of great interest due to their high photostabilizing efficiency. These two derivative groups, however, differ from each other in their action, no matter that both of them belong to the photodegradation stabilizers. Hindered amines such as 2,2,6,6-tetramethylpiperidines inhibit the process of autoxidation by transformation of the parent amines to *N*-oxyl radicals, either by reaction with peroxyl radicals or occasionally by reaction with singlet oxygen, which stops oxidative degradation by the coupling of alkyl radicals [13]. In contrast to 2,2,6,6-tetramethylpiperidines, 2-hydroxyphenylbenzotriazoles are known as UV absorbers. They are transparent to visible light and

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are supposed to dissipate the absorbed energy in a harmless manner, i.e. to convert the absorbed photon energy into heat without being chemically affected [14].

Recently, a number of papers devoted to problem of synthesis of combined stabilizers containing fragments able to act according to different stabilizing mechanisms have been published. Thus, the hindered amine fragments have been combined with either 2-hydroxybenzophenone [15,16] or 2-hydroxyphenylbenzotriazole UV absorbers [17]. A significant (synergistic) stabilizing effect against photodegradation has been determined.

In previous papers the synthesis and properties of benzo[*de*]isoquinoline-1,3-dione fluorophores, containing either an UV absorber moiety [18] or a hindered amine fragment [19] were investigated. A combination of 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole fragments through a benzo[*de*]isoquinoline-1,3-dione unit in one molecule could result in a new type of fluorescent dyes (FDs) capable of ‘‘one-step’’ dyeing and photostabilizing the polymer materials. In this paper we report the synthesis and absorption properties of novel yellow-green emitting benzo[*de*]isoquinoline-1,3-diones **5** and **8**, containing a 2-(2-hydroxyphenyl)-benzotriazole and a 2,2,6,6-tetramethylpiperidine fragments (Scheme 1).

In order to receive a more complete comparative picture for the influence of both 2-hydroxyphenylbenzotriazole and 2,2,6,6-tetramethylpiperidine fragments in the molecule of the examined compounds on their properties, a previously synthesized benzo[*de*]isoquinoline-1,3-dione derivatives **9** and **10** [18], not containing a hindered amine moiety (Scheme 2), or a UV absorber moiety in their molecules **11** [19a] as well as not containing both of them **12** [10c] were involved in the present study (Scheme 3).

2. Results and discussion

The aim of the present study was to synthesize 1,8-naphthalimide fluorescent dyes, containing both 2-(2-hydroxyphenyl)-benzotriazole and 2,2,6,6-tetramethylpiperidine fragments for simultaneously fluorescent dyeing and stabilization of polymers. It was of interest to obtain combined compounds in which the 1,8-naphthalimide unit is situated at a different position (at the benzotriazole or at the 2-hydroxyphenyl moiety) with a view to study the position effect of the benzo[*de*]isoquinoline-1,3-dione fragment on the absorption properties of the 2-(2-hydroxyphenyl)-benzotriazole UV absorbers.

2.1. Synthesis of dyes

The synthesis of the combined molecule 2-[2-(2-hydroxyphenyl)-2*H*-benzotriazol-5-yl]-benzo[*de*]isoquinoline-1,3-dione (**5**) is represented in Scheme 4.

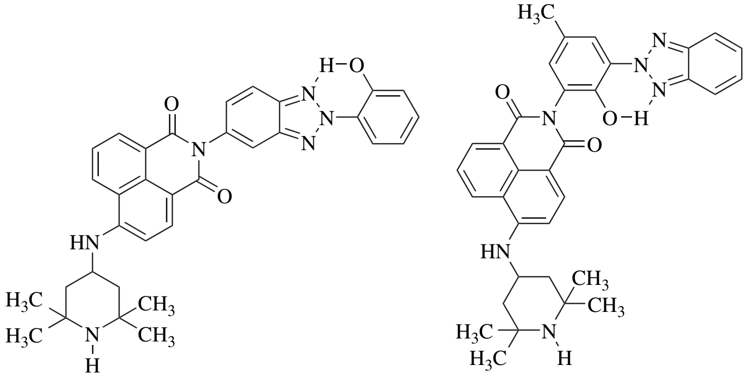
The intermediate compound **3** was obtained by condensation of 2-(2-hydroxyphenyl)-5-amino-benzotriazole (**1**) with 4-nitro-1,8-naphthalic anhydride (**2**) in glacial acetic acid at 110 °C for 8 h using a procedure described before [18]. The results obtained showed that the strong electron-accepting nitro group considerably improves the reaction ability of the starting 1,8-naphthalic anhydride (**2**).

In order to obtain fluorescent 1,8-naphthalimide dye **5** the nitro group in the intermediate **3** was nucleophilic substituted with the commercially available 2,2,6,6-tetramethylpiperidine-4-ylamine (**4**) (Fluka) in DMF at room temperature for 36 h by analogy with a method described before [19a].

To study the position effect of the benzo[*de*]isoquinoline-1,3-dione fragment on the absorption properties of the 2-(2-hydroxyphenyl)-benzotriazole UV-absorber fragments, a new combined molecule **8** was obtained, where the 1,8-naphthalimide unit is linked to the 2-hydroxyphenyl moiety of the benzotriazole ring system. The novel yellow-green emitting dye (**8**) was synthesized in two steps as already described above in the synthesis of compound **5** (Scheme 5).

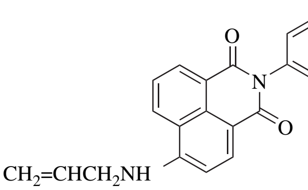
2-Allyl-6-(2,2,6,6-tetramethylpiperidin-4-ylamino)-benzo[*de*]isoquinoline-1,3-dione (**11**), not containing UV absorber fragment [19a], was synthesized by improved procedure in DMF solution at ambient temperature after nucleophilic substitution of the nitro group in 2-allyl-6-nitro-benzo[*de*]isoquinoline-1,3-dione as represented in Scheme 6.

All of the synthesized compounds were characterized by their melting points, TLC (R_f values) and UV–vis spectra



5 **8**

Scheme 1.



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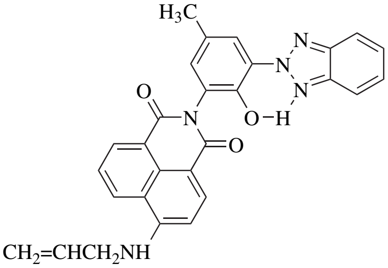

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Scheme 2.

(Table 1) and identified by elemental analysis data, FT-IR and ^{1}H NMR spectra. Dyes **5** and **8** were additionally characterized by fluorescence maxima, Stokes shifts ($\nu_A - \nu_F$) and quantum yields of fluorescence (Φ_F). The data are presented in Table 2.

2.2. Photophysical characterization of dyes

The position effect of the benzo[*de*]isoquinoline-1,3-dione fragment on the absorption properties of the 2-(2-hydroxyphenyl)-benzotriazole fragment can be seen in the UV–vis spectra (Fig. 1).

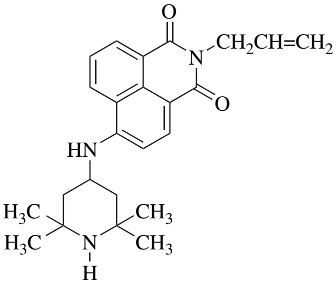
The absorption maximum of benzotriazole **1** (λ_{A1}) is 36 nm bathochromically shifted than that of benzotriazole **6**. This may be related to the position of the electron-donating amino group in the benzotriazole moiety, and in this connection, to the increased strength of the intramolecular hydrogen bond. In the benzotriazole **6** the amino group is situated in the 2-hydroxyphenyl moiety, which leads to decreased strength of the intramolecular hydrogen bond. In confirmation of the above discussion, after acylation with 1,8-naphthalic anhydride (intermediates **3** and **7**) the electron-donating activity of the amino group decreases strongly and the benzotriazole absorption of the intermediate **3** is shifted hipsochromically, while those of the intermediate **7** is shifted bathochromically. As a result of such behavior the benzotriazole absorption maxima of the intermediates **3** and **7** are brought together at $\lambda_{A1} = 342$ nm, which is retained in the spectra of the final compounds **5** and **8** (Table 1, Figs. 2 and 3).

The absorption spectra of the dyes **5** (Fig. 2) and **8** (Fig. 3) clearly show the participation of both UV absorber and 1, 8-naphthalimide units in the combined molecules. Benzotriazole fragments absorb in the UV region at $\lambda_{A1} = 338-340$ nm, while the benzo[*de*]isoquinoline-1,3-dione absorption is shifted from UV ($\lambda_{A2} = 350-351$ nm, intermediates **3** and **7**) to visible region at $\lambda_{A2} = 434$ nm (FDs **5** and **8**), which is surely connected with the substitution of the C-6 electron-withdrawing nitro group (Schemes 4 and 5).

Data presented in Table 1 and the graphics plotted in Figs. 2 and 3 show that the different substituents at both *N*-imide and C-6 atoms have a small effect on the benzo[*de*]isoquinoline-1,3-dione absorption properties by comparison with the absorption properties of the dyes, not containing a hindered amine **9** and **10** (Scheme 2) or a UV absorber **11** moiety in their molecules as well as not containing both of them **12** (Scheme 3).

Basic fluorescent characteristics of the FDs **5** and **8**–**12** such as the fluorescence (λ_F) maxima, Stokes shift ($\nu_A - \nu_F$), oscillator strength (f), fluorescent both quantum (Φ_F) and energy (E_F) yields were measured in chloroform solution and presented in Table 2.

In a chloroform solution FDs displayed intense yellow-green fluorescence due to the charge transfer in the 1,8-naphthalimide moiety from the electron-donating amino group at C-4 position to the carbonyl groups (λ_{A2}). The absorption maxima ($\lambda_{A2} = \lambda_{EX}$) of the FDs were in the UV region at 332–334 nm, while the fluorescence emission was observed in the visible region with well pronounced maxima (λ_F) at



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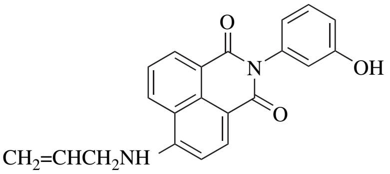

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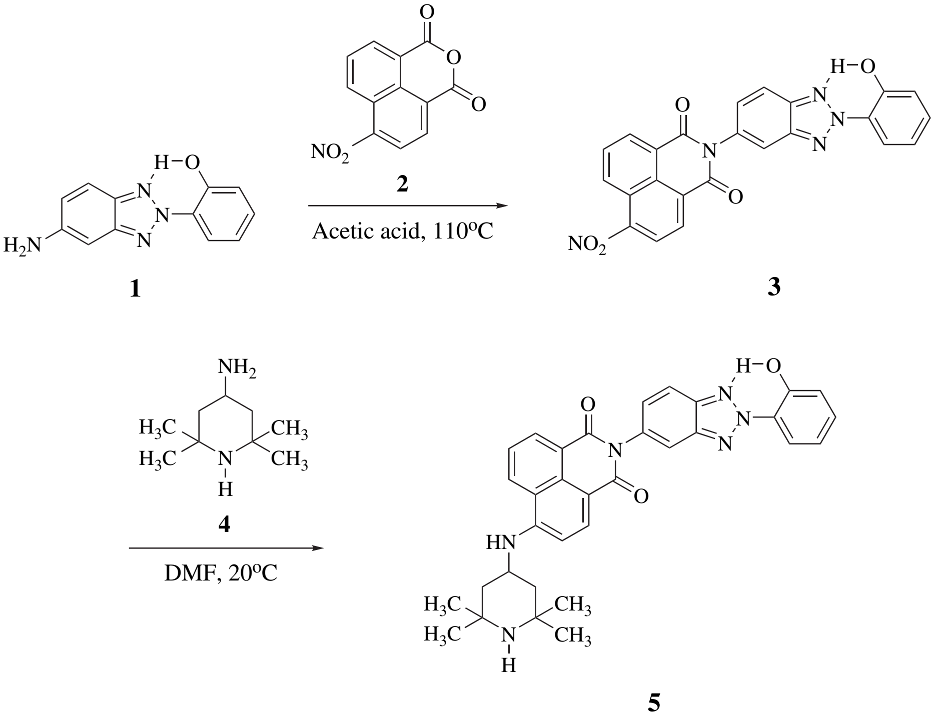
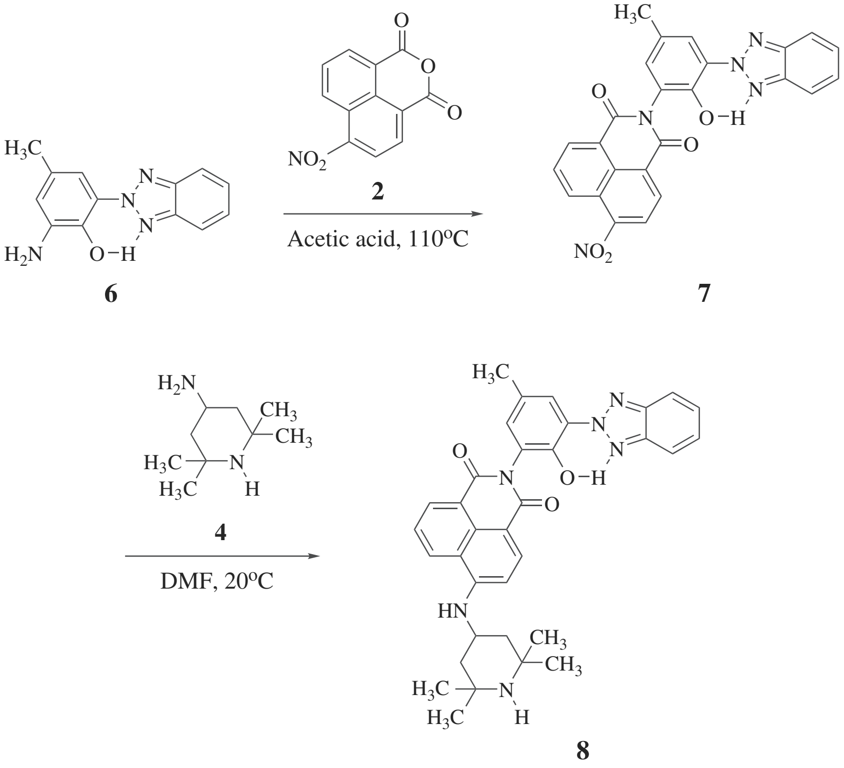
Scheme 3.



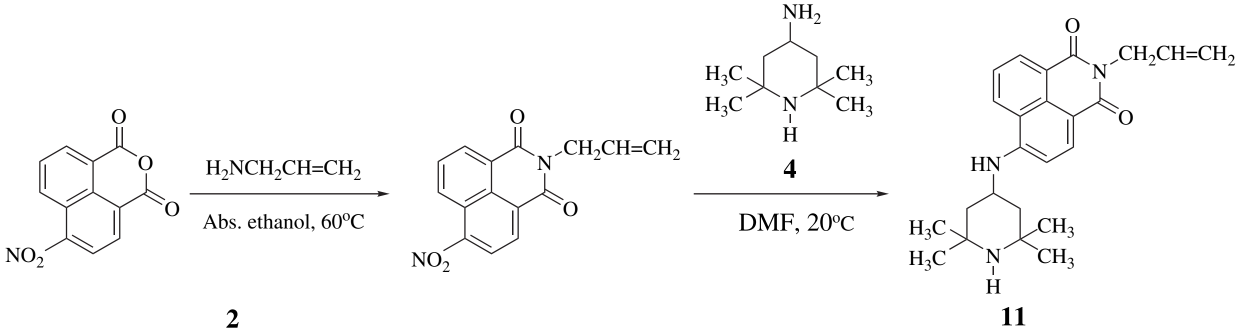
Scheme 4.

517–520 nm (Fig. 4). Data presented in Table 2 show that the different substituents at the *N*-imide and C-6 atoms have a small effect on both the absorption and the fluorescence maxima.

The Stokes shift ($\nu_A - \nu_F$) and oscillator strength (f) are important characteristics for the fluorescent compounds. The Stokes shift is a parameter that indicates the differences in the properties and structure of the fluorophores between the



Scheme 5.



Scheme 6.

ground state S_0 and the first excited state S_1. The Stokes shifts (cm^{-1}) were calculated by Eq. (1) where $\nu_A = \nu_{A2}$.

$$(\nu_A - \nu_F) = \left(\frac{1}{\lambda_A} - \frac{1}{\lambda_F}\right) \times 10^7 \tag{1}$$

The Stokes shift values of the FDs under study between 3699 cm^{-1} and 3880 cm^{-1} were common for the benzo[*de*]isoquinoline-1,3-dione derivatives [20].

The oscillator strength (f) shows the effective number of electrons whose transition from ground to excited state gives the absorption area in the electron spectrum. Values of the oscillator strength were calculated using Eq. (2) where $\Delta\nu_{1/2}$ is the width of the absorption (λ_{A2}) band (cm^{-1}) at $1/2\varepsilon_{\max}$ [21].

$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2}\varepsilon_{\max} \tag{2}$$

The values of the oscillator strength for the benzo[*de*]isoquinoline-1,3-dione dyes **5** and **8–12** were 0.238–0.314, which conform to previous investigations where 1,8-naphthalimide derivatives have oscillator strength values in the range 0.15–0.35 depending on the experimental conditions [22].

The ability of the molecules to emit the absorbed light energy is characterized quantitatively by the fluorescence quantum yield (Φ_F). The quantum yields of fluorescence were calculated using Rhodamine 6G ($\Phi_{\text{ref}} = 0.95$) as a standard according to Eq. (3) [23], where A_{ref}, S_{ref}, n_{ref} and A_{sample}, S_{sample}, n_{sample} represent the absorbance at the excited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample, respectively.

$$\Phi_F = \Phi_{\text{ref}} \left(\frac{S_{\text{sample}}}{S_{\text{ref}}}\right) \left(\frac{A_{\text{ref}}}{A_{\text{sample}}}\right) \left(\frac{n^2_{\text{sample}}}{n^2_{\text{ref}}}\right) \tag{3}$$

The energy yield of fluorescence E_F (Table 2) calculated by Eq. (4) could also be used instead of Φ_F [24].

$$E_F = \Phi_F \frac{\lambda_A}{\lambda_F} \tag{4}$$

Comparison of the fluorescence quantum yields of 6-allylamino-2-(3-hydroxyphenyl)-benzo[*de*]isoquinoline-1,3-dione (**12**) ($\Phi_F = 0.71$), not containing hindered amine and 2-hydroxyphenylbenzotriazole fragments, with those of benzo[*de*]isoquinoline-1,3-diones **9** and **10** ($\Phi_F = 0.66 - 0.67$), a combination of 1,8-naphthalimide with a 2-hydroxyphenylbenzotriazole fragment in one molecule, clearly shows (the values are approximately the same) that the combination of the two different structural units (compounds **9** and **10**) does not result in their interaction as an intramolecular quenching due to an electronic energy transfer.

As can be seen from the data presented in Table 2, the quantum yield of fluorescence for 2-allyl-6-(2,2,6,6-tetramethylpiperidin-4-ylamino)-benzo[*de*]isoquinoline-1,3-dione (**11**) (Scheme 3) is much lower (only $\Phi_F = 0.17$) in comparison

Table 1
Yields, melting points, retention factors and absorption data for benzotriazoles **1** and **6**, intermediates **3** and **7**, fluorescent dyes **5**, and **8–12** in a chloroform solution

Compound	Yield (%)	Mp (°C)	R_f	λ_{A1}[a] (nm)	log ε (l mol^{-1} cm^{-1})	λ_{A2}[a] (nm)	log ε (l mol^{-1} cm^{-1})
1	76	211–212	0.48[b]	360	4.263	–	–
3	62	>260	0.47[b]	342	4.468	351	4.002
5	67	>260	0.34[c]	340	4.509	434	4.145
6	81	213–216	0.51[b]	324	4.269	–	–
7	69	>260	0.49[b]	342	4.424	350	3.942
8	45	233–235	0.39[c]	338	4.488	434	4.142
9	68	>260	0.44[b]	340	4.457	432	4.242
10	72	144–145	0.45[b]	336	4.334	434	4.102
11	77	136–138	0.32[c]	–	–	432	4.134
12	69	153–154	0.48[b]	–	–	434	4.310

[a] λ_{A1} and λ_{A2} represent the absorption maxima of 2-(2-hydroxyphenyl)-benzotriazole and benzo[*de*]isoquinoline-1,3-dione units in the combined molecules, respectively.

[b] TLC in a solvent system *n*-heptane/acetone (1:1).

[c] TLC in a solvent system chloroform/methanol = (9:1).

Table 2
Fluorescence characteristics of compounds **5** and **8–12** in a chloroform solution at $\lambda_{EX} = \lambda_{A2}$

Compound	λ_{EX} (nm)	λ_F (nm)	Intensity [a]	$\nu_A - \nu_F$ (cm^{-1})	f	Φ_F	E_F
5	434	520	127.3	3811	0.240	0.42	0.35
8	434	519	144.4	3774	0.249	0.46	0.38
9	432	519	202.7	3880	0.293	0.66	0.55
10	434	518	203.1	3736	0.238	0.67	0.56
11	432	519	61.8	3880	0.238	0.17	0.14
12	434	517	219.3	3699	0.314	0.71	0.60

[a] Fluorescence intensity at λ_F, arbitrary units.

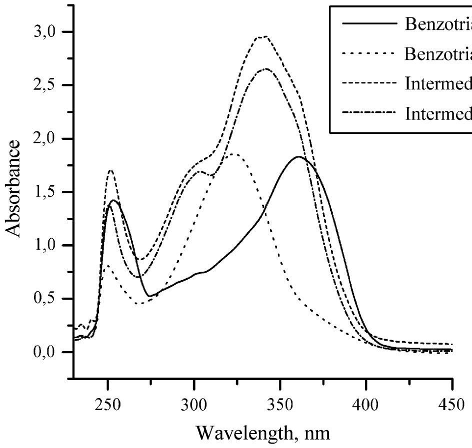


Fig. 1. UV–vis spectra of benzotriazoles **1**, **6** and intermediates **3**, **7** in a chloroform solution at concentration 10^{-4} mol l^{-1}.

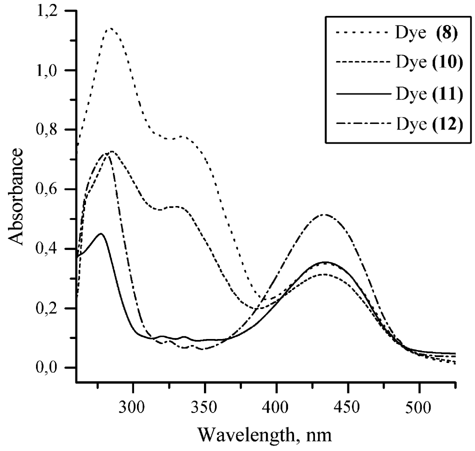


Fig. 3. UV–vis spectra of FDs **8** and **10–12** at concentration 2.5×10^{-5} mol l^{-1} in a chloroform solution.

with data for compounds **9**, **10** and **12**. This phenomenon might be caused by the possible photo-induced electron transfer (PET) from the piperidine nitrogen donor to the 4-amino-1,8-naphthalimide fluorophore through the piperidinyl ring. Thus the fluorescence of the 4-amino-1,8-naphthalimide fluorophores is quenched [7a,25]. This could be the reason for the observed decrease of the quantum yield of fluorescence for combined dyes **5** and **8**, containing 2,2,6,6-tetramethylpiperidine fragment in their molecules, related to the Φ_F of compounds **9**, **10** and **12**, containing only a 2-hydroxyphenylbenzotriazole fragment in the dye molecules (Table 2).

The results obtained suppose PET sensor properties of the fluorescent dyes, containing 4-aminopiperidine moiety at the C-6 position of the benzo[*de*]isoquinoline-1,3-dione ring system, in the presence of protons and transition metal ions, which will be the subject of our future investigations.

2.3. Photostability of the dyes

The fluorescent dyes' photostability is a very important characteristic with regard to their practical usage. To study the influence of both 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole fragments on the photostability of the target dyes **5** and **8**, solutions of the dyes in 1,2-dichloroethane (DCE) were subjected to irradiation with UV light in a SUNTEST equipment. In order to receive a more complete comparative picture of this influence, benzo[*de*]isoquinoline-1,3-diones **9** and **10**, not containing a hindered amine moiety (Scheme 2) or a UV absorber moiety **11** (Scheme 3) in their molecules as well as not containing both of them **12** (Scheme 3) were involved in the present study and investigated under the same conditions.

The kinetics of the FDs' photodegradation was monitored colorimetrically. As during the irradiation no change was observed in the absorption maximum λ_{A2} of the FDs, the correlation between the dye concentration and the time of irradiation was monitored using the method of the standard calibration curve (Fig. 5).

As seen, the photostability of the FDs **5** and **8**, containing both hindered amine and UV absorber fragments, was higher than that of FDs **9–11**, not containing either 2-hydroxyphenylbenzotriazole or 2,2,6,6-tetramethylpiperidine fragment in

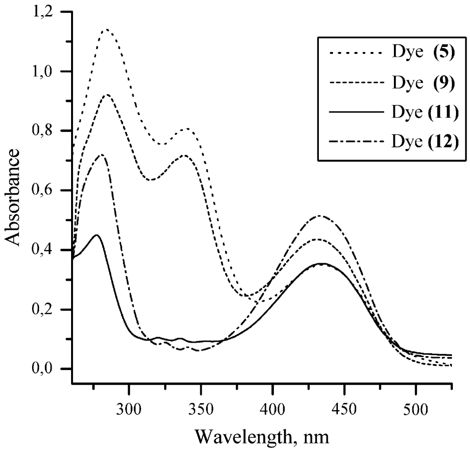


Fig. 2. UV–vis spectra of FDs **5**, **9**, **11** and **12** at concentration 2.5×10^{-5} mol l^{-1} in a chloroform solution.

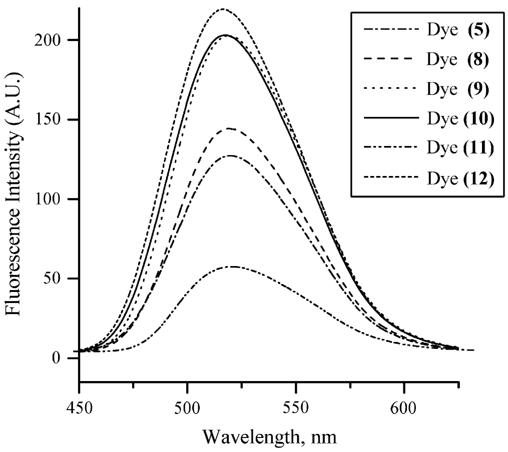


Fig. 4. Fluorescent spectra of FDs **5** and **8–12** at concentration 2.5×10^{-5} mol l^{-1} in a chloroform solution.

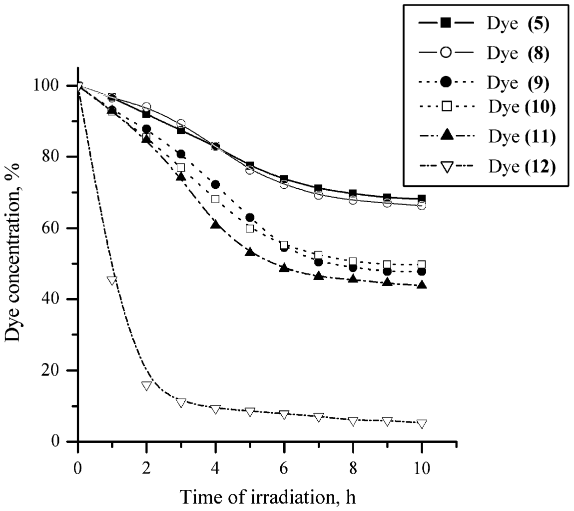


Fig. 5. Photodegradation of FDs **5** and **8–12** in a DCE solution.

their molecules, which could be explained with a "synergism" of the two stabilizer fragments combined in one molecule, differing in their action. In the case of FD **12**, not containing stabilizer fragments, the photodegradation was faster if compared to that of FDs **9–11**, especially to that of FDs **5** and **8**. Within 2 h the FD **12** solution looses significant part of its absorption maximum as a result of the photodegradation of the FD chromophoric system. The study also showed that the influence of the UV absorber fragment type (compounds **5** and **8**) on the dyes' photostability was negligible (Fig. 5).

3. Experimental

3.1. Materials

The starting 2-(2-hydroxyphenyl)-5-amino-benzotriazole **1** [17a] and 2-(2-hydroxy-3-amino-5-methylphenyl)-benzotriazole **6** [17b] as well as 4-nitro-1,8-naphthalic anhydride (**2**) [4,10c] were prepared according to the reported procedures. 2,2,6,6-Tetramethylpiperidine-4-ylamine (**4**) and allylamine (Fluka), p.a. grade, was used without purification. All solvents (Fluka, Merck) were of p.a. or analytical grade.

3.2. Methods

FT-IR spectra were recorded on a Bruker IFS-113 spectrometer at 2 cm^{-1} resolution using KBr discs. The ^{1}H NMR spectra (chemical shifts are given as δ in ppm) were recorded on a Bruker DRX-250 spectrometer, operating at 250.13 MHz. The UV–vis spectra were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature in a chloroform solution. The fluorescence spectra were taken on an SFM 25 spectrophotometer (KONTRON instruments). Fluorescence quantum yields were determined on the basis of the absorption and fluorescence spectra. Rhodamine 6G was used as standard ($\Phi_{\mathrm{ref}} = 0.95$). TLC was performed on silica gel, Fluka F60 254, 20 × 20, 0.2 mm, using as eluant the solvent system *n*-heptane/acetone (1:1) and chloroform/methanol (9:1). The melting points were determined by means of a Kofler melting point microscope.

3.3. Synthesis of fluorescent dyes

3.3.1. General preparation procedure for intermediates **3** and **7**

A suspension of 4-nitro-1,8-naphthalenedicarboxylic acid anhydride (**2**) (15 mmol) and benzotriazole **1** or **6** (15 mmol) in 90 ml of glacial acetic acid was stirred at 110 °C for 8 h. The crude product that precipitated on cooling was filtered off, washed with water and treated with 50 ml of 5% aqueous sodium carbonate. The solid phase was filtered off, washed with water and dried. Re-crystallization from acetic acid afforded the intermediate **3** or **7** as pale yellow-brown crystals.

*3.3.1.1. 2-[2-(2-Hydroxyphenyl)-2H-benzotriazol-5-yl]-6-nitro-benzo[de]isoquinoline-1,3-dione (**3**).* FT-IR (KBr), cm^{-1}: 3078 (νCH=); 3012 (νOH···N); 1712 (ν^{as}C=O); 1673 (ν^{s}C=O); 1596 (νC=C); 1528 (ν^{as}NO$_2$); 1369 (ν^{s}NO$_2$); 1344 (νN–C–N).

^{1}H NMR (250.13 MHz, CDCl$_3$) ppm: 11.09 (s, 1H, OH); 8.87 (d, 1H, $J = 8.7$ Hz, benzo[*de*]isoquinoline 7-H); 8.76 (d, 1H, $J = 7.4$ Hz, benzo[*de*]isoquinoline 9-H); 8.72 (d, 1H, $J = 8.0$ Hz, benzo[*de*]isoquinoline 5-H); 8.43 (d, 1H, $J = 7.6$ Hz, phenyl 6-H); 8.42 (d, 1H, $J = 8.0$ Hz, benzo[*de*]isoquinoline 4-H); 8.36 (dd, 1H, $J = 9.0$ Hz, $J = 1.4$ Hz, benzotriazole 6-H); 8.07 (d, 1H, $J = 9.0$ Hz, benzotriazole 7-H); 8.02 (dd, 1H, $J = 8.7$ Hz, $J = 7.4$ Hz, benzo[*de*]isoquinoline 8-H); 7.93 (d, 1H, $J = 1.4$ Hz, benzotriazole 4-H); 7.35 (dd, 1H, $J = 8.9$ Hz, $J = 1.8$ Hz, phenyl 5-H); 7.17 (dd, 1H, $J = 8.3$ Hz, $J = 1.1$ Hz, phenyl 3-H); 7.03 (m, 1H, phenyl 4-H).

Elemental analysis: Calculated for $C_{24}H_{13}N_5O_5$ (MW 451.39) C 63.86, H 2.90, N 15.52%; found C 64.12, H 2.85, N 15.61%.

*3.3.1.2. 2-(3-Benzotriazol-2-yl-2-hydroxy-5-methyl-phenyl)-6-nitro-benzo[de]isoquinoline-1,3-dione (**7**).* FT-IR (KBr), cm^{-1}: 3070 (νCH=); 3016 (νOH···N); 1710 (ν^{as}C=O); 1674 (ν^{s}C=O); 1598 (νC=C); 1540 (ν^{as}NO$_2$); 1360 (ν^{s}NO$_2$); 1336 (νN–C–N).

^{1}H NMR (250.13 MHz, CDCl$_3$ + DMSO-d_6) ppm: 11.59 (s, 1H, OH); 8.90 (dd, 1H, $J = 8.8$ Hz, $J = 0.9$ Hz, benzo[*de*]isoquinoline 7-H); 8.81 (dd, 1H, $J = 7.4$ Hz, $J = 0.9$ Hz, benzo[*de*] isoquinoline 9-H); 8.77 (d, 1H, $J = 8.1$ Hz, benzo[*de*]isoquinoline 5-H); 8.48 (d, 1H, $J = 8.0$ Hz, benzo[*de*]isoquinoline 4-H); 8.41 (d, 1H, $J = 1.4$ Hz, phenyl 4-H); 8.08 (dd, 1H, $J = 8.7$ Hz, $J = 7.4$ Hz, benzo[*de*]isoquinoline 8-H); 7.92 (dd, 2H, $J = 9.7$ Hz, $J = 3.1$ Hz, benzotriazole 4-H and 7-H); 7.51 (dd, 2H, $J = 9.7$ Hz, $J = 3.1$ Hz, benzotriazole 5-H and 6-H); 7.24 (d, 1H, $J = 1.9$ Hz, phenyl 6-H); 2.50 (s, 3H, CH$_3$).

Elemental analysis: Calculated for $C_{25}H_{15}N_5O_5$ (MW 465.42) C 64.52, H 3.25, N 15.05%; found C 64.80, H 3.19, N 15.16%.

*3.3.2. General preparation procedure for fluorescent dyes **5** and **8***

To a solution of intermediate **3** or **7** (5 mmol) in 50 ml of DMF, 0.78 g of 2,2,6,6-tetramethylpiperidine-4-ylamine (**4**) ($d = 0.91$, 5 mmol) was added at room temperature. After 24 h (TLC control in a solvent system chloroform/methanol = (9:1)), the resulting solution was poured into 300 ml of water. The precipitate was filtered off and washed with water. The crude product was dissolved in a hot solvent mixture of water (5 ml) and ethanol (100 ml), and the undissolved residue was filtered off. The filtrate was then diluted in 100 ml of water and the precipitated product was filtered off and dried. Re-crystallization from ethanol/water (50:50 vol%) afforded 1.88 g (67%) of 6-(2,2,6,6-tetramethylpiperidin-4-ylamino)-2-[2-(2-hydroxyphenyl)-2*H*-benzotriazol-5-yl]-benzo[*de*]isoquinoline-1,3-dione (**5**) and 1.29 g (45%) of 6-6-(2,2,6,6-tetramethylpiperidin-4-ylamino)-2-(3-benzotriazol-2-yl-2-hydroxy-5-methyl-phenyl)-benzo[*de*]isoquinoline-1,3-dione (**8**) as yellow-orange crystals.

*3.3.2.1. 6-(2,2,6,6-Tetramethylpiperidin-4-ylamino)-2-[2-(2-hydroxyphenyl)-2H-benzotriazol-5-yl]-benzo[de]isoquinoline-1,3-dione (**5**).* FT-IR (KBr), cm^{-1}: 3305 (νNH); 3058 (νCH=); 3010 (νOH···N); 2880 (νCH_3); 1698 (ν^{as}C=O); 1670 (ν^{s}C=O); 1660 (νC=N); 1598 (νC=C).

^{1}H NMR (250.13 MHz, $CDCl_3 + DMSO\text{-}d_6$) ppm: 11.20 (s, 1H, OH); 8.60 (dd, 2H, $J = 8.5$ Hz, $J = 7.2$ Hz, benzo[*de*]-isoquiniline 7-H and 9-H); 8.44 (d, 1H, $J = 8.5$ Hz, benzo[*de*]-isoquiniline 4-H); 8.38 (dd, 1H, $J = 8.3$ Hz, $J = 1.3$ Hz, benzotriazole 6-H); 8.07 (d, 1H, $J = 9.0$ Hz, phenyl 6-H); 7.94 (d, 1H, $J = 1.0$ Hz, benzotriazole 4-H); 7.66 (dd, 1H, $J = 8.2$ Hz, $J = 7.6$ Hz, benzo[*de*]isoquiniline 8-H); 7.40 (m, 2H, benzotriazole 7-H and phenyl 5-H); 7.21 (dd, 1H, $J = 8.3$ Hz, $J = 1.1$ Hz, phenyl 3-H); 7.08 (td, 1H, $J = 8.3$ Hz, $J = 1.2$ Hz, phenyl 4-H); 6.71 (d, 1H, $J = 8.6$ Hz, benzo[*de*]isoquiniline 5-H); 4.13 (m, 1H, piperidine CH); 3.60 (br s, 1H, NH); 2.44 (t, 2H, $J = 12.2$ Hz, piperidine CH_2); 1.66 (dd, 2H, $J = 12.2$ Hz, $J = 2.2$ Hz, piperidine CH_2);1.48 (br s, 1H, piperidine NH); 1.37 (s, 6H, piperidine $2 \times CH_3$); 1.21 (s, 6H, piperidine $2 \times CH_3$).

Elemental analysis: Calculated for $C_{33}H_{32}N_6O_3$ (MW 560.65) C 70.70, H 5.75, N 14.99%; found C 71.03, H 5.81, N 14.87%.

*3.3.2.2. 6-(2,2,6,6-Tetramethylpiperidin-4-ylamino)-2-(3-benzotriazol-2-yl-2-hydroxy-5-methylphenyl)-benzo[de]isoquinoline-1,3-dione (**8**).* FT-IR (KBr), cm^{-1}: 3308 (νNH); 3060 (νCH=); 3014 (νOH···N); 2878 (νCH_3); 1700 (ν^{as}C=O); 1668 (ν^{s}C=O); 1658 (νC=N); 1596 (νC=C).

^{1}H NMR (250.13 MHz, $CDCl_3$) ppm: 11.58 (s, 1H, OH); 8.67 (dd, 2H, $J = 8.2$ Hz, $J = 7.5$ Hz, benzo[*de*]isoquiniline 7-H and 9-H); 8.60 (d, 1H, $J = 8.3$ Hz, benzo[*de*]isoquiniline 4-H); 8.40 (d, 1H, $J = 1.2$ Hz, phenyl 4-H); 7.92 (dd, 2H, $J = 9.5$ Hz, $J = 2.9$ Hz, benzotriazole 4-H and 7-H); 7.70 (dd, 1H, $J = 8.2$ Hz, $J = 7.5$ Hz, benzo[*de*]isoquiniline 8-H); 7.47 (dd, 2H, $J = 9.6$ Hz, $J = 3.0$ Hz, benzotriazole 5-H and 6-H); 7.01 (d, 1H, $J = 1.7$ Hz, phenyl 6-H); 6.70 (d, 1H, $J = 8.3$ Hz, benzo[*de*]isoquiniline 5-H); 4.09 (m, 1H, piperidine CH); 2.49 (s, 3H, phenyl CH_3); 2.10 (dd, 2H, $J = 12.8$ Hz, $J = 2.4$ Hz, piperidine CH_2); 1.78 (br s, 1H, piperidine NH); 1.46 (t, 2H, $J = 12.8$ Hz, piperidine CH_2); 1.28 (s, 6H, piperidine $2 \times CH_3$); 1.16 (s, 6H, piperidine $2 \times CH_3$).

Elemental analysis: Calculated for $C_{34}H_{34}N_6O_3$ (MW 574.67) C 70.06, H 5.96, N 14.62%; found C 71.37, H 5.89, N 14.71%

*3.3.3. Preparation of 2-allyl-6-(2,2,6,6-tetramethylpiperi din-4-ylamino)-benzo[de]isoquinoline-1,3-dione (**11**)*

To a suspension of 4-nitro-1,8-naphthalic anhydride (**2**) (7.29 g, 30 mmol) in 60 ml of absolute ethanol, 2.25 ml of allylamine (1.71 g, $d = 0.76$, 30 mmol) was added dropwise under stirring at ambient temperature over a period of 15 min. The resulting mixture was stirred at 60 °C for 4 h. The crude product that precipitated on cooling with addition of water was treated with 50 ml of 5% aqueous sodium hydroxide to give after filtration, washing with water and drying 7.78 g (92%) of 2-allyl-6-nitro-benzo[*de*]isoquinoline-1,3-dione as pale yellow crystals.

To a solution of 2-allyl-6-nitro-benzo[*de*]isoquinoline-1,3-dione (4.23 g, 15 mmol) in 50 ml of DMF, 2.24 g of 2,2,6,6-tetramethylpiperidine-4-ylamine (**4**) ($d = 0.91$, 15 mmol) was added at room temperature. After 24 h (TLC control in a solvent system *n*-heptane/acetone = 1:1), the resulting solution was poured into 300 ml of water. The precipitate was filtered off and washed with water. The crude product was dissolved in a hot solvent mixture of water (5 ml) and ethanol (100 ml), and the undissolved residue was filtered off. The filtrate then was diluted in 100 ml of water and the precipitated product was filtered off and dried. Re-crystallization from ethanol/water (30:70 vol%) afforded 4.52 g (77%) of 2-allyl-6-(2,2,6,6-tetramethylpiperidin-4-ylamino)-benzo[*de*]isoquinoline-1,3-dione (**11**) as yellow-orange crystals.

3.3.3.1. 2-Allyl-6-nitro-benzo[de]isoquinoline-1,3-dione. FT-IR (KBr), cm^{-1}: 1705 (ν^{as}C=O); 1670 (ν^{s}C=O); 1656 (νC=N); 1598 (νC=C); 1535 ($\nu^{as}NO_2$); 1375 ($\nu^{s}NO_2$).

^{1}H NMR (250.13 MHz, $CDCl_3$) ppm: 8.83 (dd, 1H, $J = 8.1$ Hz, $J = 1.2$ Hz, benzo[*de*]isoquiniline 7-H); 8.75 (dd, 1H, $J = 7.5$ Hz, $J = 1.2$ Hz, benzo[*de*]isoquiniline 9-H); 8.70 (d, 1H, $J = 8.0$ Hz, benzo[*de*]isoquiniline 5-H); 8.41 (d, 1H, $J = 8.0$ Hz, benzo[*de*]isoquiniline 4-H); 7.98 (dd, 1H, $J = 7.5$ Hz, $J = 8.1$ Hz, benzo[*de*]isoquiniline 8-H); 5.98 (m, 1H, allyl CH=); 5.33 (dd, 1H, $J_{trans} = 17.2$ Hz, $J = 1.2$ Hz, allyl H*CH*=); 5.28 (dd, 1H, $J_{cis} = 10.4$ Hz, $J = 1.2$ Hz, allyl H*CH*=); 4.81 (dt, 2H, $J = 6.1$ Hz, $J = 1.2$ Hz, allyl NCH_2).

*3.3.3.2. 2-Allyl-6-(2,2,6,6-tetramethylpiperidin-4-ylamino)-benzo[de]isoquinoline-1,3-dione (**11**).* FT-IR (KBr), cm^{-1}: 1695 (ν^{as}C=O); 1660 (ν^{s}C=O); 1658 (νC=N); 1594 (νC=C).

^{1}H NMR (250.13 MHz, $CDCl_3$) ppm: 8.58 (d, 1H, $J = 7.3$ Hz, benzo[*de*]isoquiniline 7-H); 8.47 (d, 1H, $J = 7.9$ Hz, benzo[*de*]isoquiniline 4-H); 8.08 (dd, 1H, $J = 7.4$ Hz, $J = 1.1$ Hz, benzo[*de*]isoquiniline 9-H); 7.60 (dd, 1H,

$J = 7.4$ Hz, $J = 7.3$ Hz, benzo[*de*]isoquiniline 8-H); 6.74 (d, 1H, $J = 7.9$ Hz, benzo[*de*]isoquiniline 5-H); 5.99 (m, 1H, allyl CH═); 5.26 (dd, 1H, $J_{trans} = 17.2$ Hz, $J = 1.2$ Hz, allyl H*CH*═); 5.20 (dd, 1H, $J_{cis} = 10.4$ Hz, $J = 1.2$ Hz, allyl H*CH*═); 5.10 (d, 1H, NH, $J = 6.1$ Hz); 4.79 (d, 2H, $J = 4.9$ Hz, allyl NCH_2); 4.09 (m, 1H, piperidine CH); 2.17 (dd, 2H, $J = 11.8$ Hz, $J = 2.2$ Hz, piperidine CH_2); 1.79 (br s, 1H, piperidine NH); 1.39 (s, 6H, piperidine $2 \times CH_3$); 1.22 (m, 8H, piperidine $2 \times CH_3$ and piperidine CH_2).

3.4. Photodegradation of dyes

The studies on the photodegradation of the fluorescent dyes were performed in a solar simulator SUNTEST CPS equipment (Heraeus, Germany), supplied with an air-cooled Xenon lamp (Hanau, 1.1 kW, 765 W m^{-2}), protected with an adequate filter to simulate the solar spectrum between 290 nm and 800 nm. The photodestruction of the dyes was monitored spectrophotometrically using the method of standard calibration curve.

4. Conclusions

Novel yellow-green benzo[*de*]isoquinoline-1,3-dione fluorophores, containing hindered amine and 2-(2-hydroxyphenyl)-benzotriazole stabilizer fragments have been successfully synthesized. The basic photophysical properties of the new compounds in solution have been determined and discussed. The results obtained suppose PET sensor properties of the fluorescent dyes, containing 4-aminopiperidine moiety at the C-6 position of the benzo[*de*]isoquinoline-1,3-dione ring system, which will be the subject of our future investigations. Photodegradation of the new fluorophores has been studied and compared to other similar fluorescent dyes, not containing either UV absorber or hindered amine fragment in their molecules as well as not containing both of them. Novel fluorophores showed the best photostability in solution, which might be caused by a possible “synergism” of the two stabilizer fragments combined in one molecule , differing in their action. As a result of our investigation it can be concluded that new dyes represent the possibility of “one-step” coloration and stabilization of polymers.

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References

[1] (a) Konstantinova T, Lazarova R, Venkova A, Vasileva V. Polym Degrad Stab 2004;84:405;
(b) Grabchev I, Betcheva R. J Photochem Photobiol A Chem 2001;142:73;
(c) Grabchev I, Konstantinova T. Dyes Pigments 1997;33:197;
(d) Grabchev I, Konstantinova T, Guittonneau S, Mealier P. Dyes Pigments 1997;35:361;
(e) Konstantinova T, Mealier P, Grabchev I. Dyes Pigments 1993;22:191;
(f) Grabchev I, Konstantinova T, Mealier P, Popova T. Dyes Pigments 1995;28:41;
(g) Grabchev I, Konstantinova T. J Appl Polym Sci 1996;62:447;
(h) Grabchev I, Guittonneau S, Konstantinova T, Mealier P. Bull Soc Chem Fr 1994;131:828;
(i) Konstantinova T, Grabchev I. Polym Int 1997;43:39;
(j) Konstantinova T, Lazarova R. J Univ Chem Technol Met (Sofia) 2003;38:69;
(k) Patrick L, Whiting A. Dyes Pigments 2002;52:137;
(l) Patrick L, Whiting A. Dyes Pigments 2002;55:123.

[2] (a) Martin E, Weigand R, Pardo A. J Lumin 1996;68:157;
(b) Gruzinskii V, Kukhta A, Shakkah G. J Appl Spectrosc 1998;65:444.

[3] Tao Z-F, Qian X. Dyes Pigments 1999;43:139.

[4] Dubey K, Singh R, Mizra K. Indian J Chem 1995;34B:876.

[5] de Souza M, Correa R, Filho V, Grabchev I, Bojinov V. Pharmazie 2002;56:430.

[6] (a) Facoetti H, Robin P, Le Barny P, Schott M, Bouche C-M, Berdague P. Synth Met 1996;81:191;
(b) Morgado J, Gruner J, Walcott SP, Yong TM, Cervini R, Moratti SC, et al. Synth Met 1998;95:113;
(c) Zhu W, Hu C, Chen K, Tian H. Synth Met 1998;96:151.

[7] (a) Grabchev I, Chovelon J-M, Qian X. J Photochem Photobiol A Chem 2003;158:37;
(b) Tian H, Gan J, Chen K, He J, Song Q, Hou X. J Mater Chem 2002;12:1262;
(c) Grabchev I, Qian X, Bojinov V, Xiao Y, Zhang W. Polymer 2002;43:5731;
(d) Grabchev I, Chovelon J-M, Qian X. New J Chem 2003;27:337;
(e) Grabchev I, Qian X, Xiao Y, Zhang W. New J Chem 2002;26:920;
(f) Tian H, Xu T, Zhao Y, Chen K. J Chem Soc Perkin Trans 1999; 2:545.

[8] (a) Poteau X, Brown A, Brown R, Holmes C, Matthew D. Dyes Pigments 2000;47:91;
(b) Jia L, Zhang Y, Guo X, Qian X. Tetrahedron Lett 2004;45:3969.

[9] (a) Zhu W, Hu M, Yao R, Tian H. J Photochem Photobiol A Chem 2003;154:169;
(b) Hassheider T, Benning S, Kitzerow H-S, Achard M-F, Bock H. Angew Chem Int Ed 2001;40:2060;
(c) Cacialli F, Friend R, Bouche C, Le Barny P, Facoetti H, Soyer F, et al. J Appl Phys 1998;83:2343;
(d) Utsugi K, Takano S. J Electrochem Soc 1992;139:3610;
(e) Zhu W, Minami N, Kazaoui S, Kim Y. J Mater Chem 2003;13:2196.

[10] (a) Grabchev I, Moneva I, Wolarz E, Bauman D. Z Naturforsch 1996;51a:1185;
(b) Grabchev I, Chovelon J-M. Polym Adv Technol 2003;14:601;
(c) Grabchev I, Moneva I, Bojinov V, Guittonneau S. J Mater Chem 2000;10:1291;
(d) Scherovsky G. Makromol Chem Macromol Symp 1993;69:87;
(e) Grabchev I, Moneva I. J Appl Polym Sci 1999;74:151.

[11] Cosnard F, Wintgens V. Tetrahedron Lett 1998;39:2751.

[12] Ranby B, Rabek J. Photodegradation, photo-oxidation and photostabilization of polymers. London: Wiley; 1975.

[13] (a) Allen NS. Chem Soc Rev 1986;15:373;
(b) Kamiya Y, Niki EJellinek HH, editor. Aspects of degradation and stabilization of polymers. Amsterdam: Elsevier; 1978. p. 103.

[14] Crawford JC. Prog Polym Sci 1999;24:7.

[15] Bojinov V, Grabchev I. J Photochem Photobiol A Chem 2002;146:199.

[16] (a) Zakrzewski J, Szymanowski J. Polym Degrad Stab 2001;72:109;
(b) Zakrzewski J, Szymanowski J. Polym Degrad Stab 2000;67:279;
(c) Zakrzewski J, Szymanowski J. Polym Degrad Stab 1999;65:425;
(d) Zakrzewski J, Szymanowski J. Polym Degrad Stab 2005;87:17.

[17] (a) Bojinov V, Grabchev I. J Photochem Photobiol A Chem 2002; 150:223;
(b) Bojinov V, Grabchev I. Polym Degrad Stab 2001;74:543;
(c) Bojinov V. Photochem Photobiol Sci 2002;1:340.

[18] (a) Bojinov V, Grabchev I. J Photochem Photobiol A Chem 2005;172:308;
(b) Bojinov V, Grabchev I. Dyes Pigments 2003;59:277.

[19] (a) Bojinov V, Konstantinova T. Dyes Pigments 2002;54:239;
(b) Hrdlovic P, Chmela S, Danko M. J Photochem Photobiol A Chem 1998;112:197;
(c) Chmela S, Danko M, Hrdlovic P. Polym Degrad Stab 1999;63:159;
(d) Kollar J, Hrdlovic P, Chmela S, Sarakha M, Guyot G. J Photochem Photobiol A Chem 2004;170:151.

[20] Mata J. Adv Colour Sci Technol 1999;2:162.

[21] Gordon P, Gregory P. Organic chemistry in colour. Moskva: Chimia; 1987.

[22] (a) Grabchev I, Bojinov V, Petkov H. Dyes Pigments 2001;51:1;
(b) Yang S, Meng F, Tian H, Chen K. Eur Polym J 2002;38:911.

[23] (a) Du H, Fuh RA, Li J, Corkan A, Lindsey JS. Photochem Photobiol 1998;68:141;
(b) Kubin RF, Fletcher AN. J Lumin 1982;27:455.

[24] Grabchev I, Philipova T. Indian J Chem 1997;36B:264.

[25] Gan J, Chen K, Chang C-P, Tian H. Dyes Pigments 2003;57:21.