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Fluorescence Study of Excited-State Relaxation Processes of 2-Pyridyl-5-Aryloxazoles

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Anomalously high fluorescence spectrum Stokes' shifts of 2(4-pyridyl)-5-(4-methylphenyl)oxazole, 2(4-pyridyl)-5-(4-methoxyphenyl)oxazole, 2(4-pyridyl)-5-(4-*N,N*-dimethylaminophenyl)oxazole have been found. The fluorescence spectra of the compounds studied are shifted to longer wavelengths as the solvent dielectric constant increases. The dipole moments of these compounds increase by 3–4 times upon excitation. The fluorescence spectra of the compounds investigated are shifted to shorter wavelengths, and the fluorescence quantum yields increase as the temperature decreases. The fluorescence rate constant of 2(4-pyridyl)-5-(4-*N,N*-dimethylaminophenyl)oxazole changes slightly as the temperature decreases from 293 K (relaxed state) to 114 K (mainly nonrelaxed state). It was concluded that the anomalously high fluorescence Stokes' shift of 2-pyridyl-5-aryloxazole derivatives is caused by solvent orientation relaxation.

KEY WORDS: Pyridyloxazoles; fluorescence; relaxation; excited state.

INTRODUCTION

Earlier the processes in excited cations of pyridyloxazole [1], quinolylthiazole [2] derivatives, arylsubstituted pyridine cations [3–4], triphenylmethane dyes [5–7] were investigated. Barrierless structural relaxation (intramolecular rotation) takes place in these compounds. High fluorescence Stokes' shifts of phthalimide, naphthalene, and anthracene derivatives were explained by solvent orientation relaxation [8]. We have found anomalously high fluorescence Stokes' shifts for 2-pyridyl-5-aryloxazole derivatives in ethanol that drop to normal values as the temperature decreases. This fact indicates the existence of relaxation processes in the excited state. The object of the present work is the determination of this process mechanism. The relaxation process can be either solvent orientation or structural relaxation of the excited molecule.

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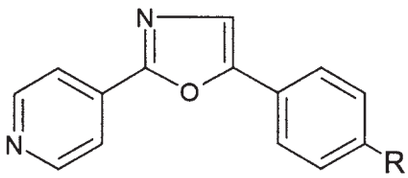
EXPERIMENTAL

We have investigated pyridylaryloxazole derivatives: 2(4-pyridyl)-5-(4-methylphenyl)oxazole **1**, 2(4-pyridyl)-5-(4-methoxyphenyl)oxazole **2**, 2(4-pyridyl)-5-(4-*N,N*-dimethylaminophenyl)oxazole **3**.



R = CH_3 (**1**), OCH_3 (**2**), $N(CH_3)_2$ (**3**)

The method of preparation of **1–3** was described earlier [9]. Solvents—heptane, dioxane, toluene, tetrahydrofuran, ethylacetate, acetone, ethanol, acetonitrile, butyronitrile, dimethylformamide, glycerol, and dimethylsulfoxide—were purified according to known methods [10]. The absorption spectra were registered by a Shimadzu UV-3100

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spectrophotometer, and the fluorescence spectra by an Elyumin 2M spectrofluorimeter. The fluorescence quantum yields were measured by comparison of the corrected fluorescence spectra areas of the compound investigated and quinine bisulphate in 1 N sulphuric acid (φ_f = 0.546) [11]. The optical densities of the solutions investigated were in the range 0.2–0.4 at the excitation wavelength. Dipole moments in the ground state were calculated by ab initio (3–21 G) geometry optimization by AM1 (HyperChem, Release 5.02 for Windows, Hypercube, Inc.). The cryostat with liquid nitrogen vapor cooling was used for absorption and fluorescence spectral measurement in the range 77–273 K. The fluorescence kinetics were registered by a SP-70 nanosecond spectrometer by the time-correlated counting of single photons with excitation by air-filled flash lamp radiation (excitation pulse duration 0.8 ns, registration channel width 0.054 ns).

RESULTS AND DISCUSSION

The absorption spectra of 2-pyridyl-5-aryloxazoles depend weakly on solvent polarity, and the fluorescence spectra are shifted considerably to lower frequencies as solvent dielectric constant increases (Table I). This indicates a considerable change of dipole moment upon excitation. The Lippert equation [12] was used for determination of the difference of molecule dipole moments in the ground and excited states (Table II):

$$hc\Delta\tilde{\nu} = \frac{2\Delta f}{a^3}(\mu^* - \mu)^2 + const$$

here $\Delta\tilde{\nu}$ is fluorescence Stokes' shift, $\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$, a is the radius of the cavity where the fluorophor molecule is located (equal to 0.8ρ, where ρ is the radius of the minimum sphere of the molecule), and c is light velocity. The increase of dipole moment upon excitation, and therefore the increase of the extent of charge transfer in the series **1–3**, is associated with increase of electron-donor ability of substituent in this series.

The fluorescence spectra of **3** at different temperatures in ethanol are shown in Fig. 1. They are shifted to shorter wavelengths by 95 nm as the temperature decreases from 290 to 77 K, and the fluorescence quantum yield (φ_f) increases from 0.36 to 1 (Fig. 2). Similar results were obtained for **1** and **2** (fluorescence spectra are shifted by 14 and 29 nm, and φ_f increase from 0.81 and 0.87 to 1, respectively). The values of fluorescence spectra shifts of **1–3** correlate with electrondonor ability of the substituents: the less the donor ability of the substituent the less the spectral shift. Electrondonor ability of substituents increases in the series $CH_3 < CH_3O < N(CH_3)_2$; therefore the fluorescence spectral shifts and the changes of the fluorescence quantum yields upon temperature decreasing from 290 to 77 K for **1** and **2** are considerably less than those for **3**. A similar temperature dependence of the fluorescence spectra is observed for the glycerol solution of **3**, and a short-wavelength shift of the fluorescence spectrum is observed in butyronitrile in a narrow temperature range, at vitrifying. These data indicate the existence of a relaxation process in the excited state. The rate of this process is determined by the temperature-dependent properties of the medium. Ethanol viscosity [13] and polarity [14] increase as the temperature decreases. If the fluorescence spectrum of **3** depends only on the solvent polarity, the fluorescence spectrum should be shifted to longer wavelengths. Therefore the short-wavelength shift of the fluorescence spectrum observed at decreasing temperature results from the ethanol viscosity increase, but not its polarity.

Because the dipole moments of **1–3** increase considerably upon excitation, the excited-state molecules become more polar than the ground-state ones. Therefore the anomalously high fluorescence Stokes' shift of 2-pyridyl-5-aryloxazole derivatives is typical for polar

Table I. Maxima of Absorption ($\tilde{\nu}_a$) and Fluorescence spectra ($\tilde{\nu}_f$) of 2-Pyridyl-5-Aryloxazoles in Various Solvents at 293 K.

Solvent	$\tilde{\nu}_a \cdot 10^{-3}$ (cm^{-1})			$\tilde{\nu}_f \cdot 10^{-3}$ (cm^{-1})		
	1	**2**	**3**	**1**	**2**	**3**
Heptane	30.9	30	27.6	27.3	25.5	22.6
Toluene	30.6	29.9	27.1	26.1	24.8	21.8
Tetrahydrofurane	30.9	29.9	27.1	25.6	24	19.6
Ethylacetate	31	30.3	27.3	25.9	23.9	19.2
Dimethylsulfoxide	30.5	29.7	26.3	24.5	22.6	17.5
Dimethylformamide	30.6	29.9	26.8	24.6	23	18
Ethanol	30.6	29.8	26.5	24.4	22.5	17.1
Acetonitrile	31	30.3	27.1	24.9	23	17.8

Table II. Dipole Moments of 2-Pyridyl-5-Aryloxazoles in the Ground (μ) and Excited (μ*) States.

Compound	μ (D)	μ* (D)	$\Delta\mu$ (D)
1	4.4	14.4	10
2	5.1	17.3	12.2
3	6.2	22.4	16.2

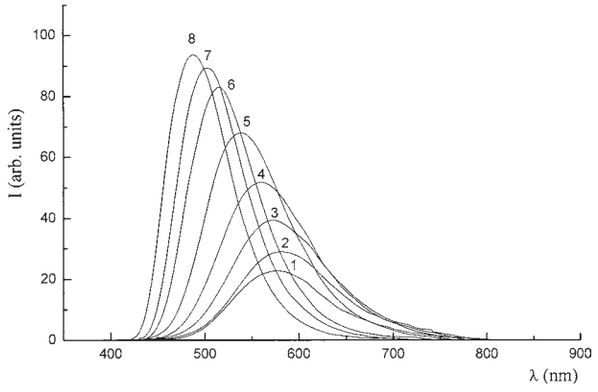

Fig. 1. Fluorescence spectra of **3** in ethanol at various temperatures (1, 290; 2, 212; 3, 191; 4, 171; 5, 151; 6, 130; 7, 114; 8, 77 K).

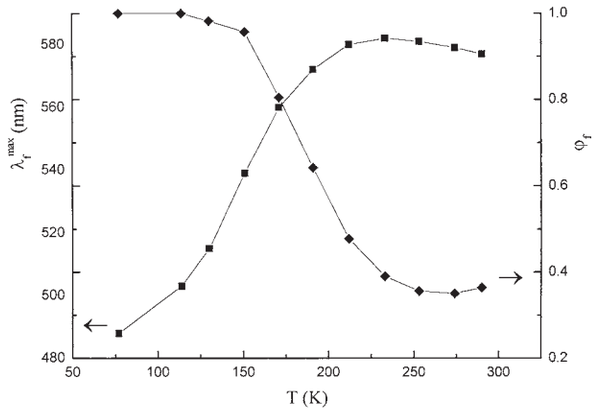

Fig. 2. The dependence of fluorescence spectral maximum and fluorescence quantum yield of **3** in ethanol on the temperature.

solvents, but in nonpolar solvents the Stokes' shift has a normal value (Table I). Thus the relaxation process mentioned above is more effective in polar solvents. The short-wavelength shift of 2-pyridyl-5-aryloxazoles fluorescence spectra with decreasing temperature (at increasing solvent viscosity) indicates that the relaxation process rate depends considerably on the solvent viscosity. This process is caused either by intramolecular rotation of fluorophor molecular fragments or by solvent orientation relaxation. In both cases the solvent orientation relaxation is inhibited upon solvent viscosity increasing; the fluorescence takes place from the state with less extent of relaxation, and fluorescence spectra should be shifted to shorter wavelengths. The considerable (123 nm) fluorescence spectrum short-wavelength shift of **3** in polymethylmethacrylate in comparison with ethanol comes from both the high viscosity and the low dielectric constant ($\varepsilon = 2.3$) of polymethylmethacrylate.

The dependence of the fluorescence rate constant (k_f) on the temperature can give important information about the relaxation process mechanism. If the relaxation process is associated with rotation of fluorophor molecular fragments, resulting in an other molecular structure, then k_f of relaxed and nonrelaxed states should differ significantly. With solvent relaxation the molecular structure is changed insignificantly; therefore in this case k_f of relaxed and nonrelaxed states should not differ considerably. We have determined the excited-state lifetimes and fluorescence quantum yields at corresponding temperatures for k_f calculation. The fluorescence kinetics was registered at the wavelength that corresponds to the fluorescence spectral maximum at a given temperature. Figure 3 shows the dependence of k_f of **3** on the temperature in ethanol. The values of k_f for relaxed ($\lambda_{reg.} = 610$ nm) and nonrelaxed ($\lambda_{reg.} = 510$ nm) states differ insignificantly ($1.8 \cdot 10^8$ and $2.7 \cdot 10^8$ c^{-1}, respectively). This shows that the excited-state relaxation process resulting in anomalously high fluorescence Stokes' shift of 2-pyridyl-5-aryloxazoles in polar solvents is caused by dipole relaxation of solvent molecules. The values of k_f in the 135–230 K temperature region are effective. They characterize the averaged emission rate from relaxed (with different relaxation extent) and nonrelaxed states.

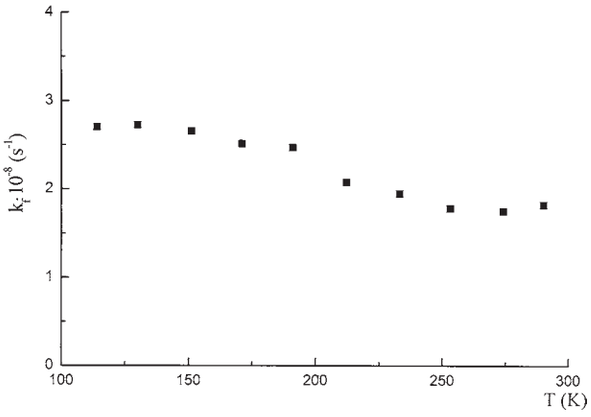

Fig. 3. The dependence of effective rate constant of radiative deactivation of excited **3** in ethanol on the temperature.

The existence of solvent orientation relaxation is confirmed by the difference of fluorescence kinetics in short- and long-wavelength regions of the fluorescence spectrum of **3** at 100–200 K in ethanol. Figure 4 shows the kinetic curves of fluorescence decay of mainly relaxed (1) and nonrelaxed (2) states. The shift of kinetic curves, one relative to other, confirms the solvent relaxation. This shift is characterized by the ratio of solvent relaxation and radiative deactivation rates. At room temperature the fluorescence observed takes place from the completely relaxed state because the relaxation rate exceeds the fluorescence rate of **3**. The fluorescence lifetimes of relaxed (2) and nonrelaxed (3) states increase as the temperature decreases, at the same time the part of the emission from the nonrelaxed state increases (Fig. 5). At 120 K and below the fluorescence takes place from the nonrelaxed state.

The relaxation times of ethanol (τ_s) at different temperatures were calculated from fluorescence lifetimes and the maxima of fluorescence spectra (Fig. 6) [15]

$$\tau_s = \frac{(\tilde{\nu}_\infty - \tilde{\nu}_m)}{(\tilde{\nu}_m - \tilde{\nu}_0)}\tau$$

where $\tilde{\nu}_m$ is the maximum of fluorescence spectrum at given temperature, $\tilde{\nu}_0$ is the maximum of fluorescence spectrum at T = 77 K (nonrelaxed state), and $\tilde{\nu}_\infty$ = the maximum of fluorescence spectrum at T = 290 K (relaxed state).

The considerable increase of the fluorescence quantum yield of the relaxed state of **3** in ethanol as the temperature decreases (Fig. 2) indicates that the efficiency of the radiationless deactivation processes decreases. The decrease of radiationless deactivation efficiency with the decrease of the temperature takes place parallel to the increase of ethanol viscosity. This makes it possible to conclude that radiationless deactivation is connected with dynamic interaction of fluorophor excited molecules with ethanol molecules by a hydrogen bond mechanism. This suggestion is confirmed by the absence of such deactivation in aprotic solvents (acetonitrile $\varphi_t = 0.86$, ethylacetate $\varphi_f = 0.8$).

Thus the anomalously high fluorescence Stokes' shift of 2-pyridyl-5-aryloxazoles is caused by solvent orientational relaxation, induced by intramolecular charge transfer, taking place upon the excitation of fluorophor molecule.

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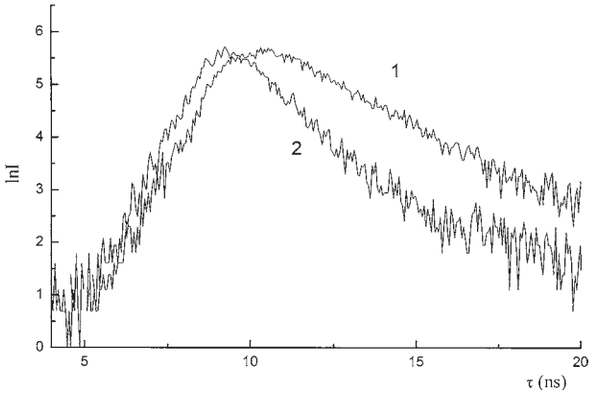

Fig. 4. The kinetic curves of fluorescence decay of relaxed (λ_{reg} = 620 nm) (1) and nonrelaxed (λ_{reg} = 510 nm) (2) states of **3** in ethanol at 191 K.

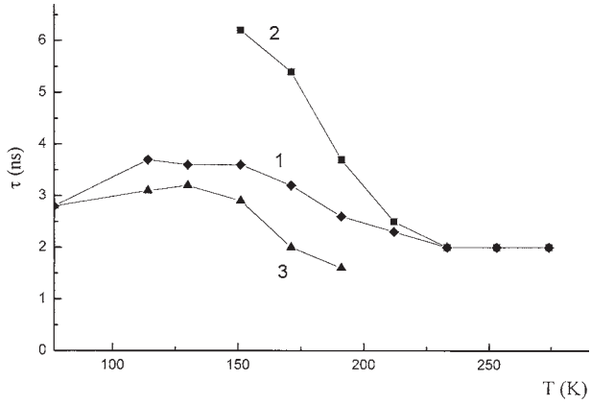

Fig. 5. The dependence of fluorescence lifetime of **3** in ethanol on the temperature: 1, λ_{reg} corresponds to the maximum of the fluorescence spectrum at given temperature; 2, λ_{reg} = 620 nm (relaxed state); 3, λ_{reg} = 510 nm (nonrelaxed state).

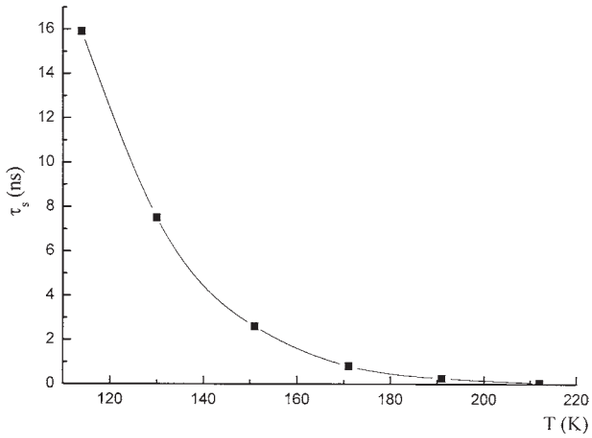

Fig. 6. The dependence of ethanol relaxation time on the temperature.

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