

SYNTHESIS OF NOVEL FLUOROPHORES – COMBINATION OF HINDERED AMINE AND UV ABSORBER IN THE MOLECULE OF BENZO[de]ISOQUINOLINE-1,3-DIONE

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ABSTRACT

Two novel benzo[de]isoquinoline-1,3-dione 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 molecule. Their absorption properties in solution have been determined and discussed. Photodegradation of the new compounds has been studied and compared to other similar fluorescent brighteners, not containing either a UV absorber or a 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 combined in one molecule two stabilizer fragments, differing in their action.

Keywords: benzo[de]isoquinoline-1,3-dione (1,8-naphthalimide), fluorescent brighteners, HALS, 2-(2-hydroxyphenyl)-benzotriazole, phase transfer catalysis, synergism, photostability.

INTRODUCTION

Fluorescent benzo[de]isoquinoline-1,3-dione derivatives due to their good spectral properties have found application in a number of areas including laser active media [1], potential photosensitive biologically units [2], fluorescent markers in biology [3], analgesics in medicine [4], light emitting diodes [5], photo-induced electron sensors [6], fluorescence switchers [7], electroluminescent materials [8], liquid crystal displays [9] and ion probes [10].

6-Alkoxy-benzo[de]isoquinoline-1,3-diones are a new type of electron-transporting emitting materials, re-emitting the absorbed light as a violet-blue fluorescence in the visible region. In the recent years they have

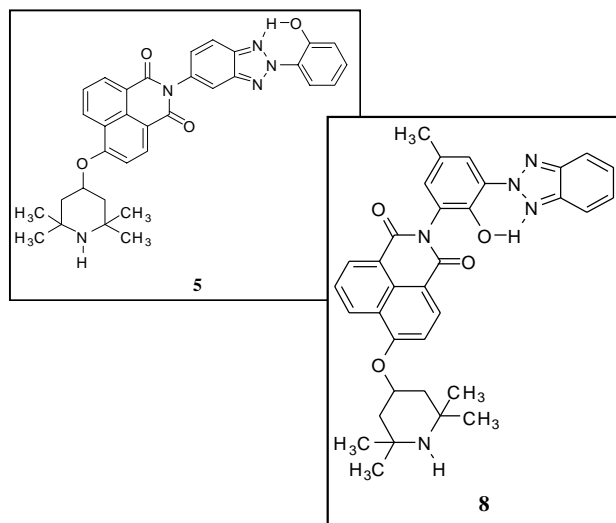
aroused the scientific interest because of their potential use as fluorophores for synthetic blue fluorescent polymers [11-16].

It is well known that all commonly used plastics degrade under the influence of sunlight. To solve the problem of polymer stabilization, a number of different stabilizers have successfully been applied. 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, though 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 and stop oxidative degradation by coupling of alkyl radicals [17]. In contrast to them, 2-hydroxyphenylbenzotriazoles are known as UV absorbers. They are transparent to visible light and convert the absorbed photon energy into heat without being chemically affected [18].

Recently, a number of papers devoted to the 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 [19] or 2-hydroxyphenylbenzotriazole [20,21] UV absorbers.

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 brighteners capable of "one-step" brightening and stabilizing of polymer materials. In this paper we report the synthesis and absorption properties of novel benzo[*de*]isoquinoline-1,3-diones **5** and **8**, containing a 2-(2-hydroxyphenyl)-benzotriazole and a 2,2,6,6-tetramethylpiperidine fragment.



EXPERIMENTAL

Materials

The starting 2-(2-hydroxyphenyl)-5-amino-benzotriazole **1** [20] and 2-(2-hydroxy-3-amino-5-methylphenyl)-benzotriazole **6** [21] as well as 4-bromo-1,8-

naphthalic anhydride **2** [22] were prepared according to the reported procedures. 2,2,6,6-Tetramethylpiperidin-4-ol **4** (Fluka), p.a. grade, was used without purification. All solvents (Fluka, Merck) were of p.a. or analytical grade.

Methods

FT-IR spectra were recorded on a Bruker IFS-113 spectrometer at 2 cm⁻¹ resolution using KBr discs. The ¹H 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. TLC was performed on silica gel, Fluka F60 254, 20 x 20, 0.2 mm, using as eluant the solvent systems *n*-heptane/acetone (1:1) and chloroform/methanol = (9:1). The melting points were determined by means of a Kofler melting point microscope.

Synthesis

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

A suspension of 4-bromo-1,8-naphthalenedicarboxylic acid anhydride **2** (15 mmol) and benzotriazole **1,6** (15 mmol) in 90 ml of glacial acetic acid was stirred at 110°C for 12 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.

6-Bromo-2-[2-(2-hydroxy-phenyl)-2H-benzotriazol-5-yl]-benzo[*de*]isoquinoline-1,3-dione (3**):** FT-IR (KBr), cm⁻¹: 3182 (ν OH); 3081 (ν CH=); 1707 (ν asC=O); 1669 (ν C=O); 1584 (ν C=C); 1346 (ν N-C-N). ¹H NMR (250.13 MHz, CDCl₃ + DMSO-*d*₆) ppm: 11.22 (s, 1H, OH); 8.60 (d, 1H, *J* = 7.3 Hz, benzo[*de*]isoquinoline 9-H); 8.59 (d, 1H, *J* = 8.6 Hz, benzo[*de*]isoquinoline 7-H); 8.43 (d, 1H, *J* = 8.4 Hz, benzo[*de*]isoquinoline 5-H); 8.37 (dd, 1H, *J* = 8.4 Hz, *J* = 1.2 Hz, benzotriazole 6-H); 8.19 (d, 1H, *J* = 8.9 Hz, phenyl 6-H); 8.08 (d, 1H, *J* = 8.4 Hz, benzo[*de*]isoquinoline 4-H); 7.94 (d, 1H, *J* = 1.1 Hz, benzotriazole 4-H); 7.81 (t, 1H, *J* = 7.9 Hz, benzo[*de*]isoquinoline 8-H); 7.39 (m, 2H, benzotriazole

ole 7-H and phenyl 5-H); 7.20 (d, 1H, $J = 8.4$ Hz, phenyl 3-H); 7.07 (t, 1H, $J = 8.3$ Hz, phenyl 4-H). Elemental analysis: Calculated for $C_{24}H_{13}BrN_4O_3$ (MW 485.29) C 59.40, H 2.70, N 11.55 %; Found C 59.18, H 2.77, N 11.66 %.

2-(3-Benzotriazol-2-yl-2-hydroxy-5-methyl-phenyl)-6-bromo-benzo[de]isoquinoline-1,3-dione (7): FT-IR (KBr), cm^{-1} : 3282 (ν_{OH}); 3064 ($\nu_{CH=}$); 1708 ($\nu^{as}C=O$); 1670 ($\nu^sC=O$); 1588 ($\nu^sC=C$); 1340 (ν_{N-C-N}). 1H NMR (250.13 MHz, $CDCl_3$) ppm: 11.66 (s, 1H, OH); 8.89 (d, 1H, $J = 8.7$ Hz, benzo[de]isoquinoline 7-H); 8.81 (d, 1H, $J = 6.8$ Hz, benzo[de]isoquinoline 9-H); 8.77 (d, 1H, $J = 8.0$ Hz, benzo[de]isoquinoline 5-H); 8.44 (d, 1H, $J = 8.0$ Hz, benzo[de]isoquinoline 4-H); 8.41 (d, 1H, $J = 1.4$ Hz, phenyl 4-H); 8.03 (dd, 1H, $J = 8.6$ Hz, $J = 7.5$ Hz, benzo[de]isoquinoline 8-H); 7.90 (dd, 2H, $J = 9.6$ Hz, $J = 3.0$ Hz, benzotriazole 4-H and 7-H); 7.48 (dd, 2H, $J = 9.7$ Hz, $J = 3.1$ Hz, benzotriazole 5-H and 6-H); 7.23 (d, 1H, $J = 1.9$ Hz, phenyl 6-H); 2.49 (s, 3H, CH_3). Elemental analysis: Calculated for $C_{25}H_{15}BrN_4O_3$ (MW 499.32) C 60.14, H 3.03, N 11.22 %; Found C 59.88, H 3.10, N 11.31 %.

General preparation procedure for combined compounds 5 and 8

To a mixture of 0.94 g of 2,2,6,6-tetramethylpiperidine-4-ol **4** (6 mmol) in 15 ml of DMF, 0.83 g of finely ground potassium carbonate (6 mmol) and 0.08 g of 18-crown-6 (0.3 mmol, 5 mol%), a solution of intermediate **3** or **7** (6mmol) in 15 ml of DMF was added at room temperature. The resulting mixture was vigorously stirred and heated to 80°C for 4 h, then cooled to room temperature and the solution was poured into 300 ml of water. The precipitate was filtered off and washed with water. The crude product was dissolved in a mixture solvent of minim water and ethanol (100 ml), and the undissolved residue was filtered off and dried. The latter then was extracted with chloroform to give after evaporation of the solvent 2.15 g (64%) of 6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-2-[2-(2-hydroxy-phenyl)-2H-benzotriazol-5-yl]-benzo[de]isoquinoline-1,3-dione **5** and 2.11 g (61%) of 6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-2-(3-benzotriazol-2-yl-2-hydroxy-5-methyl-phenyl)-benzo[de]isoquinoline-1,3-dione **8** as pale yellow crystals.

6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-2-[2-(2-hydroxy-phenyl)-2H-benzotriazol-5-yl]-benzo[de]isoquinoline-1,3-dione (5): FT-IR (KBr), cm^{-1} : 3246 (ν_{NH}); 3066 ($\nu_{CH=}$); 3018 ($\nu_{OH\cdots N}$); 2946 ($\nu^{as}CH_3$); 2892 (ν^sCH_3); 1704 ($\nu^{as}C=O$); 1668 ($\nu^sC=O$); 1620 ($\nu^sC=N$); 1598 ($\nu^sC=C$). 1H NMR (250.13 MHz, $CDCl_3$) ppm: 11.18 (s, 1H, OH); 8.61 (dd, 2H, $J = 8.4$ Hz, $J = 7.3$ Hz, benzo[de]isoquiniline 7-H and 9-H); 8.46 (d, 1H, $J = 8.4$ Hz, benzo[de]isoquiniline 4-H); 8.39 (dd, 1H, $J = 8.3$ Hz, $J = 1.3$ Hz, benzotriazole 6-H); 8.08 (d, 1H, $J = 9.0$ Hz, phenyl 6-H); 7.96 (d, 1H, $J = 1.0$ Hz, benzotriazole 4-H); 7.68 (dd, 1H, $J = 8.4$ Hz, $J = 7.3$ Hz, benzo[de]isoquiniline 8-H); 7.41 (m, 2H, benzotriazole 7-H and phenyl 5-H); 7.20 (dd, 1H, $J = 8.3$ Hz, $J = 1.1$ Hz, phenyl 3-H); 7.11 (td, 1H, $J = 8.3$ Hz, $J = 1.2$ Hz, phenyl 4-H); 6.96 (d, 1H, $J = 8.4$ Hz, benzo[de]isoquiniline 5-H); 5.05 (m, 1H, piperidine CH); 2.34 (t, 2H, $J = 12.5$ Hz, piperidine CH_2); 1.72 (dd, 2H, $J = 12.5$ Hz, $J = 2.4$ Hz, piperidine CH_2); 1.50 (br. s, 1H, piperidine NH); 1.38 (s, 6H, piperidine 2 x CH_3); 1.24 (s, 6H, piperidine 2 x CH_3).

6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-2-(3-benzotriazol-2-yl-2-hydroxy-5-methyl-phenyl)-benzo[de]isoquinoline-1,3-dione (8): FT-IR (KBr), cm^{-1} : 3242 (ν_{NH}); 3062 ($\nu_{CH=}$); 3022 ($\nu_{OH\cdots N}$); ; 2952 ($\nu^{as}CH_3$); 2896 (ν^sCH_3); 1702 ($\nu^{as}C=O$); 1666 ($\nu^sC=O$); 1618 ($\nu^sC=N$); 1596 ($\nu^sC=C$). 1H NMR (250.13 MHz, $CDCl_3$) ppm: 11.56 (s, 1H, OH); 8.65 (dd, 2H, $J = 8.3$ Hz, $J = 7.4$ Hz, benzo[de]isoquiniline 7-H and 9-H); 8.59 (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); 7.69 (dd, 1H, $J = 8.3$ Hz, $J = 7.4$ Hz, benzo[de]isoquiniline 8-H); 7.47 (dd, 2H, $J = 9.6$ Hz, $J = 3.0$ Hz, benzotriazole 5-H and 6-H); 7.10 (d, 1H, $J = 1.7$ Hz, phenyl 6-H); 6.92 (d, 1H, $J = 8.3$ Hz, benzo[de]isoquiniline 5-H); 5.09 (m, 1H, piperidine CH); 2.49 (s, 3H, phenyl CH_3); 2.16 (dd, 2H, $J = 12.6$ Hz, $J = 2.4$ Hz, piperidine CH_2); 1.68 (br. s, 1H, piperidine NH); 1.46 (t, 2H, $J = 12.6$ Hz, piperidine CH_2); 1.30 (s, 6H, piperidine 2 x CH_3); 1.16 (s, 6H, piperidine 2 x CH_3).

Photodegradation

The study on the photodegradation of the new compounds was 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). The photodestruction was monitored spectrophotometrically using the method of the standard calibration curve.

RESULTS AND DISCUSSION

The aim of the present study was to synthesize 1,8-naphthalimides, containing both 2-(2-hydroxyphenyl)-benzotriazole and 2,2,6,6-tetramethylpiperidine fragments as potential additives for simultaneous fluorescent bleaching 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 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.

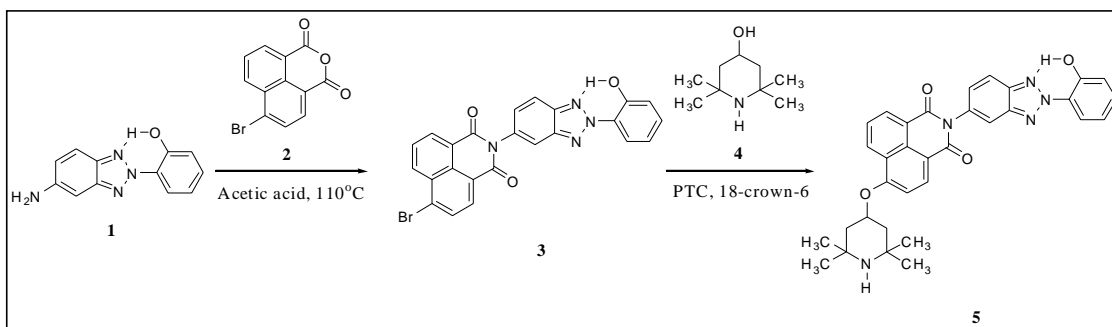
Synthesis of combined compounds

The synthesis of the combined 6-(2,2,6,6-tetramethylpiperidin-4-yloxy)-2-[2-(2-hydroxy-phenyl)-2*H*-benzotriazol-5-yl]-benzo[*de*] isoquinoline-1,3-dione **5**

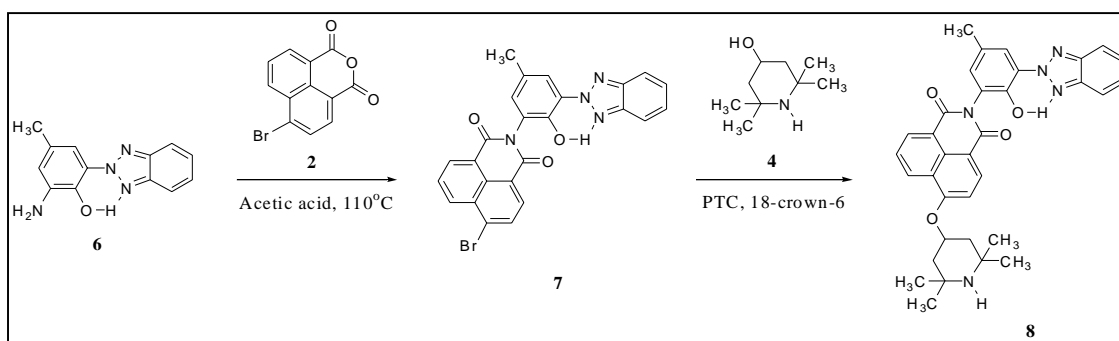
is represented in Scheme 1. The intermediate **3** was obtained by condensation of 2-(2-hydroxyphenyl)-5-amino-benzotriazole **1** with 4-bromo-1,8-naphthalic anhydride **2** in glacial acetic acid at 110°C for 12 h. In order to obtain a fluorescent 1,8-naphthalimide **5**, the bromine atom in the intermediate **3** was nucleophilically substituted with the commercially available 2,2,6,6-tetramethylpiperidin-4-ol **4** (Fluka) under phase transfer catalysis conditions in a solid/DMF two phase system at 80°C in the presence of 18-crown-6 as a phase transfer catalyst.

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 fragment, 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 fluorophore (**8**) was synthesized in two steps as was already described above in the synthesis of compound **5** (Scheme 2).

All of the synthesized compounds were characterized by their melting points, TLC (*R_f* values) and UV/Vis spectra (Tables 1 and 2) and identified by elemental analysis data, FT-IR and ¹H NMR spectra.



Scheme 1



Scheme 2

Table 1. Yields, melting points and TLC R_f values for benzo[de]isoquinoline-1,3-diones **3**, **5**, **7** and **8**.

Compound	Yield (%)	M.p. (°C)	R_f
3	48	> 260	0.58 ^a
5	68	115-118	0.47 ^b
7	51	> 260	0.59 ^a
8	41	88-90	0.51 ^b

^a TLC in a solvent system *n*-heptane/acetone (1:1); ^b TLC in a solvent system chloroform/methanol = (9:1).

Table 2. Absorption data for benzotriazoles **1**, **6**, intermediates **3**, **7** and combined compounds **5**, **8** in a chloroform solution.

Compound	λ_{A1} ^a (nm)	log ϵ (1 mol ⁻¹ cm ⁻¹)	λ_{A2} ^b (nm)	log ϵ (1 mol ⁻¹ cm ⁻¹)	f
1	360	4.263			
3	342	4.396			
5	344	4.343	358	4.080	0.327
6	324	4.269			
7	344	4.341			
8	346	4.358	362	4.039	0.288

^a λ_{A1} represents the absorption maxima of a 2-(2-hydroxyphenyl)-benzotriazole fragment.

^b λ_{A2} represents the absorption maxima of a benzo[de]isoquinoline-1,3-dione fragment.

Photophysical characterization of the synthesized 1,8-naphthalimides

The absorption spectra of the novel compounds **5** and **8** (Figure 1 and Table 2) 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 $\lambda_1 = 344-346$ nm and the benzo[de]isoquinoline-1,3-dione absorption is at $\lambda_2 = 358-362$ nm.

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 (Figures 1 and 2). The absorption maximum of benzotriazole **1** 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 ami-

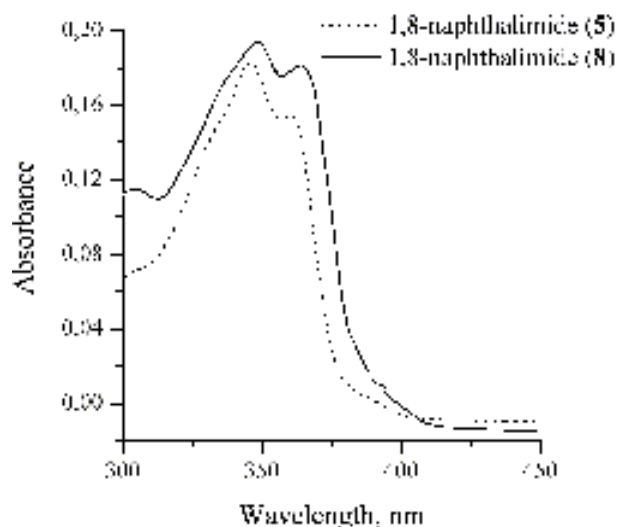


Fig. 1. Absorption spectra of combined compounds **5** and **8** in chloroform solution at concentration 10⁻⁶ mol l⁻¹.

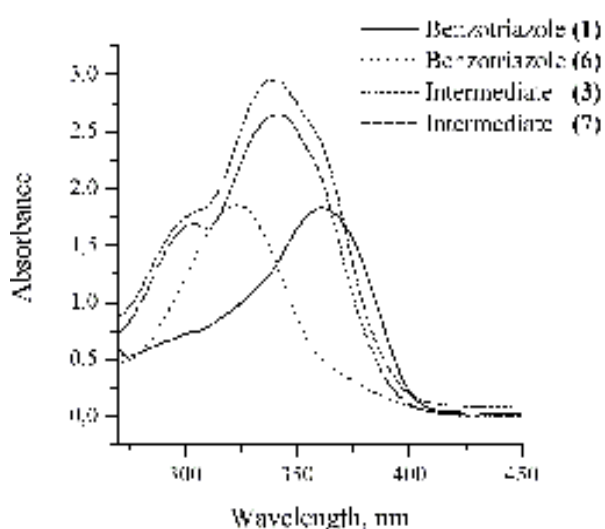


Fig. 2. UV/Vis spectra of benzotriazoles **1**, **6** and intermediates **3**, **7** in a chloroform solution at concentration 10⁻⁴ mol l⁻¹.

no group is situated in the 2-hydroxyphenyl moiety, which leads to decreased strength of the intramolecular hydrogen bond. In confirmation of the suggested above, 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 hypsochromically, while those of the intermediate **7** – bathochromically. As a result of such behavior the absorption maxima of the intermediates **3** and **7** are brought together at $\lambda_1 = 342\text{--}344\text{ nm}$, which is retained in the spectra of the final compounds **5** and **8** ($\lambda_1 = 344\text{--}346\text{ nm}$).

The oscillator strength (f) is an important characteristic for the fluorescent compounds. It shows the effective number of the 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. (1) where $\Delta\nu_{1/2}$ is the width of the absorption band (cm^{-1}) at $1/2\varepsilon_{\text{max}}$ [12].

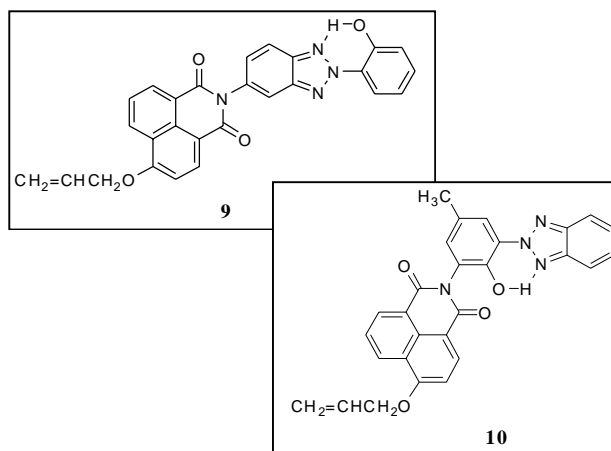
$$f = 4.32 \times 10^{-9} \Delta\nu_{1/2} \varepsilon_{\text{max}} \quad (1)$$

The values of the oscillator strength for the benzo[*de*]isoquinoline-1,3-diones **5** and **8** were 0.288–0.327, 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 [12, 23].

Photostability of the combined 1,8-naphthalimides

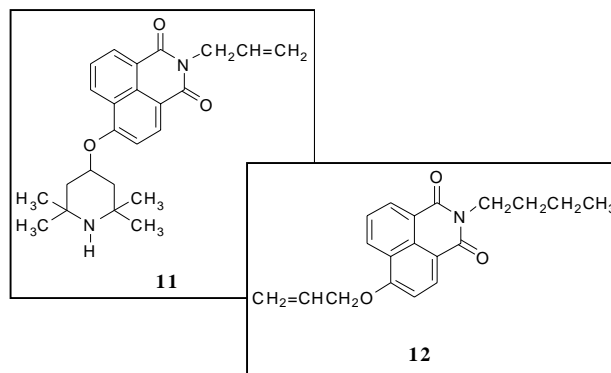
The fluorescent compounds' photostability is a very important characteristic with regard to their practical usage. To study the influence of both 2,2,6,6-tetramethylpiperidine and 2-hydroxyphenylbenzotriazole fragments on the photostability of the target 1,8-naphthalimides **5** and **8**, their solutions in DMF at a concentration of $5 \times 10^{-4} \text{ mol l}^{-1}$ were subjected to irradiation with UV light in a SUNTEST equipment.

In order to receive a more complete comparative picture for the influence of both 2-hydroxyphenylbenzotriazole and 2,2,6,6-tetramethylpiperidine fragments on the properties of the new compounds (**5** and **8**), synthesized before benzo[*de*]isoquinoline-1,3-dione derivatives **9** and **10** [24], not containing a hindered amine moiety



or a UV absorber moiety **11** (Formula 5) [25] in their molecules, as well as not containing both of them **12** [13] were involved in the present study.

The kinetics of photodegradation was monitored colorimetrically. Since during the irradiation no change



was observed in the absorption maxima of the 1,8-naphthalimides under study, the correlation between their concentration and the time of irradiation was monitored using the method of the standard calibration curve (Figure 3).

As seen, the photostability of novel compounds **5** and **8**, containing both hindered amine and UV absorber fragments, was higher than that of fluorescent brighteners **9-11**, not containing either 2-hydroxyphenylbenzotriazole or 2,2,6,6-tetramethylpiperidine fragment in their molecules, which could be explained with a “synergism” of the combined in one molecule two stabilizer fragments, differing in their action. In the case of compound **12**, not containing stabilizer fragments, the photodegradation was faster if compared to that of fluorophores **9-11**, especially to that of combined compounds **5** and **8**. Within 1 h the 1,8-naphthalimide **12**

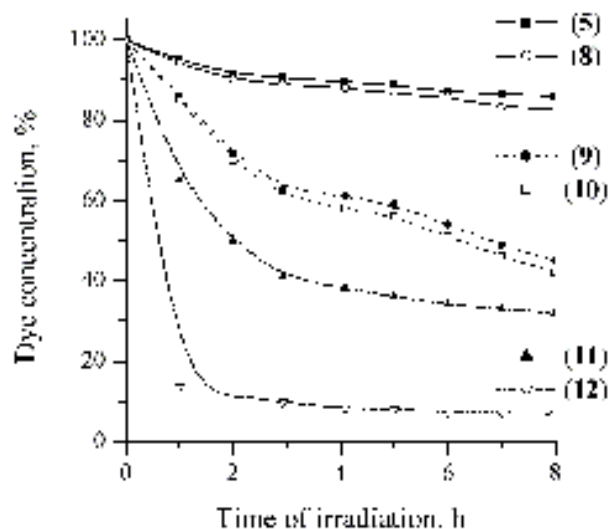


Fig. 3. Photodegradation of 1,8-naphthalimides **5**, **8-12** in a DMF solution.

solution loses its absorption maximum as a result of the photodegradation of the its chromophoric system. The study also showed that the influence of the UV absorber fragment type (compounds **5** and **8**) on the fluorophores' photostability was negligible (Figure 3).

CONCLUSIONS

Novel 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 have been determined and discussed. Photodegradation of the new compounds has been studied and compared to other similar fluorescent brighteners, not containing either a UV absorber or a hindered amine fragment in their molecules as well as not containing both of them. Novel benzo[de]isoquinoline-1,3-diones showed the best photostability in solution, which might be caused by a possible "synergism" of the combined in one molecule two stabilizer fragments, differing in their action. As a result of our investigation it can be concluded that the new benzo[de]isoquinoline-1,3-dione fluorophores present a possibility for "one-step" brightening and stabilization of polymers.

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