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Photophysical and photochemical properties of some 3-bromo-4-alkylamino-*N*-alkyl-1,8-naphthalimides

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Abstract

Photophysical properties of some 4-alkylamino-*N*-alkyl-1,8-naphthalimides and 3-bromo-4-alkylamino-*N*-alkyl-1,8-naphthalimides in ethanol solution have been investigated. It was demonstrated that the bromine atom in a C-3 position alters their properties. The bromine derivatives have a lower quantum yield of fluorescence owing to the influence of the bromine atom on the polarization of naphthalimide chromophoric system. On the other case, the photodegradation of these derivatives is higher and the reaction of photodegradation follows a pseudo first order.

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Keywords: 1,8-Naphthalimide; Bromination; Photodegradation; Photophysics

1. Introduction

1,8-Naphthalimides and their 4-substituted derivatives have been the subject of many scientific investigation including laser active media [1,2], potential photosensitive biologically active units [3], fluorescent markers in biology [4], analgetics in medicine [5,6], in solar energy collectors [7]. Recently, they have been examined as fluorescent dichroic dyes in liquid crystals for utilization in electro-optical devices [8–10]. In the recent years, some 4-aminosubstituted-1,8-naphthalimide derivatives have aroused our scientific interest because

of their potential use as polymerizable fluorophores for synthetic polymers. They possess an intense fluorescence and a very good photostability [11–14]. Due to the presence of a polymerizable group the fluorophores can polymerise with some commercial monomers, allowing to obtain copolymers with an intense fluorescence [15–19]. Novel heterogeneous photoinduced electron transfer fluorescent sensors, selective for transition metal ions or protons, being polymers regularly labelled with naphthalimide has been recently described [19].

On the other hand, some 3-bromo-4-alkylamino-*N*-alkyl-1,8-naphthalimide derivatives have been described and characterised recently by Lewis et al. with regard to their application as

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good photo chemotherapeutic inhibitors for enveloped viruses in blood and blood products [20–24].

In this paper, we report on the photophysical and photochemical properties in ethanol solution of some 3-bromo-4-alkylamino-*N*-alkyl-1,8-naphthalimide, one of them is newly synthesised. The influence of the bromine atom on the photophysical and photochemical properties is discussed.

2. Experimental

2.1. Synthesis and structural characterization

2.1.1. 4-Butylamino-*N*-butyl-1,8-naphthalimide (**Ia**)

4-Nitro-1,8-naphthalic anhydride (0.01 mol) was reacted with 0.01 mol of butylamine in boiling ethanol (100 ml) for 6 h, obtaining 4-nitro-*N*-butyl-1,8-naphthalimide. After that, water (500 ml) was added to the solution. The precipitate was filtered off, washed with water and dried under vacuum at 50 °C.

Of this product 0.01 mol were dissolved in *N,N*-dimethylformamide (50 ml) and 0.02 mol of butylamine were added. After 24 h of stirring at 25 °C 500 ml of water was added. The precipitate was filtered off, washed with water and dried under vacuum at 50 °C.

Yield: 95%; m.p. 124–125 °C (Lit. [25] 127–128 °C). R_f =0.44 (*n*-heptane/acetone 1:1); Analysis: $C_{20}H_{24}O_2N_2$ (324): calcd C 74.07, H 7.40, N 8.64; found C 73.98, H 7.32, N 8.53.

2.1.2. 3-Bromo-4-butylamino-*N*-butyl-1,8-naphthalimide (**Ia**)

4-butylamino-*N*-butyl-1,8-naphthalimide (0.01 mol) was dissolved in dichloromethane (50 ml) and 0.015 mol of bromine dissolved in 10 ml of dichloromethane were added in 30 min. After that, the solution was stirred 4 h at 20 °C. The solvent and non reacted bromine were evaporated under reduced pressure. Re-crystallization of the crude product from methanol gave the final product of 3-bromo-4-butylamino-*N*-butyl-1,8-naphthalimide as bright-yellow needles.

Yield: 68%, m.p. 87–88 °C. (Lit. [22] 170–172 °C). R_f =0.65 (*n*-heptane/acetone 1:1); 1H -NMR (DMSO- d_6 , 250 MHz ppm): 0.97 (s, 6H, $2 \times CH_3$); 1.45 (t, 4H, $2 \times CH_2$); 1.70 (m, 4H, $2 \times CH_2$); 3.62 (t, 2H, $NHCH_2$); 4.11 (t, 2H, $NHCH_2$); 4.97 (br. s, 1H, NH); 5.76 (dd, 1H, ArH-6, J =8.4; 7.5 Hz); 8.34 (d, 1H, ArH-5, J =8.4 Hz); 8.47 (d, 1H, ArH-7, J =7.5 Hz); 8.48 (s, 1 H, ArH-2). ^{13}C -NMR (DMSO- d_6 , 62.90 MHz ppm): 13.8, 13.9, 20.0, 20.4, 30.2, 33.6, 40.1, 50.6, 109.5, 113.9, 123.0, 125.0, 129.4, 130.4, 131.2, 135.3, 149.4, 162.8, 164.0; anal. $C_{20}H_{23}O_2N_2Br$ (403): calcd C 59.55, H 5.71, N 6.94; found C 59.48, H 5.63, N 7.01.

2.1.3. 4-Hexylamino-*N*-hexyl-1,8-naphthalimide (**Ib**)

4-Nitro-1,8-naphthalic anhydride (0.01 mol) was reacted with 0.01 mol of hexylamine in 100 ml boiling ethanol for 6 h thus obtaining 4-nitro-*N*-hexyl-1,8-naphthalimide. After that, 500 ml of water were added to the solution. The precipitate was filtered off, washed with water and dried under vacuum at 50 °C. Of this product 0.01 mol were dissolved in 50 ml of *N,N*-dimethylformamide and 0.02 mol of hexylamine added. After 24 h 500 ml of water were added to the solution. The precipitate was filtered off, washed with water and dried under vacuum at 50 °C.

Yield: 92%; m.p. 61–62 °C (Lit. [26] 60–62 °C). R_f =0.49 (*n*-heptane/acetone 1:1); anal. $C_{24}H_{32}O_2N_2$ (380): calcd C 75.78, H 8.42, N 7.37; found C 75.66, H 8.36, N 7.30.

2.1.4. 3-Bromo-4-hexylamino-*N*-hexyl-1,8-naphthalimide (**Ib**)

4-Hexylamino-*N*-hexyl-1,8-naphthalimide (0.01 mol) was dissolved in 50 ml of dichloromethane and 0.015 mol of bromine dissolved in 10 ml of dichloromethane were added in 30 min. After that, the solution was stirred 4 h at 20 °C. The solvent and not reacted bromine were evaporated under reduced pressure. Recrystallization of the crude product from methanol gave final product of 3-bromo-4-hexylamino-*N*-hexyl-1,8-naphthalimide as bright-yellow needles.

Yield: 65%; m.p. 58–59 °C (Lit. [20] 58–60 °C); R_f =0.72 (*n*-heptane/acetone 1:1); 1H -NMR

(DMSO- d_6 , 250 MHz ppm): 0.88 (br. s, 6H, $2\times\text{CH}_3$); 1.32 (t, 12H, $6\times\text{CH}_2$); 1.69 (br. s, 2H, NHCH_2CH_2); 1.82 (br. s, 2H, NHCH_2CH_2); 3.68 (dt, 2H, NHCH_2 , $J=7.7$ Hz); 4.11 (t, 2H, NHCH_2 , $J=7.3$ Hz); 6.6 (br. s, 1H, NH); 7.69 (dd, 1H, ArH-6, $J=8.8$; 7.3 Hz); 8.55 (d, 1H, ArH-5, $J=7.3$ Hz); 8.57 (s, 1H, ArH-2); 8.65 (d, 1H, ArH-7, $J=8.8$ Hz). ^{13}C -NMR (DMSO- d_6 , 62.90 MHz ppm): 14.0, 14.1, 22.5, 22.6, 26.4, 26.8, 28.0, 30.0, 31.3, 31.5, 40.5, 51.6, 111.9, 116.8, 123.2, 124.0, 126.3, 129.1, 130.2, 131.6, 135.2, 145.8, 162.6, 163.7; anal. $\text{C}_{24}\text{H}_{31}\text{O}_2\text{N}_2\text{Br}$ (459): calcd C 62.74, H 6.75, N 6.10; found: C 62.66, H 6.70, N 6.01.

2.1.5. 4-Dimethylamino-N-hexyl-1,8-naphthalimide (**1c**)

Of 4-dimethylamino-1,8-naphthalic anhydride 0.01 mol were reacted with 0.02 mol of hexylamine in 60 ml of boiling ethanol for 6 h. After that, 300 ml of water were added to the solution. The precipitate was filtered off, washed with water and dried under vacuum at 50 °C.

Yield: 94%; m.p. 85–86 °C; $R_f=0.36$ (*n*-heptane/acetone 1:1); anal. $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ (324): calcd C 74.07, H 7.40, N 8.64; found: C 73.91, H 7.36, N 8.58.

2.1.6. 3-Bromo-4-dimethylamino-N-hexyl-1,8-naphthalimide (**1lc**)

Of 4-dimethylamino-N-hexyl-1,8-naphthalimide (0.01 mol) were dissolved in 50 ml of dichloromethane and 0.015 mol of bromine dissolved in 10 ml of dichloromethane were added in 30 min. After that, the solution was stirred 4 h at 20 °C. The solvent and not reacted bromine were evaporated under reduced pressure. Recrystallization of the crude product from methanol give final product of 3-bromo-4-dimethylamino-N-hexyl-1,8-naphthalimide as bright-yellow needles.

Yield: 55%, m.p. 218–220 °C; $R_f=0.62$ (*n*-heptane/acetone 1:1); ^1H -NMR (DMSO- d_6 , 250 MHz ppm): 0.85 (m, 3H, CH_3); 1.10–1.40 (t, 6H, $3\times\text{CH}_2$); 1.50 (m, 2H, NHCH_2CH_2); 3.0–3.5 (m, 8H, $\text{NHCH}_2 + \text{N}(\text{CH}_3)_2$); 3.68 (dt, 2H, NHCH_2 , $J=7.7$ Hz); 4.11 (t, 2H, NHCH_2 , $J=7.3$ Hz); 6.6 (br. s, 1H, NH); 7.69 (dd, 1H, ArH-6, $J=7.2$ Hz); 8.28 (s, 1H, ArH-2); 8.42 (d, 1H, ArH-5, $J=7.2$ Hz); 8.80 (d, 1H, ArH-7, $J=7.2$ Hz). ^{13}C -NMR (DMSO- d_6 , 2.90 MHz ppm): 14.0, 22.1, 26.4, 28.9,

31.1, 35.7, 39.2, 103.1, 105.5, 118.6, 121.5, 131.9, 132.1, 132.9, 137.8, 150.8, 159.4, 161.3; anal. $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\text{Br}$ (403): calcd C 59.55, H 5.71, N 6.94; found: C 59.49, H 5.64, N 6.89.

2.2. Analysis

UV–vis spectrophotometric investigations were performed on a UVIKON 930 spectrophotometer (KONTRON instruments). The fluorescence spectra were taken on a SFM 25 spectrophotometer (KONTRON instruments). Fluorescence quantum yield of the monomeric dye have been determined on the basis of the absorption and fluorescence spectra. Rhodamine 6G was used as reference ($\Phi_0=0.88$) [27]. For all absorption measurements the dye concentration in the solution were 10^{-5} mol l^{-1} . The fluorescent measurements were in 10^{-6} mol l^{-1} . The NMR spectra were obtained on a Bruker DRX-250 spectrometer, operating at 250.13 and 62.90 MHz for ^1H and ^{13}C , respectively using a dual 5 mm probe head. The measurements were carried out in DMSO- d_6 solution at ambient temperature. The chemical shift were referenced to tetramethylsilane (TMS), standard experiments with 30° pulses, 1 s relaxation delays, 16 K time domain points, zero-filled to 64 K for protons and 32 K for carbons were performed. The distortionless enhancement by polarisation transfer (DEPT) spectra were recorded under the same conditions as the ^{13}C -NMR spectra and $\tau=(2\ ^1J_{\text{CH}})^{-1}=3.45\ \mu\text{s}$ was used. The 2D $^1\text{H}/^1\text{H}$ correlated spectra (COSY) were performed with spectral width 2000 Hz, relaxation delay 2 s, number of increments 512, size 2 K \times 2 K. The 2D $^1\text{H}/^{13}\text{C}$ heteronuclear multiple quantum coherence (HMQC) experiments were carried out with a spectral width of ≈ 2000 Hz for ^1H and 8000 Hz for ^{13}C , relaxation delay 1.5 s, FT size 1 K \times 512 W. A solar simulator (Suntest CPS+, HERAEUS), equipped with a 1.5 kW xenon arc lamp, protected with an adequate filter to simulate the solar spectrum between 290 and 800 nm, was used and the experiments were carried out in ordinary atmosphere at 20 °C. Thin layer chromatography (TLC) analysis followed on silica gel (Fluka F₆₀ 254 20 \times 20; 0.2 mm) using the solvent system *n*-heptane/acetone (1:1) as eluent.

3.1. Synthesis of 1,8-naphthalimides

3.2. ^{13}C -NMR characterisation

3.3. Photophysical properties

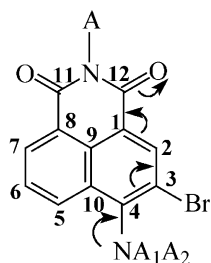
The reaction scheme shows the synthesis of compound II from compound I:

- Compound I (10-nitro-10H-phenothiazine-10-one) reacts with an amine (RNH_2) in ethanol ($\text{C}_2\text{H}_5\text{OH}$) to form an intermediate N-alkyl-10-nitro-10H-phenothiazine-10-one.
- The intermediate is then treated with DMF and RNH_2 to form N-alkyl-10-(N-alkylamino)-10H-phenothiazine-10-one.
- Finally, this intermediate is brominated using Br_2 in Cl_2CH_2 to yield compound II (8-bromo-10-(N-alkylamino)-10H-phenothiazine-10-one).

CN(C)c1ccc2c(c1)C(=O)OC(=O)c2
 $\xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{RNH}_2}$
CN(C)c1ccc2c(c1)C(=O)N(R)C(=O)c2
 $\xrightarrow[\text{Cl}_2\text{CH}_2]{\text{Br}_2}$
CN(C)c1ccc2c(c1)C(=O)N(R)C(=O)c2Br

1c
11c

Scheme 2. Synthesis of 4-*N,N*-dimethylamino-3-bromo-*N*-hexyl-1,8-naphthalimide (**IIc**).



Scheme 3.

naphthalimide molecule due to the electron donor–acceptor interaction occurring between the substituents at C-4 and the carbonyl groups from the imide structure of the chromophoric system. The donor–acceptor interaction, and the path of charge transfer of the 3-bromo-4-alkylamino-*N*-alkyl-1,8-naphthalimide derivatives are given in Scheme 3.

Table 1 presents the spectral characteristics of the 1,8-naphthalimide compounds under study in ethanol solution: the absorption (λ_A) and fluorescence (λ_F) maxima, the extinction coefficient (ϵ), Stokes shift ($\nu_A - \nu_F$), and quantum yield of fluorescence (Φ_F).

In ethanol solution the 1,8-derivatives **Ia–c** exhibit yellow-green colour with absorption maxima $\lambda_A = 439–442$ nm and intense fluorescence, whose the maxima is situated at $\lambda_F = 521–522$ nm. After the bromination, the absorption and fluorescence maxima of the respective 3-bromo derivatives **IIa–c** are hypsochromically shifted with maxima in $\lambda_A = 420–424$ and $\lambda_F = 516–518$ nm as can be seen from the presented absorption spectra of **Ib** and **IIb** in ethanol solution in Fig. 1. It is

seen that the absorption curves in the visible region is similar without vibrational structure.

In Figs. 2 and 3 are presented as an example the absorption and fluorescent spectra of **Ib** and **IIb** in ethanol solution. In both cases, the fluorescence curve appears approximately as mirror image of the absorption, which indicates that the molecular structure of the dyes is maintained in the excited state and that fluorescence emission prevails.

In all cases the extinction coefficients in the visible region are high, indicating that the long wavelength band of the absorption spectra is a band of charge transfer /CT/, due to π, π^* electron transfer on $S_0 \rightarrow S_1$ transition. The bromine derivatives exhibit lower extinction values due to the different polarization of the 1,8-naphthalimide chromophoric system.

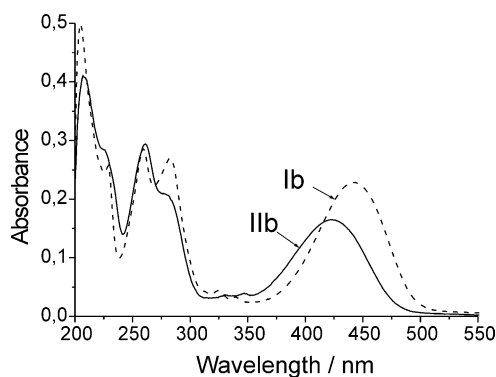
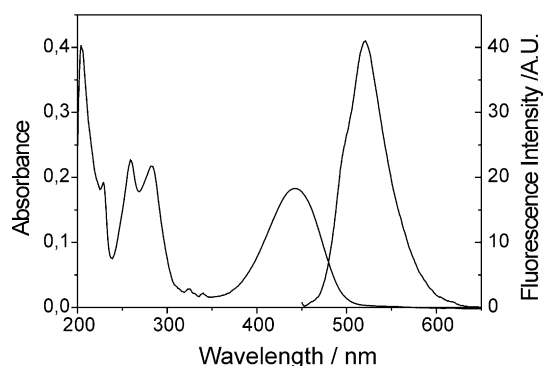
Fig. 1. Absorption spectra of naphthalimide derivatives **Ib** and **IIb**.Fig. 2. Absorption and fluorescence spectra of naphthalimide derivative **Ib**.

Table 1
Photophysical and photochemical characteristics of naphthalimide derivatives I and II in ethanol solution (see text)

	Ia	IIa	Ib	IIb	Ic	IIc
λ_A / nm	442	425	442	424	439	420
ϵ / l mol ⁻¹ cm ⁻¹	18,300	14,000	22,900	16,400	8600	7670
λ_F / nm	521	517	521	518	522	516
$\nu_A - \nu_F$ / cm ⁻¹	3460	4187	3400	4279	3622	4430
Φ_F	0.55	0.50	0.71	0.60	0.16	0.14
Kp / s ⁻¹ × 10 ⁻⁷	22.11	0.151	20.43	0.143	21.15	0.157

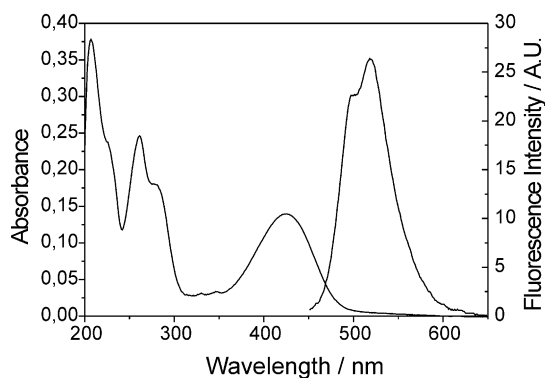


Fig. 3. Absorption and fluorescence spectra of naphthalimide derivative **IIb**.

The Stokes shift is a parameter which indicates the difference in the properties and structure of the dyes between the ground state S_0 and the first excited state S_1 and was found using Eq. (1).

$$\nu_A - \nu_F = (1/\lambda_A - 1/\lambda_F) \times 10^7 \text{ cm}^{-1} \quad (1)$$

The values of the Stokes shift for compounds **Ia–c** are in the $3400\text{--}3622 \text{ cm}^{-1}$ region, which is in accordance with other investigations [11–14] on the similar 1,8-naphthalimide derivatives. As can be seen from Table 1 the 3-bromo derivatives have higher values. The observed larger Stokes shift in this case is due to the different polarization of naphthalimide molecule in the presence of bromine atom in position C-3 and connected with energy losses during the transition into the excited state.

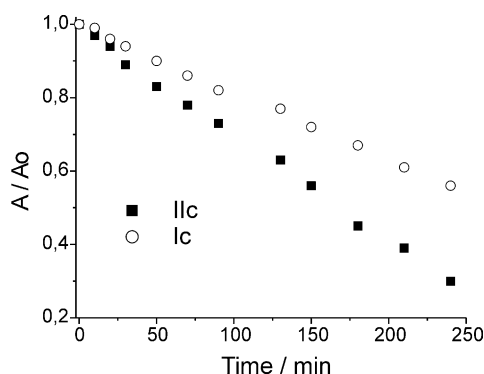


Fig. 4. Photodegradation of 1,8-naphthalimide derivatives **Ic** and **IIc** in ethanol solution.

The fluorescence efficiency of 1,8-naphthalimides is estimated by measuring their quantum yield Φ_F on the basis of the absorption and fluorescence spectra.

As seen from the data in Table 1, the 1,8-naphthalimides **Ia–c** have quantum yield $\Phi_F = 0.16\text{--}0.71$. The respective bromine derivatives have lower quantum yield $\Phi_F = 0.14\text{--}0.60$ due to the electron accepting nature of the bromine atom. In this case, for 3-bromo derivatives, the results show that no-emitting phenomena compete with fluorescence in the $S_1\text{--}S_0$ decay. In the case of **Ic** and **IIc** derivatives with a dimethylamino substituent in C-4 position the lower values of Φ_F is due to the possible rotation of methyl groups with stretching of the molecule beyond its plane and to corruption of its planar structure. The orbital interaction between of the substituent $\text{--N}(\text{CH}_3)_2$ and π -electron system of the chromophore becomes weaker, resulting in a decrease of the dipole transition moment of the 1,8-naphthalimide derivatives.

3.4. Photodegradation

The photostability of the 3-bromo-4-alkyl-amino-*N*-alkyl-1,8-naphthalimide derivatives has also been investigated. Fig. 4 shows the kinetics of photodegradation of the compounds **Ic** and **IIc** in ethanol solution. It has been found that the photodegradation follows a pseudo first order of reaction. In general the presence of bromine atom in *ortho* position to amino substituent affects the

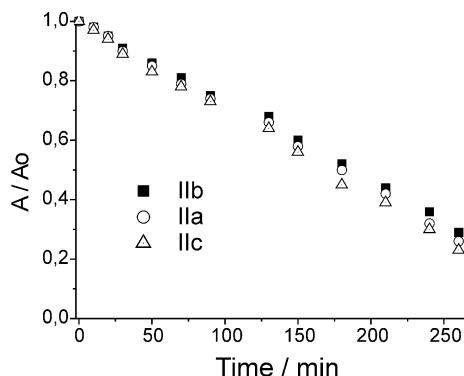


Fig. 5. Photodegradation of 1,8-naphthalimide derivatives **IIa–c** in ethanol solution.

photodegradation. In Table 1 the calculated rate constants K_p of the 4-alkylamino-*N*-alkyl-8-naphthalimide and 3-bromo-4-alkylamino-*N*-alkyl-1,8-naphthalimide derivatives photodegradation are listed. As seen the degradation is higher in the case of the bromine derivative. In Fig. 5 the photodegradation of compounds **IIa–c** is presented. It is seen that the more photostabilising effect has been observed in the case of compounds **IIc** with a dimethylamino substituent in position C-4.

4. Conclusions

The photophysical properties of some 3-bromo-4-alkylamino-*N*-alkyl-1,8-naphthalimide derivatives in ethanol solution have been investigated. It was demonstrated that in the presence of bromine atom in position C-3 the polarization of naphthalimide molecule is different from the respective non-substituted derivatives. The bromine derivatives have a lower quantum yield of fluorescence, which is due to the influence of the bromine atom on the polarization of naphthalimide chromophoric system. The reaction of photodegradation of all 1,8-naphthalimide derivatives under study follows a pseudo first order. 3-bromo substituted 1,8-naphthalimide derivatives **IIa–c** have more higher photodegradation in ethanol solution compared with non substituted derivatives **Ia–c**.

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