Radiationless deactivation of excited molecules of 4-aminonaphthalimides

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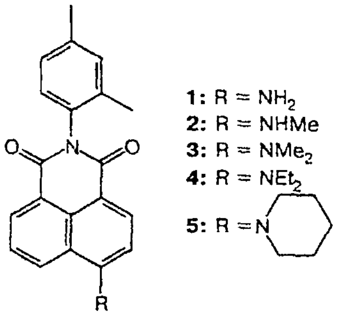
The effects of alkylation of the 4-amino group, polarity and viscosity of a solvent, and temperature on the fluorescence of *N*-(2,4-dimethylphenyl)imides of 4-amino-1,8-naphthalenedicarboxylic acid were studied. A decrease in the temperature and polarity of a solvent and an increase in its viscosity cause the rate of radiationless deactivation of 4-dimethylaminonaphthalimide to decrease and have almost no effect on the rate of emissive deactivation of excited state. The abnormally low efficiency of fluorescence of 4-dimethylaminonaphthalimide in polar low-viscosity media at room temperature is associated with the formation of a nonfluorescent charge-transfer state. The increase in the rate of radiationless deactivation of 4-aminonaphthalimide in the alkylation of its amino group is associated with the increase in its electron-donor ability.

Key words: 4-aminonaphthalimide, fluorescence, radiationless deactivation, donor-acceptor interaction.

Derivatives of 4-aminonaphthalimides are used as active laser media[1] and fluorescent labels.[2] The luminescent properties of these compounds are strongly dependent on the structure of the molecule and solvent. The fluorescence of naphthalimides containing the 4-amino- or 4-monoalkylamino group is characterized by a high quantum yield independent of the solvent, whereas the quantum yield of fluorescence of 4-(*N*,*N*-dialkylamino)naphthalimides is strongly dependent on the nature of the solvent.[2,3] The nineteen-fold decrease in the quantum yield of fluorescence in ethanol on going from 4-amino- to 4-(*N*,*N*-dialkylamino)naphthalimide has been explained by the violation of planarity of the dialkylaminonaphthalimide molecule.[3] The strong effect of substitution in the amino group on luminescent properties of derivatives of 4-aminobenzonitriles, coumarins, and other compounds is associated with a change in the extent of the charge transfer in the excited state[4–6] and in the molecular structure (with a change in hybridization[5] and rotation of the fragments[4,6]). A rearrangement of the closest environment of the molecule or a change in its structure in the excited state results in the dependence of the efficiency of fluorescence of such systems on the viscosity and polarity of the medium.[4,6]

In this work, the effects of the structure of the 4-amino substituent, of the polarity and viscosity of a solvent, as well as the effect of temperature on the fluorescent properties of *N*-(2,4-dimethylphenyl)imides of 4-amino-1,8-naphthalenedicarboxylic acid were studied to elucidate the reasons for the different fluorescent abilities of 4-amino- and 4-(*N*,*N*-dialkylamino)naphthalimides.[1–5]



Experimental

Absorption and fluorescence spectra were recorded on a Shimadzu UV-3100 spectrophotometer and an Elyumin 2M spectrofluorimeter, respectively. The kinetics of fluorescence was studied on a nanosecond ORTEC spectrometer by photon counting. The quantum yield of fluorescence (φ) was determined by comparing the areas under the curves of corrected fluorescence spectra of the compound under study with those of a solution of quinine bisulfate in 1 N H_2SO_4 (φ = 0.546).[7] Polymeric films were prepared by slow evaporation of solutions of 4-aminonaphthalimides and poly(methyl methacrylate) (PMMA) in purified acetone and those of polyvinyl alcohol (PVA) in water on a glass surface. The procedure for preparation of 4-aminonaphthalimides has been described previously.[8]

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Table 1. The wavelengths of maxima of the absorption spectra (λ_a/nm), those of the fluorescence spectra (λ_f/nm), and the quantum yields of fluorescence (φ) of compounds **1**, **3**, and **4** in various solvents and polymeric films

Solvent	**1**			**3**			**4**		
	λ_a	λ_f	φ	λ_a	λ_f	φ	λ_a	λ_f	φ
Octane	—	—	—	390	460	0.70	—	—	—
Benzene	—	—	—	393	495	0.81	—	—	—
Toluene	402	481	0.91	404	492	0.79	410	502	0.74
Dioxane	412	510	0.92	404	512	0.61	—	—	—
Chloroform	406	492	0.96	415	503	0.96	—	—	—
Diisopropyl ether	—	—	—	397	484	0.68	—	—	—
Diethyl ether	415	501	0.80	399	506	0.50	403	511	0.53
Ethyl acetate	415	513	0.78	404	515	0.35	411	527	0.10
Ethyl benzoate	416	504	0.79	413	514	0.65	—	—	—
Tetrahydrofuran	418	507	0.79	409	513	0.37	414	527	0.13
Methylethylketone	420	515	0.90	411	524	0.08	419	536	0.02
Acetone	420	519	—	413	531	—	—	—	—
Butyronitrile	417	518	0.76	417	530	0.10	—	—	—
Benzonitrile	414	506	0.86	411	515	0.65	420	543	0.31
Acetonitrile	416	520	0.76	424	545	0.01	—	—	—
DMF	431	527	0.75	421	530	0.01	—	—	—
Methanol	—	—	—	427	545	0.01	—	—	—
Ethanol	437	536	0.57	426	537	0.02	421	553	0.01
n-Propanol	—	—	—	423	535	0.03	—	—	—
n-Butanol	—	—	—	421	532	0.04	—	—	—
n-Hexanol	—	—	—	419	530	0.08	—	—	—
n-Nonanol	—	—	—	415	524	0.17	—	—	—
Glycerol	—	—	—	446	550	0.11	—	—	—
Ethylene glycol	—	—	—	438	545	0.02	—	—	—
PMMA	414	495	—	407	504	—	—	—	—

The solvents and acids were purified and dehydrated following the known procedure.[9]

Results and Discussion

The substitution of the hydrogen atoms of the amino group in the 4-aminonaphthalimide molecule by alkyl substituents results in the hypsochromic shift of the absorption spectra (except for those obtained in toluene, chloroform, and acetonitrile) and in the bathochromic shift of the fluorescence spectra (Table 1, Fig. 1). An increase in the polarity of the solvent causes a bathochromic shift of both the absorption and fluorescence spectra of compounds **1**, **3**, and **4** (see Table 1).

The noticeable solvatochromism and solvatofluorochromism of 4-aminonaphthalimides makes it possible to estimate the dipole moments of these molecules in the excited state (μ^*) using the method of spectral shifts.[10] The values of half-sums of the frequencies of maxima in the absorption and fluorescence spectra of compounds **1**, **3**, and **4** satisfactorily correlate with the values of the functions of the universal interaction

$$F(\varepsilon,n) = \frac{2n^2+1}{n^2+2}\cdot\frac{\varepsilon-1}{\varepsilon+2}+\frac{n^2-1}{n^2+2}$$

and $$U(\varepsilon,n) = \frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right),$$

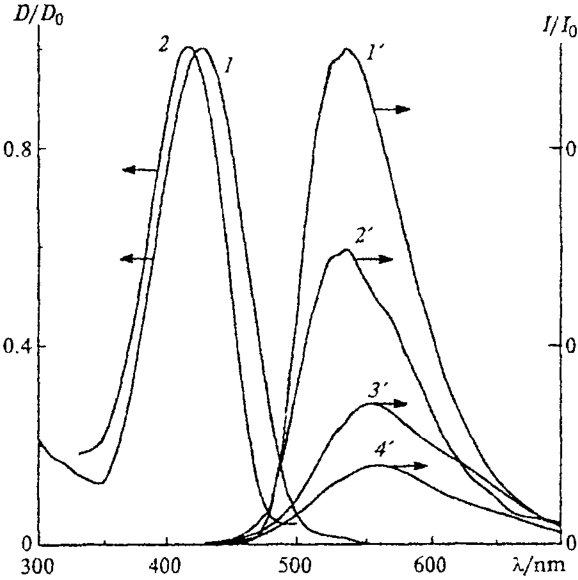

Fig. 1. Absorption spectra (*1*, *2*) and fluorescence spectra (*1′—4′*) of compounds **1** (*1*, *1′*) and **3** (*2*, *2′*), **4** (*3′*) and **5** (*4′*) in ethanol. The intensity of fluorescence of **3**, **4**, and **5** is multiplied by a factor of 4, 4, and 2, respectively.

where ε and n are the dielectric constant and the refractive index of the solvent, respectively (Fig. 2). Assuming that the dipole moments of the compounds studied are

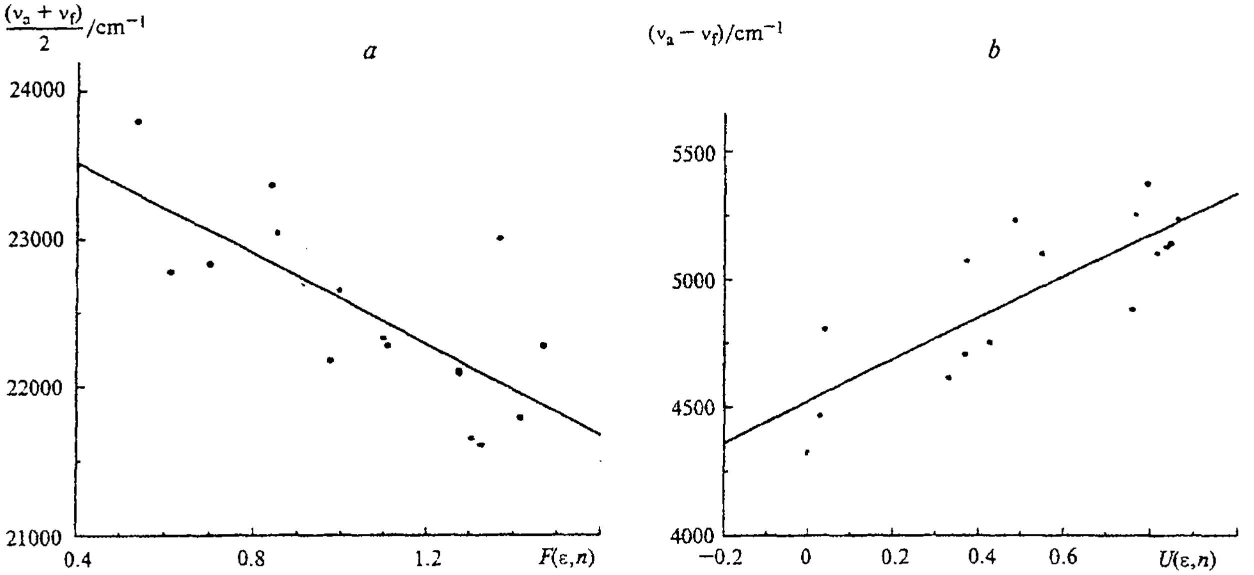

Fig. 2. The dependence of the values of the half-sum of frequencies of the maxima in the absorption and fluorescence spectra $(\nu_a + \nu_f)/2$ (*a*) and that of the Stokes shift of fluorescence $(\nu_a - \nu_f)$ (*b*) of compound **3** on the values of the functions of universal interaction.[10]

mainly due to the donor-acceptor interaction in the 4-aminonaphthalimide fragment and that the dipole moments of the studied 4-aminonaphthalimides and 4-dimethylamino-*N*-(*n*-butyl)naphthalimide (μ = 4.29 D)[2] in the ground state are equal, we get μ^* = 9.5±2.1, 8.1±1.6, and 6.4±2.0 D for compounds **1**, **3**, and **4**, respectively, and the change in the direction of the dipole moment upon excitation will be equal to 3±2°, 12±5°, and 11±5°, respectively. The Onsager radii of the molecules were estimated using the formula $r = (3V/4\pi)^{1/3}$, where V is the molecular volume (V = 0.39, 0.42, and 0.46 nm^3 for **1**, **3**, and **4** respectively). It follows from the aforesaid that the absolute values of the dipole moments of 4-aminonaphthalimides increase while their directions remain nearly unchanged at excitation. This might be associated with partial transfer of the electron from the donor amino group to the acceptor fragment of the molecule. The dipole moments of molecules **1**, **3**, and **4** in the excited states do not differ within the limits of experimental error. This indicates that for these compounds the transition to the excited state is most likely of the same nature and is accompanied by partial transfer of an electron from the amino group to the naphthalimide fragment.

Unlike aminonaphthalimides **1** and **2**, the quantum yield of fluorescence of *N*,*N*-dialkylsubstituted 4-aminonaphthalimides **3**—**5** strongly depends on the nature of the solvent (see Table 1) and temperature. The decay of fluorescence of **3** obeys a one-exponential law. The lifetime of fluorescence of **3** (τ) is changed in parallel with the change in the quantum yield of fluorescence. The rate constant of the fluorescence emission $k_f = \varphi/\tau$ decreases by a factor of 1.3 on going from benzene to tetrahydrofuran, while the rate constant of radiationless deactivation $k_d = (1 - \varphi)/\tau$ increases by a factor of 3 (Table 2). This points to the fact that the dependence of the quantum yield of fluorescence of **3** on the nature of the solvent is mainly dictated by changes in the rate of radiationless deactivation.

To elucidate the regularities of the solvent effect on the rate of radiationless deactivation of *N*,*N*-dialkylaminonaphthalimides, we studied the dependences of the quantum yield of fluorescence of **3** and **4** on the polarity and viscosity of the solvent and on temperature. In low-polarity solvents, compounds **3** and **4** effectively fluoresce at room temperature (see Table 1). The quantum yield of fluorescence of these aminonaphthalimides substantially decreases on going to the more polar solvents. A parallel change in the φ values for **3** and **4** and in the empirical parameter of polarity of the solvent $E_t(30)$[11] for low-viscosity solvents (Fig. 3) shows that the rate of radiationless deactivation of *N*,*N*-dialkylaminonaphthalimides increases as the polarity of the solvent increases.

The quantum yield of fluorescence of **3** in viscous media (glycerol) is appreciably higher than that expected from the dependence of the φ value on the

Table 2. The quantum yields of fluorescence (φ), lifetimes of excited state (τ), and the rate constants of fluorescence emission ($k_f = \varphi/\tau$) and radiationless deactivation ($k_d = (1 - \varphi)/\tau$) for compound **3**

Solvent	φ	τ/ns	$k_f \cdot 10^8$/s^{-1}	$k_d \cdot 10^8$/s^{-1}
Benzene	0.71	5.64±0.06	1.26±0.02	0.52±0.01
Diethyl ether	0.50	5.00±0.04	1.00±0.01	1.00±0.01
Tetrahydrofuran	0.40	4.01±0.02	1.00±0.01	1.50±0.02

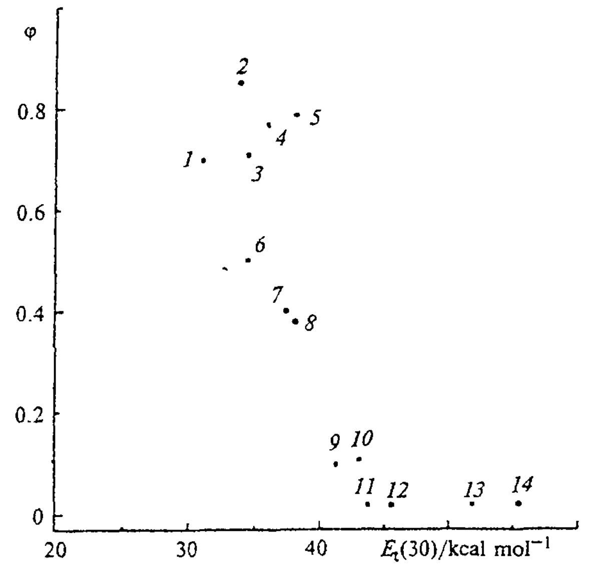

Fig. 3. The dependence of the φ values for compounds **3** and **4** on the empirical parameter of polarity of the solvent $E_T(30)$: *1* — octane, *2* — toluene, *3* — benzene, *4* — dioxane, *5* — ethyl benzoate, *6* — diethyl ether, *7* — tetrahydrofuran, *8* — ethyl acetate, *9* — methylethylketone, *10* — butyronitrile, *11* — DMF, *12* — acetonitrile, *13* — ethanol, and *14* — methanol.

polarity of the medium for low-viscosity solvents (see Fig. 3). The fluorescence of **3** and **4** in PMMA and PVA films is close in intensity to that of **1**. A substantial increase in the intensity of fluorescence of **3** and **4** in the series of alcohols (MeOH, ethylene glycol, glycerol, and PVA) makes it possible to conclude that the increase in the viscosity of the solvent results in a decrease in the rate of radiationless deactivation of 4-(*N*,*N*-dialkylamino)naphthalimides.

The quantum yield of fluorescence of compounds **3** and **4** in polar solvents increases appreciably as temperature decreases (by a factor of 35 for **3** in ethanol as the temperature decreases from 298 to 77 K). This can be associated with a decrease in the rates of both the temperature-activated and viscosity-dependent radiationless deactivation of the solvent. In the general case, the apparent activation energy of the temperature quenching of fluorescence of **3** is defined by the expression

$$\frac{d\ln(1/\varphi - 1/\varphi_0)}{d(1/T)} = -\frac{E_a}{R} + \frac{d\ln A}{d(1/T)} - \frac{d\ln k_f}{d(1/T)},$$

where φ_0 is the quantum yield of fluorescence in the absence of temperature-activated deactivation processes, E_a is the activation energy of radiationless deactivation, and A is the pre-exponential factor. The quantum yield of fluorescence in ethanol at 77 K (φ_0 = 0.92, 0.89, and 0.90 for **3**, **4**, and **5**, respectively) was used as the φ_0 value.

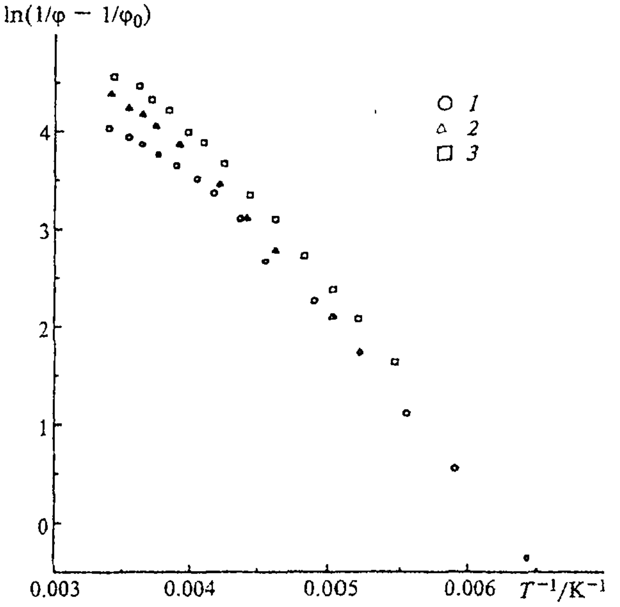

Fig. 4. The dependence of the quantum yield of fluorescence of compounds **3** (*1*), **4** (*2*), and **5** (*3*) in ethanol on temperature.

The dependence of ln(1/φ − 1/φ_0) on 1/T for dialkylaminonaphthalimides in ethanol is nonlinear (Fig. 4), which can be associated with the fact that the viscosity and polarity of the solvent increase as the temperature decreases. Since the temperature dependence of viscosity in the temperature interval under study is satisfactorily described by an exponential function, the nonlinear character of the dependence of ln(1/φ − 1/φ_0) on 1/*T* is most likely due to the fact that the polarity of the medium changes as temperature decreases. The activation energy E_a = 2.5±0.1 kcal mol^{-1} determined on the linear portion of this dependence in the 150—250 K interval is close to the energy of activation of the viscous flow of ethanol (E_η = 3.14 kcal mol^{-1}).[12]

Thus, unlike 4-aminonaphthalimides containing an unsubstituted or monoalkylated amino group, 4-(*N*,*N*-dialkylamino)naphthalimides have an effective channel of radiationless deactivation of the singlet excited state. The rate of radiationless deactivation increases as the solvent polarity increases, the viscosity of the solvent decreases, and the temperature increases.

The fact that the rates of radiationless deactivation of excited 4-(*N*,*N*-dialkylamino)naphthalimides increase as the polarity of the medium increases suggests that the radiationless process in this system is connected with a transition from a state of local excitation to a nonfluorescent state of higher polarity (a charge-transfer state). The fact that the rates of formation of this state decrease as the viscosity of the solvent increases can be associated with retardation of orientational relaxation of the solvent and/or with that of the process of structural relaxation in the fluorophore molecule.

The substantial increase in the efficiency of radiationless deactivation (the rate of transition to the charge-transfer state) in the alkylation of the amino group of aminonaphthalimide can be associated with the increased electron-donor ability of the amino group. This ability can be characterized by the ionization potential and proton affinity.[13] Since the ionization potentials of amines decrease in the sequence NH_3, NH_2Me, $NHMe_2$, and $NHEt_2$ (234.3, 205, 188, and 181 kcal mol^{-1}, respectively),[13] it should be expected that the energy of the charge-transfer state decreases in the sequence **1**, **2**, **3**, and **4**. A comparison of the proton affinities of amines NH_3, NH_2Me, NH_2Et, morpholine, $NHMe_2$, and $NHEt_2$ (204.0, 214.1, 217.0, 219.4, 220.6, and 225.9 kcal mol^{-1}, respectively)[14] results in an analogous sequence (**1**, **2**, **5**, **3**, and **4**).

Thus, the decrease in the temperature and polarity of the solvent and the increase in the viscosity of the medium lead to the decreased rate of radiationless deactivation of **3** and have almost no effect on the rate of emissive deactivation of the excited state. The abnormally low efficiency of fluorescence of **3** in polar low-viscosity media at room temperature is associated with the formation of a nonfluorescent charge-transfer state. The increase in the rate of radiationless deactivation in the alkylation of the amino group of aminonaphthalimide is due to the increase in the electron-donor ability of the amino group.

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