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Synthesis and transient absorption spectra of derivatives of 1,8-naphthalic anhydrides and naphthalimides containing 2,2,6,6-tetramethylpiperidine; triplet route of deactivation

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Abstract

Novel probes represented 4-substituted 1,8-naphtalic anhydride and 1,8-naphthalimide as a chromophore and sterically hindered amine in the form of parent amine as well as stable nitroxyl radical form were synthesized. Laser flash photolysis was used to examine the triplet route of deactivation. The formation of the triplet state occurred at 355 nm laser excitation exhibiting the absorption in the range 360–700 nm. Triplet states of 1,8-naphthalic anhydride chromophore were quenched by oxygen with rate constant about 2×10^9 dm^3 mol^{-1} cm^{-1} for unsubstituted and 4-bromo substituted derivatives. The 4-dimethylamino substitution of 1,8-naphthalic anhydride exhibited the triplet state, which was not quenched by oxygen or 1-oxo-2,2,6,6-tetramethylpiperidine (TEMPO). The same effect of 4-dimethylamino substitution was observed on the triplet state of *N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide.

In the series of 4-bromo-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide derivatives, the weak transient triplet absorption was observed for 1-oxo derivative. Probably, the decay of triplet state of 1,8-naphthalimide chromophore is fast due to combination of two effects: paramagnetic effect of free *N*-oxyl radical and heavy atom effect of bromo substituent.

Keywords: 2,2,6,6-Tetramethylpiperidine; 1,8-Naphthalic anhydrides; Laser flash photolysis; Transient absorption spectra; Triplet; Quenching

1. Introduction

Free radicals of the *N*-oxyl type attract attention because they influence the photophysical and photochemical processes due to their paramagnetic effect [1–9]. Quenching of singlet and triplet states of aromatic hydrocarbons and ketones was studied in detail.

Fluorescence probes of several types have been prepared in which simple aromatic chromophore was combined with a free radical centre of the *N*-oxyl type. Formation or decay of the free radical is connected with switching off or on of the chromophore emission as a result of intramolecular quenching [10–17].

Mechanism of inter- or intramolecular quenching of excited states by *N*-oxyls is not well established even after such an extensive studies. The following processes are discussed:

- catalytic enhancement of intersystem crossing as a result of an increase in spin-orbital coupling due to the paramagnetic effect,
- catalytic enhancement of the efficiency of internal conversion,
- transfer of electronic energy of resonance or exchange type,
- transfer of electron and formation of cation or anion radical.

The majority of mechanistic studies of quenching of the singlet state of aromatic hydrocarbons with *N*-oxyl radicals concluded that enhancement of intersystem crossing is the most probable route for dissipation of energy. Quenching of a triplet state occurs through internal conversion [1–9]. The

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photophysical process is a preferred route for deactivation of excited state by intramolecular quenching as well [10–17].

The photoinitiated intramolecular electron transfer from *N*-oxyl to diimide under formation of diimide monoanion has been observed recently [18]. These studies indicate that *N*-oxyl radical is able to quench the excited state by different mechanisms depending on the structure of the couple quenchee-quencher and medium.

Recently time resolved electron spin resonance (TR-EPR) has been used to investigate the chemically induced dynamic electron polarization (CIDEP) generated between a *N*-oxyl and the triplet state of thioxanthonedioxide derivatives in a molecules where these moieties are covalently linked [19]. Two mechanisms have been proposed to explain the quenching of the triplet state by *N*-oxyl radical. One is radical triplet pair mechanism and another is electron spin polarization transfer.

In this paper the triplet route of deactivation has been explored for chromophore as substituted 1,8-naphthalic anhydride and for related probes consisting of chromophore/amine and chromophore/*N*-oxyl with 4-bromo-1,8-naphthalimide as chromophore in methanol solution. Previously, it was found that the unsubstituted 1,8-naphthalimide combined with 1-oxo-2,2,6,6-tetramethylpiperidine-4-yl structural unit exhibited the most effective route of triplet deactivation among combined probes with naphthalene and pyrene as chromophores [20]. Therefore, transient triplet absorption spectra of substituted 1,8-naphthalic anhydride and related 1,8-naphthalimide were studied in detail in order to better understand the routes of triplet deactivation.

2. Experimental

Methanol was for UV spectroscopy. 1,8-Napthalic anhydride was analytical grade (Aldrich, Steinheim, Germany). The free radicals: 1-oxo-2,2,6,6-tetramethylypiperidine (TEMPO) was commercial product (Aldrich, Steinheim, Germany).

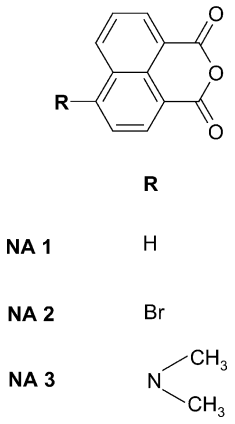
1,8-Naphthalic anhydride (NA1) and 4-bromo naphthalic anhydride (NA2) were commercial products (Aldrich, Steinheim, FRG). The structures of probes used in this paper are shown in Schemes 1 and 2. New probes NA3, DMANI and BNI1-3 were prepared according to the following procedures.

2.1. 4-Dimethylamino-1,8-naphthalic anhydride (NA3)

4-Bromo-1,8-naphthalic anhydride (1.11 g, 4 mmol) was dissolved in 3-methyl-1-butanol (28 ml) and solution was heated under stirring to 132 °C and 3-dimethylamino-propionitrile (1.6 g, 16 mmol) was added and stirred 12 h. The formed crystals were than filtered out and washed with water and with cool isohexane to yield 0.8 g (83%) of orange crystals. Melting point (m.p.) 208–210 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.16 (s, 6H, 2x C$\underline{H}_3$-N), 7.10 (d, J = 8.3 Hz, 1H, C$\underline{H}$ (napht.-3), 7.67 (t, 1H, C$\underline{H}$ (napht.-6), 8.40–8.60 (m, 3H, C$\underline{H}$ (napht.).

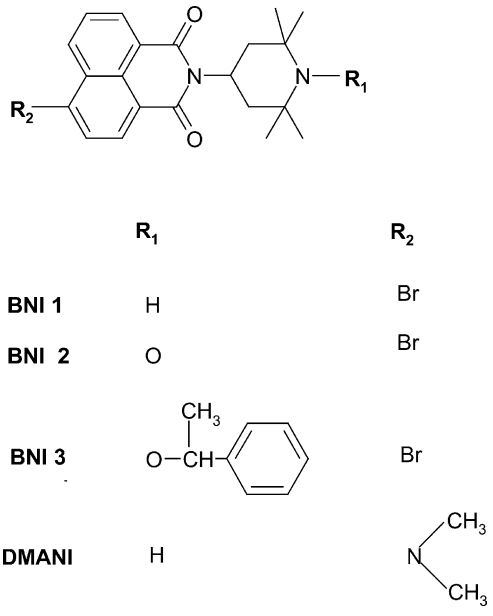
GC-MS *m*/*z*: 241[M], 197, 168, 154, 126.



Scheme 1.

2.2. 4-Bromo-N-(2,2,6,6-tetramethyl-4-piperidinyl)-1, 8-naphthalimide (BNI1)

4-Bromo-1,8-naphtalic anhydride (2.2 g, 8 mmol) was dissolved in 15 mL of DMF and 4-amino-2,2,6,6-tetramethylpiperidine (1.25 g, 8 mmol) in 15 mL of DMF was slowly added (40 min) under stirring and after this time AcOH (1.5 mL) was added. Mixture was stirred at room temperature for 40 min and 12 h at 100 °C. Reaction mixture was cooled and washed with diethylether (40 ml). Yellow solid was filtered off, crystallized from hexane and purified by column chromatography (dichloromethane/methanol 5:1). R_f of the product was 0.6. Yield 2.1 g (64%) of gray crystals with m.p. 205–207 °C.



Scheme 2.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 6H, 2x C$\underline{H}_{3ax}$), 1.37 (s, 6H, 2x C$\underline{H}_{3eq}$), 1.70 (m, 2H, 2x C$\underline{H}$H), 2.50 (m, 2H, 2x CH$\underline{H}$), 5.65 (m, 1H, C$\underline{H}$–N), 7.85 (t, 1H, C$\underline{H}$ (napht.-6)), 8.10 (d, J = 7.8 Hz, 1H, C$\underline{H}$ (napht.)), 8.40 (d, J = 8.1 Hz, 1H, C$\underline{H}$ (napht.)), 8.55 (d, J = 7.8 Hz, 1H, C$\underline{H}$ (napht.)), 8.65 (d, J = 7.8 Hz, 1H, C$\underline{H}$ (napht.)).

^{13}C-NMR ($CDCl_3$): (=28.1 (2C, $\underline{C}H_3$), 34.9 (2C, $\underline{C}H_3$), 40.8 (2C, 2x $\underline{C}H_2$–CH), 47.5 (1C, $\underline{C}$H–N), 51.8 (2C, 2x $\underline{C}$–N), 122.7 and 123.5 (2C, $\underline{C}$(1), $\underline{C}$(8)), 128.2–133.1 (8C, (napht.)), 164.3 (2C, $\underline{C}$=O).

FTIR (KBr) (cm^{-1}): ν(C=O) 1699, ν(C=O) 1657, $\delta(CH_3)$-dublet 1358, 1342, ν(napht.) 779.

GC-MS m/z: 416[M]$^+$, 401, 399, 124.

2.3. 4-Bromo-N-(1-oxo-2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI2)

Parent amine BNI1 (0.44 g, 1.6 mmol) was dissolved in 30 mL of dichloromethane and cooled to 0 °C. Under stirring, 3-chloroperoxy-benzoic acid (0.5 g, 2.9 mmol) was added in small portions during 15 min. Originally transparent solution became orange. The mixture was then warmed to room temperature and stirred for another 4 h. Reaction mixture was extracted with aqueous K_2CO_3 solution and with water. Organic layer was dried over anhydrous sodium sulfate and the solvent was removed. Crude product was purified by column chromatography using a mixture of dichloromethane/isohexane 3: 1. The product was crystallized from hexane to yield slightly orange crystals (0.42 g, 61%), m.p. 220–224 °C. Structure and purity of the radical was proved by FTIR and EPR spectroscopy as well as by TL chromatography.

FTIR (KBr) (cm^{-1}): ν(C=O) 1701, ν(C=O) 1659, ν(N–O) 1375, $\delta(CH_3)$-dublet 1358 and 1342, ν(napht.) 779. N–O stretching vibration ν(N–O) of 4-acroylamino-1-oxy-2,2,6,6-tetramethyl-piperidine was observed at 1365 cm^{-1} [21].

2.4. 4-Bromo-N-(1-(1-phenylethyl)oxo-2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI3)

BNI2 (0.6 g, 1.4 mmol), $Mn(OAc)_3$ (1.3 g, 5.6 mmol) and styrene (0.58 g, 5.6 mmol) were suspended in 25 mL solvents mixture (ethanol/toluene/acetic acid 2: 2: 1) and stirred vigorously at room temperature. $NaBH_4$ (0.32 g, 8.4 mmol) was added slowly in very small portions and reaction was checked by TLC. After addition the mixture was filtered and washed three times with dichloromethane. The organic layers were combined, concentrated and the residue was dissolved in 30 mL of dichloromethane. The solution was washed with aqueous $NaHCO_3$ solution and with water. Organic layer was separated, dried over Na_2SO_4 and the solvent was removed. Purification by column chromatography, eluting with 2:1 dichloromethane/isohexane, gave a colorless wax. Crystallization from isohexane yielded white crystals (0.58 g, 77%) m.p. 174–177 °C.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.70 (s, 3H, C$\underline{H}_{3ax}$), 1.20 (s, 3H, C$\underline{H}_{3ax}$), 1.34 (s, 3H, C$\underline{H}_{3eq}$), 1.39 (s, 3H, C$\underline{H}_{3eq}$), 1.40–1.60 (m, 2H, 2x C$\underline{H}$H), 1.50 (d, J = 6.6 Hz, 3H, C$\underline{H}_3$–CH–Ph), 2.70–2.90 (m, 2H, 2x CH$\underline{H}$), 4.80 (m, 1H, C$\underline{H}$–Ph), 5.50 (m, 1H, C$\underline{H}$–N), 7.25–7.40 (m, 5H, Ph), 7.80 (t, 1H, C$\underline{H}$ (napht.-6)), 8.00 (d, J = 8.1 Hz, 1H, C$\underline{H}$ (napht.)), 8.33 (d, J = 7.8 Hz, 1H, C$\underline{H}$ (napht.)), 8.50 (d, J = 7.8 Hz, 1H, C$\underline{H}$ (napht.)), 8.59 (d, J = 7.2 Hz, 1H, C$\underline{H}$ (napht.)).

^{13}C-NMR ($CDCl_3$): δ = 20.8 (1C, $\underline{C}H_3$–CH–Ph), 23.4 (2C, $\underline{C}H_3$), 34.0 and 34.5 (2C, $\underline{C}H_3$), 41.6 (2C, 2x $\underline{C}H_2$–CH–N), 46.0 (1C, $\underline{C}$H–N), 60.7 and 60.9 (2C, 2x $\underline{C}$–N), 83.3 (1C, $\underline{C}$H–Ph), 122.7 and 123.6 (2C, $\underline{C}$(1), $\underline{C}$(8)), 126.8–133.0 (8C, napht. and 5C, Ph.), 145.6 (1C, $\underline{C}$(Ph)), 164.3 (1C, $\underline{C}$=O).

FTIR (KBr) (cm^{-1}): ν(C=O) 1701, ν(C=O) 1663, $\delta(CH_3)$-dublet 1361 and 1343, ν(napht.) 778, ν(phenyl) 700.

2.5. 4-Dimethylamino-N-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (DMANI)

BNI1 (4.2 g, 1 mmol) was dissolved in 3-methyl-1-butanol (8 mL) and warmed to 132 °C. 3-(Dimethylamino)propionitrile (0.4 g, 4 mmol) was added and the reaction mixture were stirred for 12 h. The formed crystals were filtered off, washed with water and then with cooled isohexane. Crystallization from dichloromethane gave 0.25 g of orange crystals, which were a mixture of starting material and the required product according to TLC. Column chromatography (Al_2O_3) using a mixture of dichloromethane/isohexane/methanol 6:6:1 afforded yellow crystals (90 mg, 24%), m.p. 187–190 °C. Sample for analysis was obtained by repeated crystallization from dichloromethane.

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 6H, 2x C$\underline{H}_{3ax}$), 1.37 (s, 6H, 2x C$\underline{H}_{3eq}$), 1.65 (m, 2H, 2x C$\underline{H}$H), 2.50 (m, 2H, 2x CH$\underline{H}$), 3.11 (s, 6H, 2x C$\underline{H}_3$–N), 5.70 (m, 1H, C$\underline{H}$–N), 7.10 (d, J = 8.1 Hz, 1H, C$\underline{H}$ (napht.-3)), 7.70 (t, 1H, C$\underline{H}$ (napht.-6)), 8.40–8.60 (m, 3H, C$\underline{H}$ (napht.)).

^{13}C-NMR ($CDCl_3$): δ = 28.0 (2C, $\underline{C}H_{3ax}$), 34.9 (2C, $\underline{C}H_{3eq}$), 40.9 (2C, 2x $\underline{C}H_2$–CH), 44.8 (2C, 2x $\underline{C}H_3$–N), 46.8 (1C, $\underline{C}$H–N), 52.0 (2C, 2x $\underline{C}$–N), 113.4 (2C, $\underline{C}$(1), $\underline{C}$(8)), 115.5 (1C, $\underline{C}$(3)), 123.6–132.6 (6C, (napht.)), 156.8 (1C, $\underline{C}$(4)), 164.8 and 165.3 (2C, $\underline{C}$=O).

GC-MS m/z: 379[M], 365, 267, 241, 124.

Absorption spectra were recorded on M40 (C. Zeiss, Jena, Germany) and on UV 160 (Shimadzu, Japan). EPR spectrum was measured with X-band spectrometer E-4 Varian (USA) interfaced on PC with program Symphonia Bruker. Measurements of transient absorption spectra in the time scale 20 ns to 500 μs were carried out on a nanosecond laser flash photolysis LKS 60 from Applied Photophysics Ltd. (London, England). The laser excitation at 355 nm (third) from Quanta Ray GCR 130-1 Nd:YAG (pulse width ∼9 ns) was used in right angle geometry with respect to the monitor-

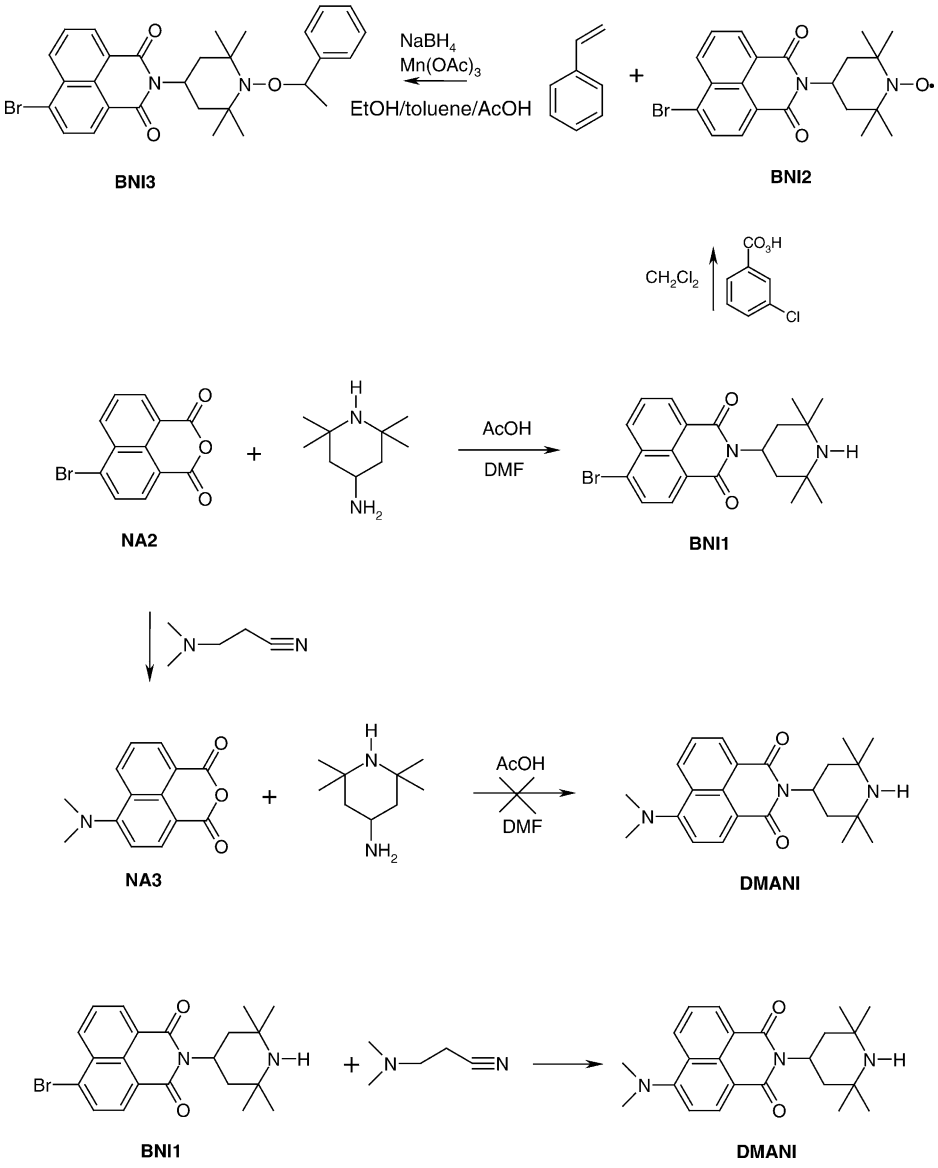
ing light beam. The transient absorbance at the pre-selected wavelength was monitored by a detection system composed of a pulsed Xe-lamp (150 W), monochromator and a 1P28 photomultiplier. A unit controlled synchronizing of the pulse lamp, programmable shutters and high voltage power supply with laser output. The signal from photomultiplier was displayed on digital osciloscope (HP 54522A) and analyzed on 32 bit RISC work station [22,23].

3. Results and discussion

3.1. Synthesis

The synthetic approach we pursued is depicted in Scheme 3. 4-Bromo-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI1) was prepared by the reaction of 4-bromo-1,8-naphthalic anhydride (NA2) and equimolar amount of 4-amino-2,2,6,6-tetramethylpiperidine in DMF. Solid crude product was crystallized from hexane, but some starting material was still present. After purification by column chromatography the final product was recieved in high purity. The structure was confirmed using ^{1}H-NMR (Fig. 1), ^{13}C-NMR, FTIR and mass spectroscopy.

Transformation of parent amine to stable nitroxyl radical can be done with different oxidation agents. The advantage of using 3-chloroperoxobenzoic acid is its very high selectivity to oxidized >NH to >NO$^{\bullet}$ and reasonable simple purification of final product. In our case direct oxidation of BNI1 with 3-chloroperoxy-benzoic acid in dichloromethane was successful, giving a 4-bromo-*N*-(1-oxo-2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI2) in 61% yield as or-



Scheme 3.

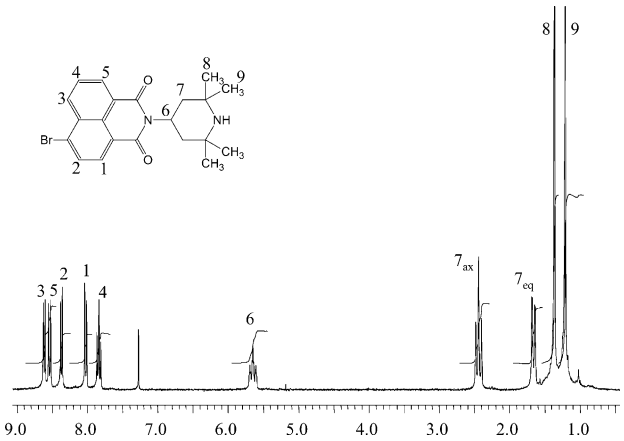


Fig. 1. ^{1}H-NMR spectrum of 4-bromo-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI1) in $CDCl_3$.

ange crystals. The purity of BNI2 was checked by EPR spectroscopy. Quantitative measurements were performed in benzene solutions ($c = 1 \times 10^{-3}$ mol/dm^3). Integral of EPR spectra for BNI2 was compared with the integral of standard measured under the same conditions. As the standard 4-hydroxy-2,2,6,6-tetramethyl-piperidine-*N*-oxyl was used. EPR spectrum of the BNI2 as well as standard were triplets with equal line intensities. The values of integrals are proportional to the number of radicals so the relative concentration c_r provides information about amount of radical in the BNI2. We assume that the concentration of radicals in the standard is 100%. The value c_r for BNI2 was 95%, which is the proof of the very high purity. Purity was checked by TLC too.

Synthesis of alkoxyamine 4-bromo-*N*-(1-(1-phenylethyl) oxo-2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI3) from this nitroxide was accomplished by the addition of styrene in the presence of $Mn(OAc)_3$ as a catalyst. The most efficient conditions were obtained using a solvent mixture ethanol/toluene/acetic acid 2:2:1. Acetic acid increases the solubility of the $Mn(OAc)_3$, so only a four-fold excess of $Mn(OAc)_3$ and styrene is needed. Using of pure acetic acid yields only the hydroxylamine as a sideproduct.

Conversion of 4-bromo-1,8-naphtalic anhydride (NA2) to 4-dimethylamino-1,8-naphthalic anhydride (NA3) was provided by the reaction with 3-(dimethylamino)-propionitrile, which was prepared by the addition reaction of dimethylamine with acrylonitrile in ethanol. Thus, treatment of 3-(dimethylamino)propionitrile with NA2 in polar solvent, afforded dimethylaminoderivate NA3 in a very good yield.

Following conversion of NA3 to 4-dimethylamino-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (DMANI) using the same procedure as in the case of preparation of BNI1 from 4-bromo-1,8-naphtalic anhydride was unsuccessful and only many unidentified products were formed. Using a BNI1 as a starting material solved this problem. BNI1 was treated with an excess of 3-(dimethylamino)propionitrile to provide a 1:1 mixture of desired product and unreacted BNI1. Careful column chromatography gave the crude product which was crystallized from dichloromethane obtaining yellow crystals of 4-dimethylamino-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide in high purity. To our knowledge the compounds BNI1, 2, 3 and DMANI are newly synthesized.

3.2. Spectral measurement

Effect of substituent in position 4 of naphthalene ring on the absorption spectra is shown in Fig. 2. Spectra of unsubstituted 1,8-naphthalic anhydride (NA1) and 4-bromo-1,8-naphthalic anhydride (NA2) are very similar. Just very small bathochromical shift of several nanometer can be seen in the case of bromo-derivative in comparison with unsubstituted anhydride. However, substantial changes can be seen by introduction of dimethylamino group to naphthalene ring.

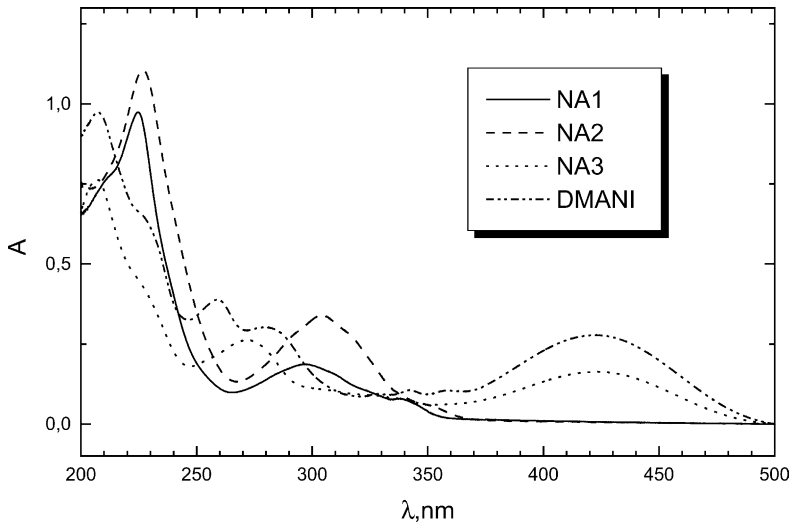


Fig. 2. Absorption spectra of 1,8-naphthalic anhydride (NA1), 4-bromo-1,8-naphthalic anhydride (NA2), 4-dimethylamino-1,8-naphthalic anhydride (NA3) and 4-dimethylamino-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (DMANI) in methanol.

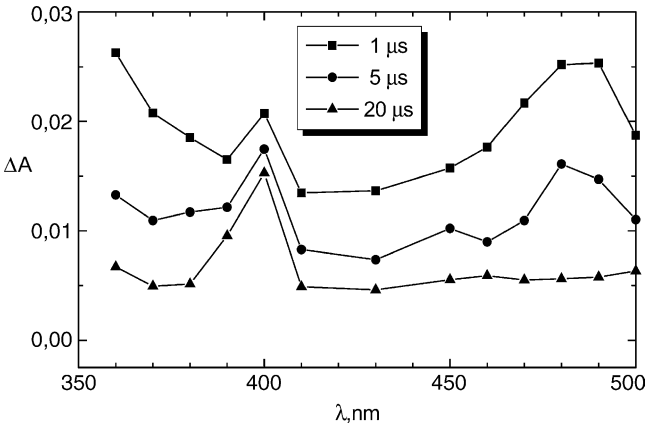


Fig. 3. Time resolved transient absorption spectra of 1,8-naphthalic anhydride NA1 at 355 nm excitation in methanol.

Clearly, the substitution of electron donating dimethylamino group in the position 4 of naphthalene ring in the case of 1,8-napthalic anhydride (NA3) as well as in the case of 1,8-naphthalimide (DMANI) shifts the long wavelength band bathochromically from ca. 300 to 425 nm.

Absorption spectra indicate that the 355 nm excitation is feasible for unsubstituted 1,8-naphthalic anhydride (NA1) and derivatives derived from it NA2, NA3 and DMANI. In the case of NA1 and 2 the excitation occurs at the long wavelength edge while it occurs at short wavelength edge for NA3 and DMANI. Concentration of all solutions used for laser flash photolysis experiment was used according to the absorption at 355 nm. All solutions had at this wavelength roughly the same absorption ca. 0.6 to secure similar population of excited states. The transient triplet absorption spectrum of 1,8-naphthalic anhydride NA1 exhibits two distinct maxima (Fig. 3). First maximum around 400 nm, practically does not decay during the time scale used, contrary to the second one around 480 nm which decays. It means that they

Table 1
Kinetic data of decay of probes based on 1,8-naphthalic anhydride NA1–NA3 and 1,8-naphthalimide DMANI at 355 nm excitation in methanol

Probe[a]	Conditions[b]	λ[c] (nm)	F[d]	k[e] (A[f]) (s^{-1})	k_q[g] ($dm^3\,mol^{-1}\,s^{-1}$)
NA1	Air	480	M	1.49×10^6	$0.57. \times 10^9$
	N_2	480	B	2.35×10^5 (51%)	
				4.00×10^4 (49%)	
	N_2	480	M	1.00×10^5	
	N_2/Q_2	480	M	1.28×10^7	2.54×10^9
NA2	Air	500	M	2.34×10^6	0.99×10^9
	N_2	500	M	1.59×10^5	
	N_2/Q_1	500	M	2.62×10^6	
	N_2/Q_2	500	M	1.47×10^7	2.94×10^9
NA3	Air	650	M	2.24×10^4	0
	N_2	650	M	3.30×10^4	
	N_2/Q_3	650	M	3.70×10^4	4.0×10^5
DMANI	Air	650	M	3.87×10^4	0
	N_2	650	M	4.07×10^4	
	N_2/Q_3	650	M	2.33×10^4	0

[a] Structure of the probe according to Schemes 1 and 2.
[b] Experimental conditions: air – aerated solutions, N_2 – bubbling with stream of nitrogen for 10 min. Q – quencher TEMPO at concentration, $Q_1 = 0.001$, $Q_2 = 0.005$, $Q_3 = 0.01$ mol dm^{-3}.
[c] Monitoring wavelength.
[d] Fitting to monoexponential M, or biexponential B.
[e] Rate constant of the decay.
[f] Fraction at the bimolecular decay.
[g] Bimolecular rate constant of quenching by oxygen (oxygen concentration $c = 2.4 \times 10^{-3}$ mol dm^{-3} [23]) and 1-oxo-2,2,6,6-tetramethylpiperidine (TEMPO).

are two different excited states concerning the lifetime. The decay of transient absorption at 480 nm of NA1 in methanol is about 10 times more rapid in the presence of oxygen ($k = 1.49 \times 10^6\ s^{-1}$, Table 1) than in nitrogen atmosphere $\sim 1 \times 10^5\ s^{-1}$, which is clearly biexponential. Surprisingly, the triplet of NA1 is quenched more efficiently by free nitroxyl radical 1-oxo-2,2,6,6-tetramethyl-piperidine (TEMPO) than by ground state of oxygen (Table 1). The bromo substituted

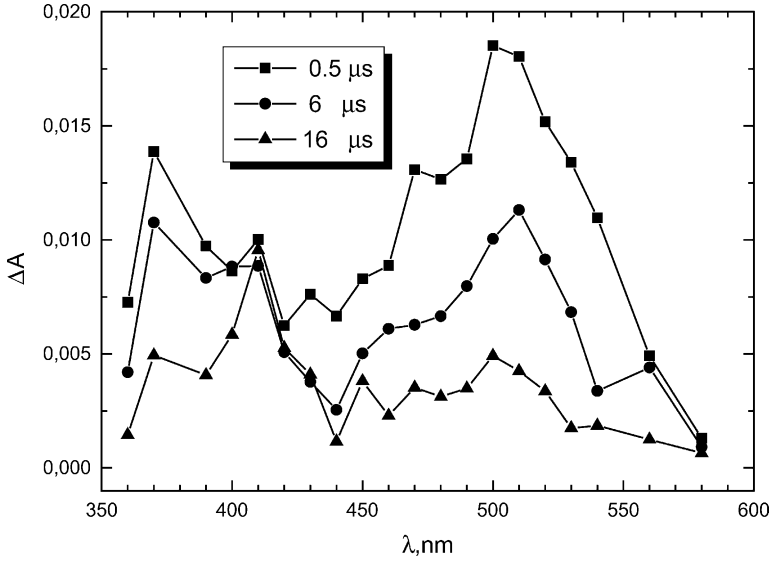


Fig. 4. Time resolved transient absorption spectra of 4-bromo-1,8-naphthalic anhydride NA2 in methanol at 355 nm excitation.

derivative NA2 (Fig. 4) shows similar features with some additional maxima at 370 and 510 nm. Under the same condition the overall absorption is weaker indicating lower concentration of triplet state. By bromo substitution, heavy atom effect was introduced to the molecular system. One can expect that the heavy atom effect will increase the deactivation routes and consequently lower measurable triplet concentration might be expected. Again the triplet of NA2 is more effectively quenched by free nitroxyl radical –TEMPO – than by oxygen. Bimolecular rate constant k_q of quenching of NA1 and NA2 with oxygen is 1×10^9 dm^3 mol^{-1} s^{-1} and for TEMPO (Q) k_q is higher 3×10^9 dm^3 mol^{-1} s^{-1}. In accord with previous studies with probes based on naphthalene, quenching of derivatives containing different substituent in position 4 with *N*-oxyls as well as with oxygen is well below diffusion-controlled limit for these 1,8 naphthalic anhydride derivatives as well. The decays of transient absorption fit monoexponential but in nitrogen atmosphere the decay is better described by biexponential with fast rate 2.35×10^5 s^{-1} and slow rate 4.0×10^4 s^{-1}.

Dimethylamino group in position 4 of 1,8-naphthalic anhydride – NA3 or naphthalimide – DMANI results in the shift of transient triplet absorption maxima of NA3 and DMANI (Figs. 5 and 6) above 600 nm. The intensity especially in the case of DMANI was much lover. These triplets were difficult to quench with oxygen as well as by TEMPO. For NA3 the estimated value of k_q was around 4×10^5 dm^3 mol^{-1} s^{-1} that is five orders of magnitude lower than diffusion-controlled limit. Clearly, this dimethylamino substitution on 1,8-naphthalic anhydride or imide frame lowers the formation of triplet state under the same conditions and also lowers its energy so that it is difficult to quench it by oxygen and TEMPO.

In comparison with nonsubstituted as well as 4-bromo-substituted 1,8-naphthalic anhydride (NA1 and NA2) which

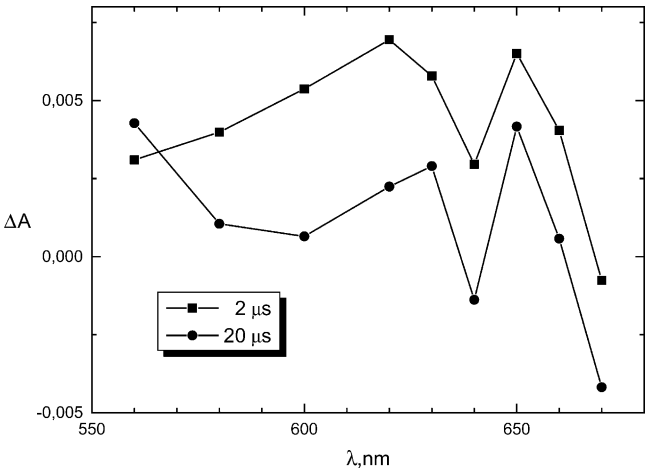


Fig. 6. Time resolved transient absorption of 4-dimethylamino-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide DMANI at 355 nm excitation in methanol.

have in UV absorption spectra maximum of the longest wavelength band around 300 nm (Fig. 2), *N*-substituted derivatives of 4-bromo-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI1–BNI3) have absorption maximum shifted to the longer wavelength at 340 nm (Fig. 7). The absorption spectra of 4-bromo-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide in polar methanol are not influenced by substitution on sterically hindered nitrogen. The longest wavelength bands show some vibrational resolution. When these derivatives are probed by 355 nm excitation, they exhibit similar behaviour as derivatives without substitution in position 4 of naphthalene ring [20]. The triplet transient absorption spectra of parent amine (BNI1) and alkoxyaminoether (BNI3) (Figs. 8 and 9) exhibit maxima around 480 and 380 nm in nitrogen. Additional band is at

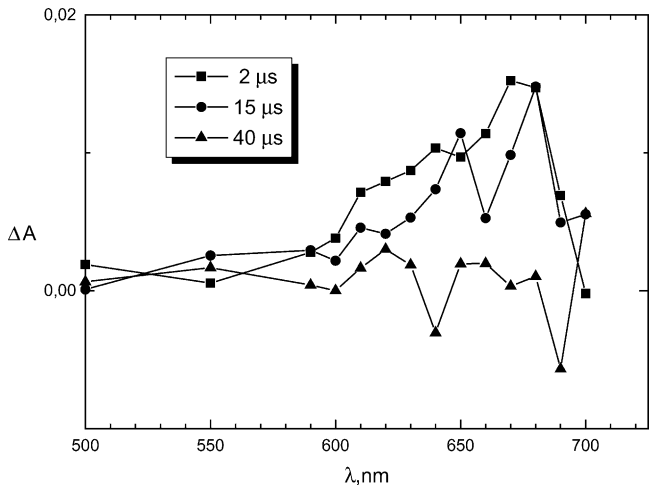


Fig. 5. Time resolved transient absorption spectra of triplet 4-dimethylamino-1,8-naphthalic anhydride NA3 in methanol at 355 nm excitation.

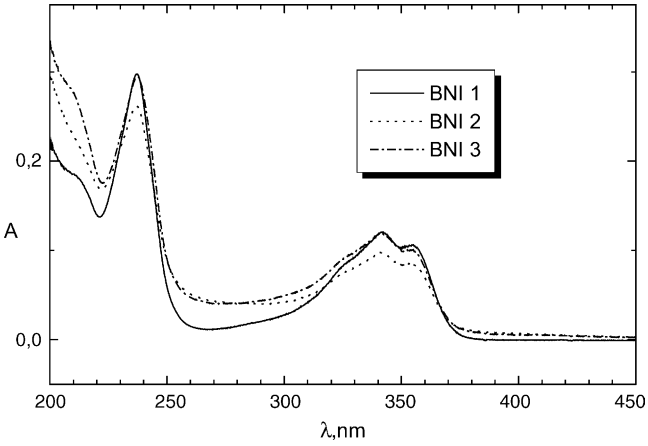


Fig. 7. Absorption spectra of 4-bromo-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI1), 4-bromo-*N*-(1-oxo-2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI2), and 4-bromo-*N*-(1-(1-phenylethyl)oxo-2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI3) in methanol.

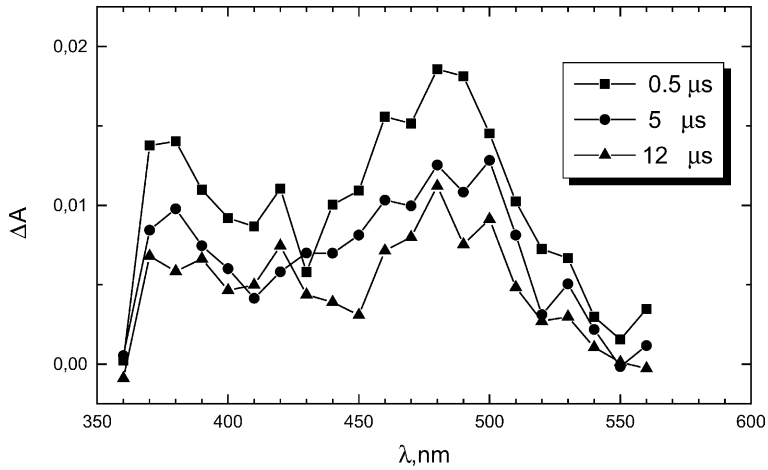


Fig. 8. Time resolved triplet absorption spectra of 4-bromo-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI1) in methanol at 355 nm excitation.

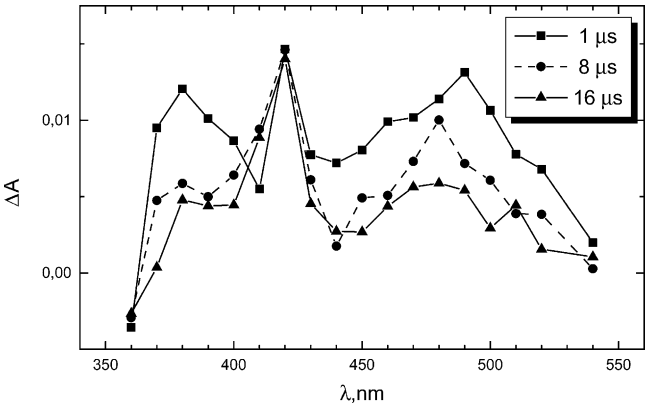


Fig. 9. Time resolved triplet absorption spectra of 4-bromo-*N*-(1-(1-phenylethyl)oxo-2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide (BNI3) in methanol at 355 nm.

420 nm which does not decay in the case of BNI3. In this case also, the quenching of triplet BNI1 and BNI3 by oxygen is less effective as by TEMPO (Table 2).

No (or extremely weak transient) absorption spectra was observed for stable nitroxyl radical BNI2. Excited triplets are quenched by nitroxyl radical which is part of the molecule. This intramolecular quenching is faster than the shortest time we can use for measurement. This is the similar behaviour as in the case of nonsubstituted derivative (2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide described in [20]. Moreover in this case we have shown that this free nitroxyl radical is able to quench first itself and after than act as an effective quencher for another chromophore.

In conclusion one can state that the triplet state of 1,8-naphthalic anhydride or imide substituted in position 4 is influenced strongly by electron donating dimethylamino group and less effectively by bromine. Combination of 4 bromine group, having heavy atom effect, with free *N*-oxyl radical, having paramagnetic effect, in the same molecule results in formation of very efficient deactivation channel and triplet state is difficult to observed in sub microsecond region.

Table 2
Kinetic data of decay of triplet of derivatives of 4-bromo-*N*-(2,2,6,6-tetramethyl-4-piperidinyl)-1,8-naphthalimide BNI1–BNI3 at 355 nm excitation in methanol

Probe[a]	Conditions[b]	λ[c] (nm)	F[d]	k[e] (s^{-1})	k_q[f] ($dm^3\ mol^{-1}\ s^{-1}$)
BNI1	Air	470	M	2.35×10^6	0.92×10^9
	N_2	470	M	1.36×10^5	
	N_2/Q_1	470	M	2.09×10^6	
	N_2/Q_2	470	M	9.97×10^6	
	N_2/Q_3	470	M	2.88×10^7	2.84×10^9
BNI2	Air	470	—	Weak signal	
	N_2	470	—	Weak signal	
BNI3	Air	470	M	2.22×10^6	0.87×10^9
	N_2	470	M	1.34×10^5	
	N_2/Q_1	470	M	2.51×10^6	2.37×10^9
	N_2/Q_2	470	M	1.15×10^7	2.30×10^9

[a] Structure of the probe according to Scheme 2.
[b] Experimental conditions: air – aerated solutions, N_2 – bubbling with stream of nitrogen for 10 min. Q = quencher TEMPO at concentration, Q_1 = 0.001, Q_2 = 0.005, Q_3 = 0.01 mol dm^{-3}.
[c] Monitoring wavelength.
[d] Fitting to monoexponential M.
[e] Rate constant of the decay.
[f] Bimolecular rate constant of quenching by oxygen (oxygen concentration $c = 2.4 \times 10^{-3}$ mol dm^{-3} [23]) and 1-oxo-2,2,6,6-tetramethylpiperidine (TEMPO).

Acknowledgements

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