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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

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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).

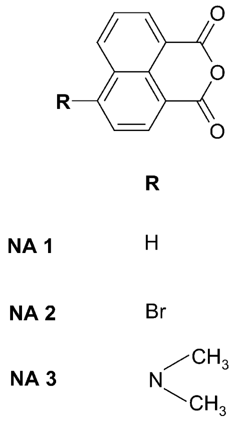
1,8-Naphthalic anhydride (NA1) and 4-bromo naphthalic anhydride (NA2) were commercial products (Aldrich, Steinheim, FRG). The structures of probes used in this paper are shown in Schemes 1 and 2. New probes NA3, DMANI and BNI1-3 were prepared according to the following procedures.

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.).

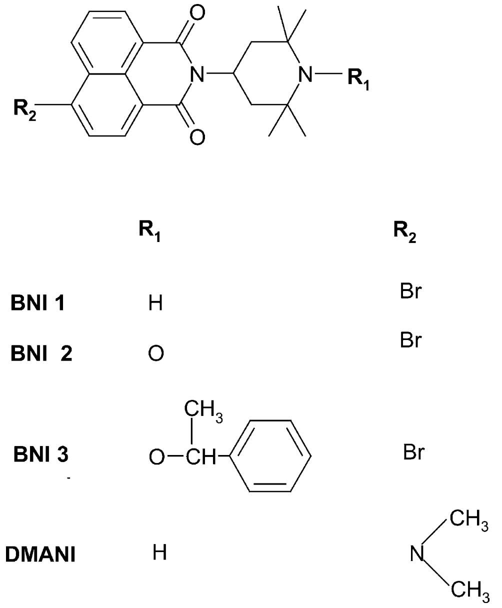
GC-MS m/z: 241[M], 197, 168, 154, 126.



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.