

Spectral Characteristics of Bifunctional Fluorescence Probes Based on Naphthalene: Comparison in Solution and Polymer Matrix

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Spectral properties of bifunctional fluorescence probes of esters of 1-naphthoic and 1-naphthylacetic acids with methanol, 2,2,6,6-tetramethyl-4-hydroxypiperidine, its *N*-oxyl and chloride in solution and in polymer matrix were studied. Esters of 1-naphthoic acid exhibit broad absorption and emission bands which shift bathochromically in going from nonpolar to polar solvents. Esters of 1-naphthylacetic acid exhibit absorption spectrum typical for naphthalene chromophore which is not influenced by the polarity of solvent or polymer matrix. The different spectral behaviour of derivatives of 1-naphthylacetic and 1-naphthoic acids stresses the role of methylene bridge between the naphthyl ring and ester group in esters of 1-naphthylacetic acid whereas there is the direct interaction in the esters of 1-naphthoic acid. The fluorescence lifetime of esters of 1-naphthoic acid is in the range of 2–4 ns and it decays as monoexponential with some approximation. Intermolecular quenching of esters of 1-naphthoic acid by *N*-oxyls is effective and occurs as a diffusion-controlled process. Intramolecular quenching, which proceeds in *N*-oxyls derived from esters of 1-naphthoic and 1-naphthylacetic acids, is equally effective in solution and in polymer matrices. Small medium effect on intramolecular quenching supports the conclusion that the new radiationless channel is opened in the presence of paramagnetic centre for dissipation of electronic energy.

Free radicals of the *N*-oxyl type attract attention for two reasons. First of all they are intermediates in the course of stabilization of polymers, mainly polyolefins, by sterically hindered amines [1–4]. Secondly, the free radicals influence the photophysical and photochemical processes due to their paramagnetic effect [5–13]. Quenching of singlet and triplet states of aromatic hydrocarbons and ketones was studied in detail.

Recently fluorescence probes 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 [14].

Mechanism of inter- or intramolecular quenching of excited states by *N*-oxyls is not unequivocally established. 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 a singlet state of aromatic hydrocarbons with *N*-oxyl radicals concluded that enhancement of intersystem crossing

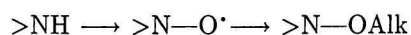
is the most probable route for dissipation of energy. Quenching of a triplet state occurs through internal conversion [5–13].

The photophysical process is a preferred route for deactivation of excited state by intramolecular quenching as well [14].

On the other hand, the photoinitiated intramolecular electron transfer from *N*-oxyl to diimide under formation of diimide monoanion has been observed recently [15].

These studies indicate that *N*-oxyl radical is able to quench the excited state by different mechanisms depending on the structure of the couple quencher—quencher and medium.

The transformation of the parent amine to *N*-oxyl radical, its alkyl ether and regeneration of *N*-oxyl plays a key role in the course of stabilization of polyolefins by hindered amines [1–3]. The process seems to be rather complex and involves several partial photochemical, thermal, and catalytic steps. This process occurs in the bulk of the stabilized polymer during the induction period when there is no accumulation of oxygen-containing groups in polymer. The content of low-molecular light stabilizer is around 0.01 mol kg⁻¹. At this content level it is rather difficult to monitor the transformation



in detail. Fluorescence probes based on 1-naphthoic and 1-naphthylacetic acids with hindered amine centre could monitor this transformation during photooxidation because the *N*-oxyl could switch off fluorescence. This might be rather sensitive indication of *N*-oxyl formation.

In this paper the spectral properties of fluorescence probes of aromatic hydrocarbon/amine and aromatic hydrocarbon/*N*-oxyl derived from 1-naphthoic and 1-naphthylacetic acids, respectively, were compared in solution and polymer matrix in the concentration range commonly used in stabilization. The intermolecular quenching of probes with parent amine and related compounds by *N*-oxyls was compared with intramolecular quenching. The influence of medium on intramolecular quenching was established.

EXPERIMENTAL

Naphthalene and anthracene (Lachema, Brno) were zonally refined. Solvents cyclohexane (Merck, Darmstadt), ethanol, and methanol were used for UV spectroscopy. Chloroform and tetrahydrofuran (Lachema, Brno) were anal. grade reagents.

2,2,6,6-Tetramethyl-4-hydroxypiperidine (4HOTMP), 1-oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine (4HOTMPNO) and its 4-acyloxy derivative (4AcOTMPNO) were the same as in [16].

Methyl 1-naphthoate (*Ib*) was prepared by acid-catalyzed esterification of 1-naphthoic acid (BDH, Poole, England) as pale yellow liquid. Yield 3.5 g, 65 %.

2,2,6,6-Tetramethyl-4-piperidinyl 1-naphthoate (*Ic*) was prepared by reesterification of *Ib* (3.5 g; 0.02 mol) with 2,2,6,6-tetramethyl-4-hydroxypiperidine (4HOTMP) (3.2 g; 0.02 mol) catalyzed by tetrabutylorthotitanate in heptane under reflux. In order to shift the equilibrium the alcohol (3.2 g; 0.02 mol) was added additionally. Crude product was obtained chromatographically on silica gel (L100/400, Lachema, Brno) by elution with the mixture benzene—methanol saturated with ammonium ($\varphi_r = 9 : 1$). It was crystallized from hexane and white crystals (m.p. = 48—51°C) were obtained. Yield 1.1 g; 20 %. IR spectrum (CCl_4), $\tilde{\nu}/\text{cm}^{-1}$: 1714 (C=O), 1134 (C—O, ester), 783 (naphthyl in hexane as solvent). ^1H NMR spectrum (CDCl_3), δ : 1.25 (s, 6H, $2 \times \text{CH}_3$, 2 + 6 axial), 1.35 (s, 6H, $2 \times \text{CH}_3$, 2 + 6 equat.), 1.4 (m, 2H, CH_2 , 3 + 5 axial), 1.45 (s, 1H, NH), 2.15 (m, 2H, CH_2 , 3 + 5 equat.), 5.55 (m, 1H, $>\text{CH}-\text{O}$), 7.5—8.9 (m, 7H, naphthyl).

1-Oxo-2,2,6,6-tetramethyl-4-piperidinyl 1-naphthoate (*Id*) was prepared by oxidation of amine *Ic* (1 g; 0.0033 mol) in hexane (15 cm^3) by 3-chloroperbenzoic acid (1.2 g; 0.0069 mol) at room temperature for several days. The crude product after evaporation of solvent was purified chromatographically on silica gel (L100/400) with chloroform as eluent. The red crys-

tals (m.p. = 98—101°C, Ref. [14] gives m.p. = 100—102°C) were obtained by crystallization from ethanol. Yield 0.7 g, 65 %.

2,2,6,6-Tetramethyl-4-piperidinyl(1-naphthoate)-ium chloride (*Ie*) precipitated from diethyl ether solution (50 cm^3) of parent amine *Ic* (1 g; 0.0033 mol) after dropwise addition of methanol saturated with HCl (3.065 cm^3 , 0.0033 mol) as white powder (m.p. = 246—249°C). Yield 0.89 g, 80 %.

The same route of synthesis was used for derivatives of 1-naphthylacetic acid as well.

Methyl 1-naphthylacetate (*Iib*) was prepared by acid-catalyzed esterification of acid (Lachema, Brno) with methanol and was obtained as pale yellow liquid. Yield 8 g, 80 %.

2,2,6,6-Tetramethyl-4-piperidinyl 1-naphthylacetate (*Iic*) was prepared by reesterification of *Iib* (8 g; 0.04 mol) with 4HOTMP (6.3 g; 0.04 mol) in *n*-heptane (150 cm^3) catalyzed by tetrabutylorthotitanate at the boiling point. Crude product was obtained chromatographically. Crystallization from methanol yielded white crystals with m.p. = 59—61°C. Yield 3.5 g, 27 %. IR spectrum (CCl_4), $\tilde{\nu}/\text{cm}^{-1}$: 1730 (C=O), 1169 (C—O, ester), 787 (naphthyl in hexane as solvent). ^1H NMR spectrum (CDCl_3), δ : 1.1 (s, 6H, $2 \times \text{CH}_3$, 2 + 6 axial), 1.15 (m, 3H, CH_2 , 3 + 5 axial and NH), 1.2 (s, 6H, $2 \times \text{CH}_3$, 2 + 6 equat.), 1.9 (m, 2H, CH_2 , 3 + 5 equat.), 4.05 (s, 2H, $-\text{CH}_2-\text{CO}$), 5.2 (m, 1H, $>\text{CH}-\text{O}$), 7.4—8.0 (m, 7H, naphthyl).

1-Oxo-2,2,6,6-tetramethyl-4-piperidinyl 1-naphthylacetate (*Iid*) was prepared by oxidation of parent amine *Iic* (1 g; 0.003 mol) with 30 % hydrogen peroxide (1.7 cm^3 in 1.3 cm^3 of water) in the presence of ethylenediaminetetraacetic acid (0.02 g) and sodium wolframate (0.01 g) in methanol (8.5 cm^3). The reaction mixture was stirred for 24 h at room temperature. Product after liquid chromatography was a red viscous liquid which did not crystallize as in [14]. Yield 0.6 g, 57 %.

2,2,6,6-Tetramethyl-4-piperidinyl(1-naphthylacetate)ium chloride (*Iie*) was prepared by precipitation of diethyl ether solution of *Iic* (1 g; 0.033 mol) with methanol saturated with HCl (3.065 cm^3 , 0.033 mol). The white powder was decomposed at 268°C. Yield 0.65 g, 61 %.

Polymer films doped with fluorescence probes were prepared in two ways: by casting from solution and by hot pressing of impregnated polymer powders. Films of polystyrene (PS) (Chemische Werke Huels, F.R.G.), poly(methyl methacrylate) (PMMA) (Diacon, ICI, England) were prepared by casting 0.5—2 mg of probe in 1 cm^3 of chloroform solution of polymer ($\rho = 5 \times 10^{-2} \text{ g cm}^{-3}$) on a glass plate (28 mm \times 35 mm). The solvent was evaporated slowly. Films of poly(vinyl chloride) (PVC) (Neralit, Spolana Neratovice) were prepared by casting tetrahydrofuran solution ($\rho = 5 \times 10^{-2} \text{ g cm}^{-3}$) similarly. Content of the

Table 1. Absorption Spectra of Probes Derived from Naphthalene

Probe	Solvent ^a	λ_{\max}/nm ($\log(\epsilon/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}))$)
<i>Ia</i>	E	297 (3.70), 226 (5.24)
<i>Ib</i>	Cy	286 (4.33), 221 (4.74), 207 (4.81)
	E	300 (3.74), 236 (4.60)
<i>Ic</i>	Cy	286 (4.18), 221 (4.52), 208 (4.58)
	E	298 (3.74), 235 (4.70)
<i>Id</i>	Cy	286 (4.13), 233 (4.40), 219 (4.50), 208 (4.59)
	E	301 (3.83), 233 (4.54)
<i>Ie</i>	E	301 (3.76), 233 (4.68)
	W	298 (3.74), 234 (4.30), 219 (4.52), 213 (4.51)
<i>IIa</i>	Cy	314 (2.38), 287 (3.62), 278 (3.78), 267 (3.71), 223 (4.80)
	E	316 (2.51), 278 (4.08)
<i>IIb</i>	Cy	314 (2.54), 292 (3.76), 282 (3.93), 272 (3.83), 224 (4.95)
	E	316 (2.38), 294 (3.78), 285 (3.94), 273 (3.83), 263 (3.64)
<i>IIc</i>	Cy	314 (2.55), 289 (3.77), 281 (3.92), 270 (3.85), 223 (4.97)
	E	316 (2.45), 293 (3.81), 283 (3.92), 273 (3.86), 263 (3.68)
<i>IId</i>	Cy	314 (2.59), 291 (3.80), 280 (3.95), 270 (3.90), 223 (4.92)
	E	333 (2.30), 316 (2.90), 292 (3.79), 282 (3.93), 272 (3.87)
<i>IIe</i>	E	316 (2.51), 293 (3.83), 283 (4.02), 274 (3.92), 263 (3.72)
	W	316 (2.55), 291 (3.60), 283 (3.76), 274 (3.68), 263 (3.47), 224 (4.76)

a) Cy - cyclohexane, E - ethanol, W - water.

probe was in the range 0.02–0.1 mol kg⁻¹.

Films of isotactic polypropylene (iPP) (Slovnaft, Bratislava) were prepared by hot pressing of powders impregnated with the probe. Polymer powder (2 g), probe (10–25 mg), and 10 cm³ of dichloromethane were mixed and allowed to stand for 24 h. After removing the solvent under vacuum the mixture was homogenized. Part of it (1 g) was pressed for 2 min at 190°C. The thickness of films was 0.1–0.15 mm and content of probe was 0.02 mol kg⁻¹.

Absorption spectra were taken on Specord UV VIS and M-40 (Zeiss, Jena) instruments in nonpolar cyclohexane and polar ethanol. All relevant data on UV spectra are summarized in Table 1.

IR spectra were measured on Specord IR-75, M-80 (Zeiss, Jena) and Impact 400 (Nicolet, F.R.G.) apparatuses.

Emission spectra were recorded on spectrofluorimeter Perkin—Elmer MPF-4 (Perkin—Elmer, Norfolk, Conn., U.S.A.) which was connected through interface and A/D convertor to microcomputer [17] for data collection, processing, and plotting on an XY 4110 plotter (Laboratorní přístroje, Prague). Emission of solution was measured in a 1 cm cuvette in the right angle arrangement. Emission of polymer films was measured in front face arrangement on the solid sample holder. In both cases the relative quantum yield was determined using anthracene as standard which fulfils the following requirements: 1. good solubility in solvents of different polarity and good compatibility with polymer matrices, 2. absorption and emission in the same region as the probes under study, 3. availability in high purity, 4. small or no influence on the spectral properties by the medium. The relative quan-

tum yields in solution and in film were determined according to the relation [18]

$$\phi_r = \frac{P \cdot (1 - 10^{-AS}) \cdot n^2 \cdot (2 - r_{ns})}{PS \cdot (1 - 10^{-A}) \cdot n_s^2 \cdot (2 - r_n)}$$

where P and PS are the areas under fluorescence curves of probe and standard, respectively, A and AS are absorptions of probe and standard, at the wavelength excitation, n and n_s are refractive indices, and r_n and r_{ns} are emission anisotropies on excitation by unpolarized light of probe and standard, respectively. No correction was made on emission anisotropy due to excitation by unpolarized light.

The fluorescence lifetime measurements were performed on a LIF 200 (Lasertechnik, Berlin) which operates as a stroboscope. The output signal was digitalized and transferred to the microcomputer [19]. The decay curves were evaluated by the simple phase plane method [20]. The standard deviation $G^{1/2} = \sum((I_{\text{exp}} - I_{\text{calc}})^2/n)^{1/2}$, where I_{exp} and I_{calc} are intensities of emission, experimental and calculated, respectively, is used to judge if the decay is monoexponential. The decay curve satisfies the monoexponential if $G^{1/2}$ is lower than 5%. The spectral data concerning the emission spectra are given in Table 2.

The quenching experiments were performed in aerated ethanol solutions. The Stern—Volmer plots were constructed by evaluating the areas under fluorescence curves without and with quencher using the home-made software. The pertinent data concerning the quenching are given in Table 3.

¹H NMR spectra were measured on a 300 MHz AM-300 instrument (Bruker, F.R.G.).

Table 2. Emission Spectra of Probes Based on Naphthalene in Solution and Polymer Matrix

Probe	M ^a	λ_{\max}/nm (I_r) ^b	ϕ_r^c	τ/ns^d	$G^{1/2}$ e
Ia	Cy	348 (1.00)	0.13		
	E	369 (1.00)	0.07	2.9	4.9
	iPP	360 (1.00)	1.07	1.6	8.3
	PS	370 (1.00)	1.65	2.6	2.8
	PMMA	356 (1.00)	0.34	2.6	7.9
Ib	PVC	374 (1.00)	0.71	1.4	4.6
	Cy	345 (1.00)	0.23		
	E	370 (1.00)	0.90	2.8	4.5
	iPP	335 (0.61), 346 (1.00)	0.45	2.3	8.5
	PS	359 (1.00)	0.58	2.0	4.6
Ic	PMMA	358 (1.00)	0.49	3.9	8.1
	PVC	359 (1.00)	0.71	1.4	7.9
	Cy	346 (1.00)	0.13		
	E	370 (1.00)	0.90	2.9	4.5
	iPP	335 (1.00)	0.53	2.1	8.7
Id	PS	357 (1.00)	0.51	2.3	5.8
	PMMA	358 (1.00)	0.35	2.7	8.2
	PVC	357 (1.00)	0.15	1.5	13.6
	Cy	348 (1.00)	0.035		
	E	372 (1.00)	0.05		
Ie	iPP	334 (1.00), 349 (0.98)	0.13		
	PS	359 (1.00)	0.1		
	PMMA	358 (1.00)	0.07		
	PVC	358 (1.00)	0.05		
	E	374 (1.00)	1.15	3.5	4.0
IIa	W	394 (1.00)	0.87		
	iPP	334 (1.00), 397 (0.87)	0.41	1.2	7.4
	PS	360 (1.00)	0.44	2.1	5.0
	PMMA	358 (1.00)	0.44	1.7	9.8
	PVC	378 (0.23), 423 (1.00)	0.98	44.8	4.8
IIb	Cy	330 (0.77), 342 (1.00)	0.02		
	E	329 (1.00), 339 (0.98)	0.08		
	iPP	330 (0.87), 342 (1.00)	0.74		
	PS	331 (1.00), 343 (0.98)	0.35		
	PMMA	341 (1.00)	1.11		
IIc	PVC	342 (1.00)	0.26		
	Cy	330 (0.67), 343 (1.00)	0.02		
	E	328 (1.00), 340 (1.00)	0.10		
	iPP	343 (1.00)	0.61		
	PS	331 (0.96), 343 (1.00)	0.32		
IIe	PMMA	330 (0.88), 341 (1.00)	0.78		
	PVC	330 (0.99), 341 (1.00)	0.25		
	Cy	330 (0.66), 343 (1.00)	0.02		
	E	328 (1.00), 340 (0.77)	0.08		
	iPP	331 (0.97), 342 (1.00)	0.88		
IIc	PS	331 (1.00), 343 (0.91)	0.30		
	PMMA	340 (1.00)	1.06		
	PVC	329 (1.00), 341 (0.98)	0.29		
	Cy	344 (1.00)	0.005		
	E	328 (1.00), 340 (0.79)	0.02		
IIe	iPP	334 (1.00)	0.28		
	PS	329 (1.00)	0.08		
	PMMA	341 (1.00)	0.35		
	PVC	330 (1.00)	0.08		
	W	323 (1.00), 332 (0.89)	0.04		
IIe	iPP	333 (1.00)	0.04		
	PS	330 (1.00), 342 (0.81)	0.27		
	PMMA	341 (1.00)	0.99		
	PVC	334 (1.00)	0.28		

a) Medium. Symbols are explained in Experimental and in Table 1. b) Wavelength at the maximum of emission band (relative intensity to the band with the highest intensity). c) Relative quantum yield to anthracene. d) Lifetime determined by the method of phase plane [20]. e) Standard deviation.

Table 3. Intermolecular Quenching of Fluorescence Probes Based on Naphthalene with *N*-Oxyls in Ethanol^a

Probe	K_{sv}	τ	$k_q \cdot 10^{10}$
	$\text{dm}^3 \text{ mol}^{-1}$	ns	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Anthracene	144	3.9	3.7
<i>Ia</i>	152	2.9	5.2
<i>Ib</i>	132	2.8	4.7
<i>Ic</i>	172	2.9	5.9
<i>Ie</i>	154	3.5	4.4
Naphthalene	2100 ^b		
<i>Iic</i>	2100 ^b		

a) K_{sv} was determined by 4HOTMPNO and 4AcOTMPNO. b) Combination of screening and quenching effect of *N*-oxyl due to the excitation at $\lambda = 280 \text{ nm}$ where the quencher absorbs.

RESULTS AND DISCUSSION

Two extreme assumptions are considered for evaluation of the effect of polymer matrix on spectral properties and photophysical and photochemical processes:

1. Polymer matrix is sufficiently inert even at room

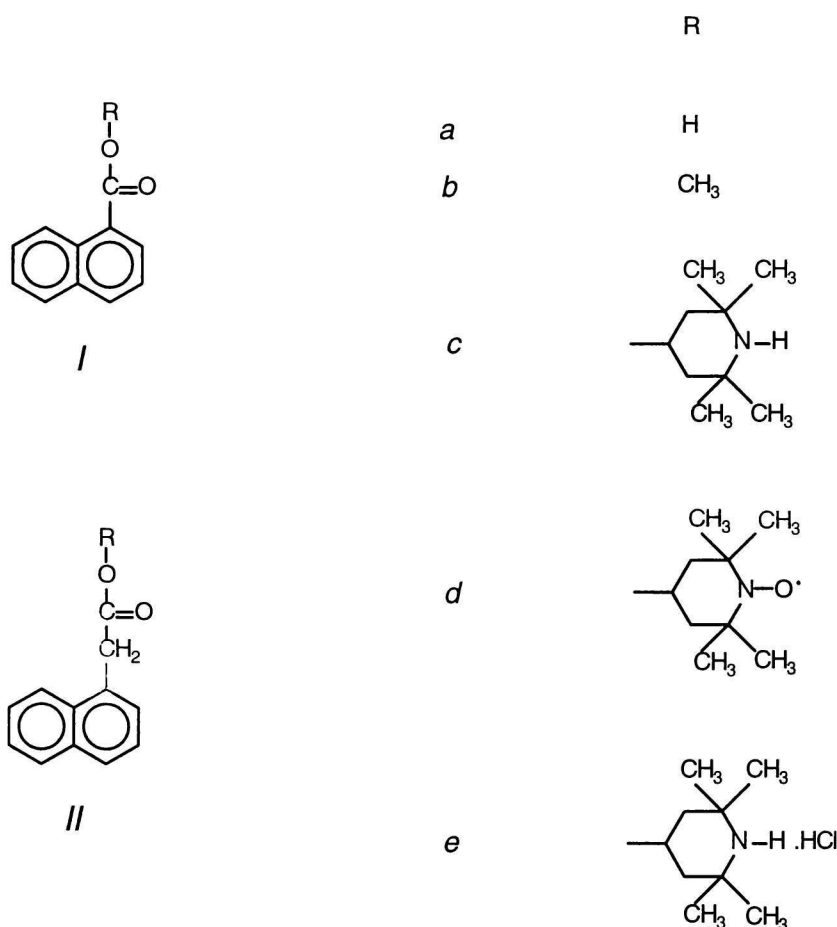
temperature so that it has no effect.

2. Polymer matrix exhibits the same effect as solvent of equal polarity.

For application of fluorescence probes in degradation studies of polymers it is necessary to know the response of probes on the changing environment in the course of photooxidation.

Bifunctional fluorescence probes based on naphthalene which combine the simple chromophore with sterically hindered amine will be suitable for monitoring in the course of degradation when their spectral properties will be little influenced by the surroundings. Therefore, the effect of the medium on spectral properties of the probes and on photophysical processes like intramolecular quenching was studied.

Probes derived from 1-naphthoic acid (*Ia*, Scheme 1) as methyl ester (*Ib*), 2,2,6,6-tetramethyl-4-piperidiny ester (*Ic*) and its *N*-oxyl (*Id*) and chloride (*Ie*) exhibit the longest wavelength broad absorption band at $\lambda = 285 \text{ nm}$ in cyclohexane. In going to polar ethanol this band shifts bathochromically 10–15 nm (Table 1). The intensity of this band expressed as $\log \epsilon$



Scheme 1

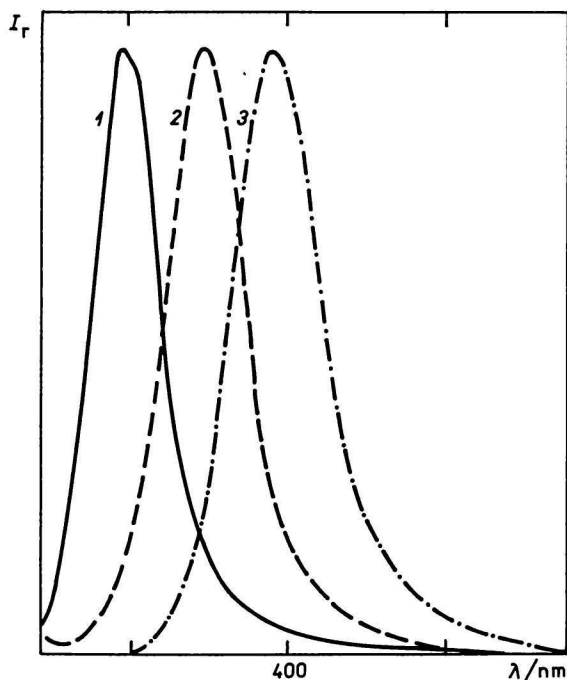


Fig. 1. Emission spectrum of probe *Ic* in 1. cyclohexane, 2. ethanol, and 3. *Ie* in water.

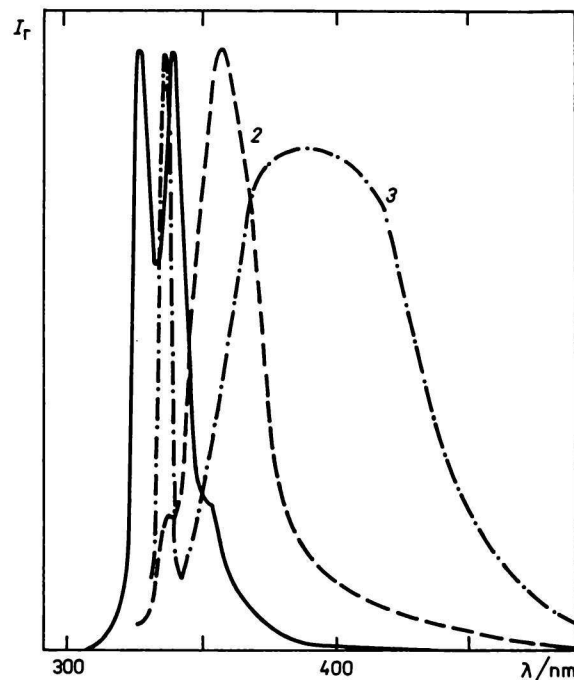


Fig. 2. Emission spectrum of 1. naphthalene, 2. *Ic*, 3. *Ie* in iPP.

is about 4.0 being higher in nonpolar than in polar solvent.

Probes derived from 1-naphthylacetic acid (*IIb*—*IIe*) exhibit absorption spectra typical for naphthalene chromophore. For all derivatives well resolved vibrational structure is observed which does not depend on the polarity of solvent and it is preserved even in the polar water. Similarly, the intensity of absorption is not influenced by polarity of the solvent, either.

Absorption spectra of probes are more sensitive to surroundings when the ester group substitutes the naphthalene ring directly. In this case no vibrational structure is observed, either.

Fluorescence spectra of probes of the 1-naphthoic acid (*I*) type show a broad emission band without any vibrational structure. The emission shifts bathochromically when going from nonpolar to polar solvents (Fig. 1). Relative quantum yield in nonpolar solvent is rather low (Table 2) but it is higher in polar solvents. In polymer matrices the position of the emission maximum correlates qualitatively with its polarity. In nonpolar iPP the maximum is in the same position as in nonpolar cyclohexane (Fig. 2). In more polar matrix it is shifted bathochromically as in a more polar solvent. The probe *Ie* exhibits large broadening of the emission band in iPP (Fig. 2). On the other hand, fluorescence of this probe is bathochromically shifted in PVC in comparison with the emission in other matrices under equal content of the dopant (Fig. 3). Surprisingly, this probe seems to be not sufficiently compatible with the polar PVC matrix. The probe *Ie*

forms some aggregates when prepared by casting from solution. Bathochromically shifted excimer-like emission in these aggregates originates from preformed excimer sites. Relative quantum yields of probes of the 1-naphthoic acid type in polymer matrices lie between low values 0.1 in nonpolar solvents and high values about 1 in polar ones (Table 2).

Since the emission band of type *I* probes is rather broad, it is possible to be excited with wavelength of nitrogen laser 337 nm at the concentration above $0.001 \text{ mol dm}^{-3}$. The lifetimes of probes in solvents and polymer matrices are similar and they are in the range 1–4 ns (Table 2). The lifetimes were determined by deconvolution with the simple phase plane method [20] and are fitted to monoexponential. The fluorescence in solution decays according to monoexponential satisfactorily because the standard deviation $G^{1/2}$ is lower than 5%. On the other hand, the standard deviation for decay of fluorescence in polymer matrices is higher than 5%. Polystyrene seems to be the most suitable matrix because $G^{1/2}$ is the lowest and comparable with $G^{1/2}$ in solution. In PVC the shorter lifetimes of probes are observed. The lifetime of polar *Ie*, which exhibits rather broad band in iPP, lies in the range 1–4 ns. This probe exhibits in PVC longer lifetime about 44 ns. This supports the conclusion that the red-shifted emission originates from an aggregate. This type of emission was not observed in solution in the concentration range 10^{-5} – $10^{-2} \text{ mol dm}^{-3}$.

Emission spectra of probes derived from 1-naphthylacetic acid (type *II*) are the same as the fluorescence spectrum of naphthalene. The vibrational structure

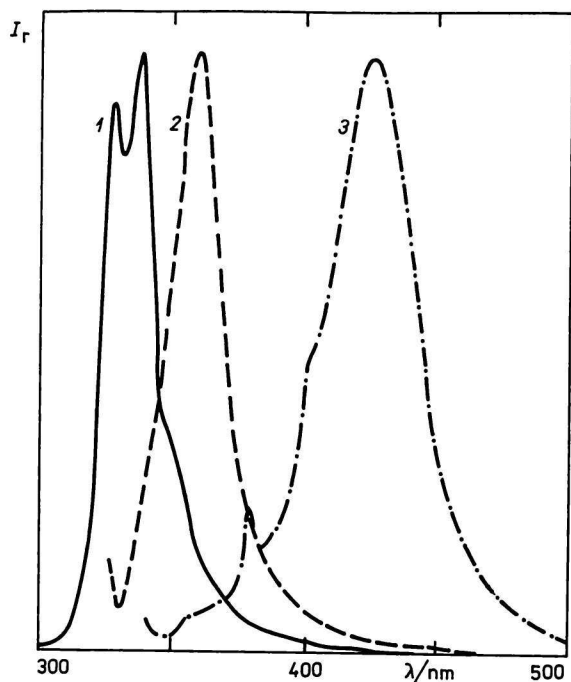


Fig. 3. Emission spectrum of 1. naphthalene, 2. *Ic*, 3. *Ie* in PVC.

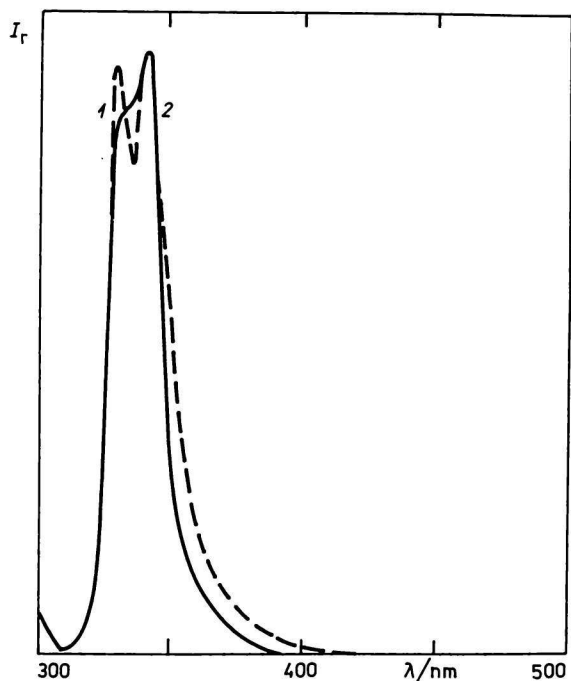


Fig. 4. Emission spectrum of *IIc* in 1. iPP, 2. PMMA.

of the emission is preserved in all derivatives under study even for the polar probe *IIe* in water. However, the ratio of the intensity of the vibrational bands changes depending on the medium. Better resolution of vibrational structure is observed in nonpolar matri-

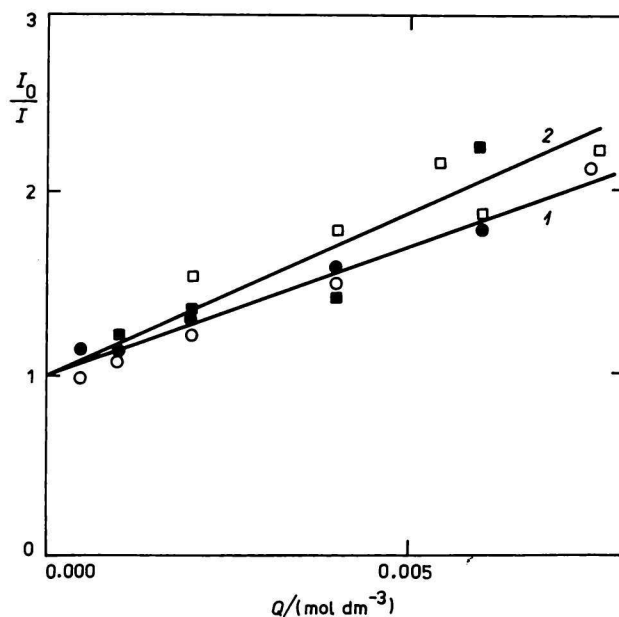


Fig. 5. Stern—Volmer plot of quenching in ethanol of 1. anthracene with 4HOTMPNO (open circles) and 4AcOTMPNO (full circles), 2. *Ic* with 4HOTMPNO (open squares) and 4AcOTMPNO (full squares).

ces (Fig. 4). Relative quantum yields of emission are lower for probes of the type *II* than for the type *I* especially in polar solvents and in polymer matrices. For probes of the type *II*, the more intense fluorescence is observed in polymer matrices than in solution. Probably, some hindrance of the rotation of the side group on naphthalene chromophore in polymer matrix causes the closure of the dissipation channel. Consequently, more intense emission is observed. The lifetime of probes of this type was not determined because it was not possible to obtain measurable emission by 337 nm excitation even at the concentration 0.01 mol dm^{-3} on LIF 200.

The intramolecular quenching of probes of the type *I* with free radicals of the *N*-oxyl type is effective. The Stern—Volmer plot is linear (Fig. 5) with the slope K_{sv} given as product of lifetime and bimolecular quenching rate constant k_q for anthracene and *Ic* and two quenchers of the *N*-oxyl type. The slope is higher for *Ic* than for anthracene. Using K_{sv} from this plot and lifetime of anthracene, the value of $k_q = 4 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was calculated which is higher than the value of rate constant of the diffusion-controlled bimolecular reaction $k_d = 8 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ calculated using the Smoluchowski relationship for ethanol [12]. For the couple anthracene/*N*-oxyl, this calculation might underestimate the diffusion coefficients or the radii of collisions of quenchee and quencher. The values of k_q for probes of the type *I* are in the same range as that for anthracene (Table 3). Higher value

of k_q in some cases might be due to underestimation of the lifetime. Aromatic hydrocarbons were donors in the most studies of quenching by *N*-oxyl radicals [5–12]. However, the involvement of the ester group cannot be completely excluded in quenching of probes of the type *I*.

Suitable parameter for evaluation of intramolecular quenching in probes with the bound *N*-oxyl is the ratio of emission of parent amine to the emission of *N*-oxyl. This ratio is about 3 in nonpolar cyclohexane. In polar ethanol this ratio is about 18. In polymer matrices this ratio is in the range 3–5. The rate of intramolecular quenching was estimated to be 10^8 – 10^{10} s⁻¹ [14], which is comparable to the rate constant of intermolecular quenching. The intramolecular quenching, however, is more effective in the system where chromophore is bound with the quencher than the intermolecular one when the rate constants of both processes are equal. At low concentration of the probe as 10^{-5} mol dm⁻³, the hundred times higher concentration of quencher is needed to achieve the same intermolecular quenching as compared with intramolecular.

Several authors [9, 12] concluded that the mechanism operating at quenching of aromatic singlets is the increase in the rate of the intersystem crossing. At quenching of aromatic triplet it is the increase in the rate of internal conversion to the ground state due to the paramagnetic effect of free radical. This conclusion was extended to the adducts of naphthalene chromophore/*N*-oxyl as well [14]. Observed small effect on intramolecular quenching when going from nonpolar solvent to polymer matrix supports the conclusion that the new channel for dissipation of energy is opened or the existing is more efficient. The higher efficiency in polar solvents indicates, however, that the involvement of some electron transfer cannot be completely excluded.

In conclusion, the probes of the type *I* exhibit more intense emission than the probes of the type *II*. The type *I* probes are more sensitive to the polarity of medium. The intermolecular quenching of the parent probes by *N*-oxyl occurs with equal rate as the intramolecular quenching with bound *N*-oxyls but the efficiency of the latter is higher under equal conditions.

Small medium effect on intramolecular quenching supports the conclusion that the photophysical process is involved more likely than the electron transfer.

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