

The Dynamics of Intramolecular Excited State Relaxation of *N*-Anthryl Substituted Pyridinium Cations

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N-(1-Anthryl)-2,4,6-trimethyl-pyridinium (**I**), *N*-(2-anthryl)-2,4,6-trimethyl-pyridinium (**II**) and 10-(1-anthryl)-1,2,3,4,5,6,7,8-octahydro-acridinium cations (**III**) with anomalously high fluorescence Stokes' shift have been investigated. Fluorescence kinetics analysis at various temperatures showed that in the range 293–77 K, the radiative deactivation rate constants (k_f) increase by 5.5 to 30 times. The low-temperature time-resolved emission spectra of **I–III** were found to be consistent with the model: $A \rightarrow A^* \leftrightarrow B^*$ where A^* is the local excited twisted form and B^* is the relaxed more planar, bent conformer of the molecule. The rate constants of the excited relaxed state formation (k_1) and back reaction (k_{-1}) of compounds studied were estimated.

KEY WORDS: Intramolecular structural relaxation; time-resolved emission spectra; *N*-anthryl substituted pyridinium cations.

INTRODUCTION

The investigation of spectral-luminescent behavior of *N*-(1-anthryl)-2,4,6-trimethyl-pyridinium (**I**) and *N*-(2-anthryl)-2,4,6-trimethyl-pyridinium (**II**) cations showed, that in the ground state these molecules are mainly acoplanar with a very small admixture of biradical conformers, which are weakly allowed by the torsional vibrations [1]. At the excitation, the π -systems of two parts of these cations overlap stronger, favoring the charge transfer from anthryl fragment to pyridinium ring. It results in an anomalously high fluorescence Stokes' shift. The charge transfer increases the electronic density at pyridinium nitrogen atom and its sp^3 hybridization produces, supposedly, bent molecular structure. The recent study of the excited cation **I** has revealed the large increase of the radiative deactivation rate constant k_f as

the temperature decreases from 293 to 77 K (6 times for ethanol and 15 times for butyronitrile) [2]. The crucial effect of the medium viscosity on the relaxation degree was shown. The purpose of the present work is to trace the excited state relaxation dynamics of relative cations **I–III** by means of time-resolved fluorescence measurements in a nanosecond range at different temperatures and to give a quantitative description of this dynamics.

EXPERIMENTAL

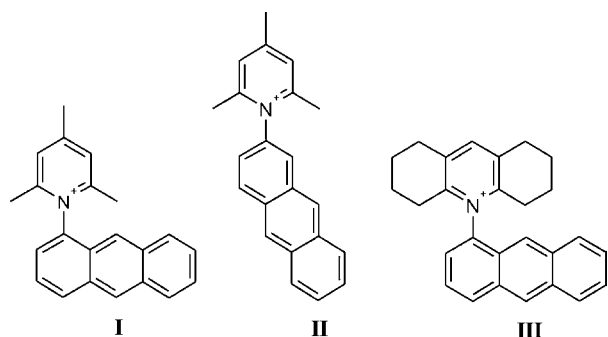
Compounds

N-(1-Anthryl)-2,4,6-trimethyl-pyridinium (**I**) and *N*-(2-anthryl)-2,4,6-trimethyl-pyridinium (**II**) were synthesized in the form of perchlorates (anion ClO_4^-) by known methods [3,4] and used as received. Ethyl acetate, dichloromethane, 1,2-dichloroethane, chloroform, isopropanol, *n*-butanol, acetone, butyronitrile, ethanol, acetonitrile, water and PMMA were of spectroscopic grade quality. Ethanol was dehydrated by the distillation with CaH_2 prior use. Ethyl acetate was purified by the distillation with K_2CO_3 prior use.

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Scheme 1.

^1H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) using CDCl_3 as solvent. The absorption and fluorescence spectra were recorded on an UV-3100 spectrophotometer and an Elyumin-2M spectrofluorimeter. The absorption and fluorescence measurements at low temperatures were carried out by a homemade cryostat with an adjustable flow of cooled nitrogen vapors through spectroscopic Dewar vessel. The standard quinine bisulfate solution in 1 *N* sulfuric acid ($\varphi_f = 0.546$) [5] was used for fluorescence quantum yield measurements. The fluorescence quantum yields at low temperatures were calculated considering the absorption spectra recorded at the same temperatures as the corresponding fluorescence spectra by Eq. (1):

$$\varphi_i = \varphi_0 \frac{S_i(1 - 10^{-D_0})}{S_0(1 - 10^{-D_i})} \quad (1)$$

where φ_i and φ_0 are the fluorescence quantum yields of the sample at T_i and 293 K; S_i and S_0 the area under quantum-corrected fluorescence spectra, D_i and D_0 the optical densities at the excitation wavelength at T_i and 293 K. The dipole moment changes at the excitation were calculated using the Lippert function [6].

The fluorescence kinetics was recorded by a nanosecond SP-70 spectrometer by the method of 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). The accumulation of the signal for the determination of $k_f(T)$ function was carried out at the wavelengths corresponding to the steady-state emission spectra maxima, recorded at the same temperatures. The decay times were fitted using the iterative deconvolution procedure, which allowed a time resolution down to 0.1 ns and a precision of better than 0.1 ns. The measurements of fluorescence kinetics at low temperatures were carried out using the same spectroscopic Dewar vessel. The time-resolved emission spectra (TRES)

were calculated from the set of kinetic curves obtained at different wavelengths at equal accumulation times and constant temperature.

Synthesis of 10-(1-Anthryl)-1,2,3,4,5,6,7,8-Octahydro-Acridinium Perchlorate (III)

1,2,3,4,5,6,7,8-Octahydroanthrylium perchlorate [4] (0.289 g, 1 mmol) and 1-aminoanthracene (0.193 g, 1 mmol) were boiled in 50 mL of acetic acid for 1 hr. The mixture was cooled, diluted by 200 mL of ethyl ether. The residue was filtered off, washed with a small portion of ethyl ether (yield 92%). The product was purified by a double recrystallization from a mixture of 83% (v/v) ethyl ether and acetonitrile to give the brown brilliant crystals of 10-(1-anthryl)-1,2,3,4,5,6,7,8-octahydroacridinium perchlorate. M.p. 312–313°C (decomp.)

^1H NMR (δ , ppm, *J*/Hz); 1.74–1.95 (m, 8H, 4CH₂); 2.11–2.85 (m, 4H, 2CH₂); 3.00–3.20 (m, 4H, 2CH₂), 7.51–8.15 (m, 8H, H of anthracene); 8.28 (d, 6.7 Hz, 1H, H(2) of anthracene); 8.65 (c, 1H, H(9) of octahydroacridinium). IR (vaseline oil) ν (cm⁻¹) 1620, 1595 (C=N, C=C); 1090 (ClO₄⁻). Anal. Calc. For C₂₇H₂₆ClNO₄ (%): C, 69.98; H, 5.66; Cl, 7.64, N, 3.02. Found: C, 69.98; H, 5.77; Cl, 7.80; N, 3.11.

RESULTS AND DISCUSSION

The fluorescence spectra of **I–III** have an anomalously high Stokes' shift due to excited state intramolecular charge transfer between electron donor (anthryl fragment) and electron acceptor (pyridinium ring) in the molecules (Fig. 1, Table I). To estimate the charge transfer degree in the excited cations the absorption and fluorescence spectra of **I–III** in various solvents at 293 K were measured. The corresponding dependence of fluorescence Stokes' shift $\tilde{\nu}_{a-f}$ versus solvent polarity parameter Δf is shown in Fig. 2. The calculated dipole moment changes are indicated in Table I. It is evident, that the excited states of **I–III** have the pronounced charge transfer from anthryl to pyridinium fragments. $\Delta\mu$ is also dependent on the substituent position. The large difference between $\Delta\mu$ values in the isomeric **I** and **II** can be explained by the longer charge transfer distance for the latter. It is worth to note, that $\tilde{\nu}_{a-f}$ are anomalously large even in the solvents of relatively small polarity.

At the gradual decrease of the temperature from 293 to 77 K, the fluorescence spectra of **I–III** in ethanol demonstrate the common behavior: the continuous short-wavelength shift, accompanied by the essential increase of fluorescence quantum yield (Fig. 3B). The wide

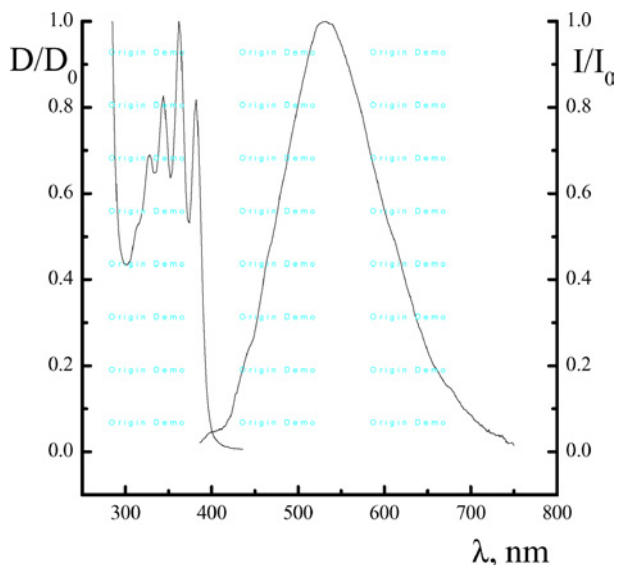


Fig. 1. The absorption (I) and the fluorescence (I') spectra of **II** in ethanol at 293 K.

structureless band at room temperature is transformed into structured one resembling the spectrum of anthracene at 77 K. The corresponding absorption spectra show only the increase of absorption intensity with the temperature decrease (Fig. 3A). The form and the position of the emission spectra of **I–III** in PMMA at 293 K are close to those in ethanol at 160 K. These observations indicate, that in highly viscous media the relaxation process is inhibited practically completely. It means, that both in PMMA at 293 K and in frozen ethanol the orthogonal position of cations fragments is apparently conserved at the excitation. As already has been mentioned, if the relaxation is associated with a mutual rotation of fluorophor molecular fragments, resulting in another molecular structure, then k_f of relaxed and nonrelaxed state should differ significantly [2]. Indeed, k_f values at 293 and 77 K, calculated by the equation $k_f = \varphi_f/\tau$ differ by 5.5 times for **I**, 9.9 times for **II** and 30 times for **III** (Table I, Fig. 4). Such great difference could not be explained only by the exponential increase of ethanol relaxation time with temper-

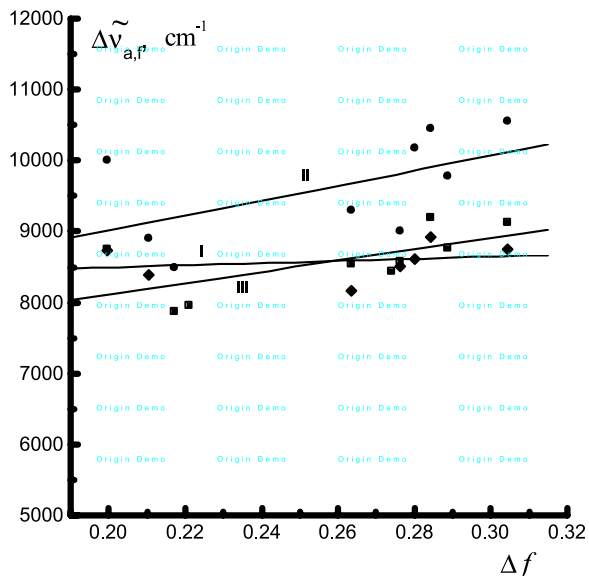


Fig. 2. The dependence of fluorescence Stokes' shift $\tilde{\nu}_{a-f}$ on the solvent polarity parameter Δf for the compounds: **I–III** at 293 K.

ature decrease. It supports the structural character of the process.

As the relaxation under study is significantly inhibited at the temperature decrease the relaxation activation energy E_a may be calculated from the experimentally obtained dependence $k_f(T)$. The presence of two excited molecular forms – initial and relaxed ones allow to introduce a two-state $LE \leftrightarrow CT$ model. Let us suppose, that only rate constant of forward reaction (k_1) depends largely on the temperature; $k_1(T_i) \gg k_{-1}(T_i)$ and $k_1(T_i) \gg k_d^{LE}$. k_d^{LE} is the non-radiative rate constant of the local excited species. In low temperature region $\varphi_f \approx \varphi_f^{LE}$. The value E_a may be calculated from the slope of a plot of $\ln(1/\varphi_f - 1)$ versus $1/T$ according to Eq. (2):

$$\ln\left(\frac{1}{\varphi_f} - 1\right) = \ln\left(\frac{A}{k_f^{LE}}\right) - \frac{E_a}{RT} \quad (2)$$

where A denotes the pre-exponential constant in the Arrhenius equation, k_f^{LE} is the fluorescence rate constant of

Table I. Absorption (λ_{abs}) and Fluorescence (λ_{fl}) Band Maxima, Fluorescence Quantum Yields (φ_f), Fluorescence Lifetimes (τ), Averaged Fluorescence Radiative Rate Constants (\bar{k}_f), Dipole Moment Changes ($\Delta\mu = \mu_e - \mu_g$), and Relaxation Activation Energy (E_a) of Compounds **I–III** in Ethanol

Compound	λ_{abs} (nm)	λ_{fl} (nm)	φ_f (293 K)	φ_f (77 K)	τ , ns (293 K)	τ , ns (77 K)	$\bar{k}_f \times 10^{-7}$, s ⁻¹ (293 K)	$\bar{k}_f \times 10^{-7}$, s ⁻¹ (77 K)	$\Delta\mu$ (D)	E_a (kJ/mol)
I	369	535	0.014	0.55	2.1	15	0.67	3.67	4.3	3.9 ± 0.1
II	362	535	0.019	1.0	1.8	9.6	1.06	10.46	15	9.0 ± 0.5
III	368	537	0.0068	0.86	2.6	11.1	0.26	7.78	15	6.0 ± 0.3

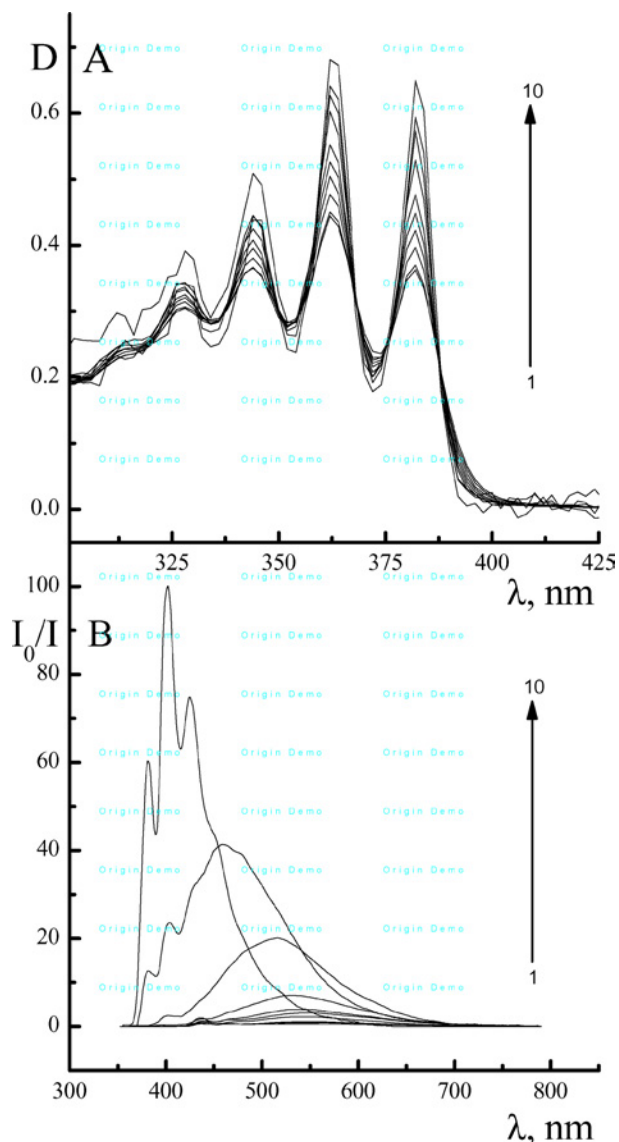


Fig. 3. The absorption (A) and the fluorescence spectra (B) of **II** in ethanol at decreasing temperature: 1(294), 2(273), 3(253), 4(232), 5(214), 6(198), 7(173), 8(151), 9(130) and 10 (115 K). $\lambda_{\text{exc}} = 362$ nm.

the initial, local excited species. The obtained values of E_a are shown in Table I. It is necessary to mention, that two different slopes of the function $\ln(1/\varphi_f - 1)$ in high and low temperature regions obtained in [7] apparently have the origin primarily in the theoretically calculated corrections for the density changes of the solvent. The experimental measurements of the absorption spectra at decreasing temperature give other values of corrections and thus other φ_f values. The resulting slopes of the lines become almost equal. That is the reason of the discrepancy between E_a calculated in [7] for **I** (15.6 kJ/mol) and

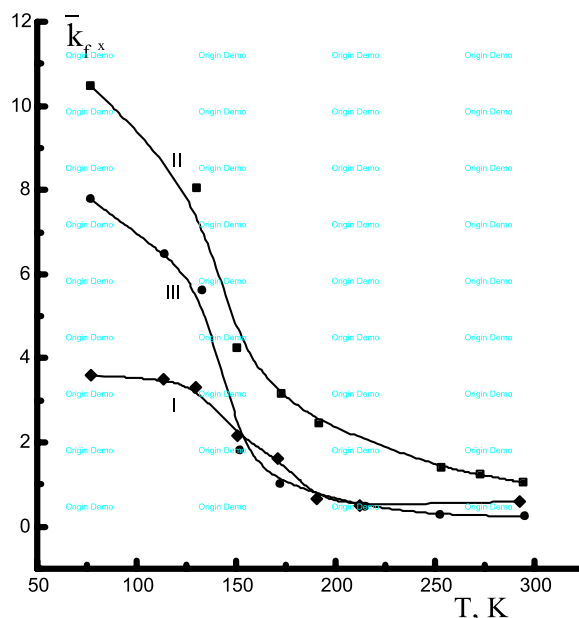


Fig. 4. The averaged radiative rate constants \bar{k}_f^x of the compounds **I–III** in ethanol at various temperatures in the range 293–77 K.

our result (3.9 kJ/mol). Indeed, the proximity of the fluorescence spectrum position of **I** in PMMA at 293 K to the spectrum in ethanol at 77 K indicates a minor influence of the temperature itself on k_1 .

To trace the dynamics of the relaxation we performed a series of the time-resolved fluorescence measurements of **I–III** in ethanol. Because of the rapid relaxation at room temperature it is necessary to measure the fluorescence at relatively low temperatures where the relaxation times are changed from picosecond to nanosecond range and become greater than the resolution time of the apparatus. The appearance and gradual rise of a longwavelength shoulder of the initial band of **III** at 133 K is shown in Fig. 5A. The increase of a longwavelength emission band and disappearance of the initial one is observed at 152 K (Fig. 5B). At 191 K TRES of **III** do not demonstrate any essential changes with time. The same picture as a whole was observed for **I** and **II**. The rate constants of the excited relaxed state formation (k_1) and back reaction (k_{-1}) of compounds studied were estimated according to Eq. (3) [8]:

$$\frac{S_i}{S'_i} = \frac{k_f}{k'_f} \left(\frac{k_{-1}/k_1 + e^{-(k_1+k_{-1})t}}{1 - e^{-(k_1+k_{-1})t}} \right) \quad (3)$$

where S_i and S'_i are the squares under the short and the longwavelength TRES bands, fitted as single Gaussian functions at the time delay t_i , k_f and k'_f are the emission rate constants of a LE and a CT (relaxed state) at given

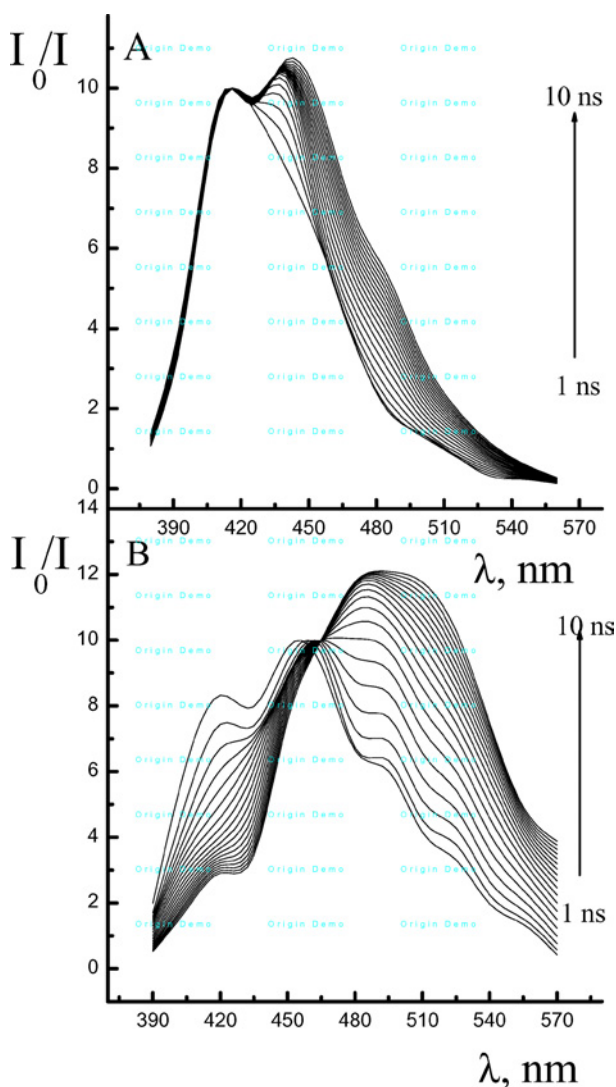


Fig. 5. The time-resolved emission spectra of **III** in ethanol at: (A) 133 K, and (B) 152 K. The time interval after excitation is changed from 1 to 10 ns. The increment is equal to 0.5 ns.

temperature. Because of the complicated picture of time-resolved fluorescence spectra, we managed to calculate the values k_1 and k_{-1} only in two cases: for **II**, 151 K ($7.4 \times 10^8 \text{ s}^{-1}$, $4.5 \times 10^7 \text{ s}^{-1}$) and for **III**, 133 K ($4.1 \times 10^9 \text{ s}^{-1}$, $1.7 \times 10^7 \text{ s}^{-1}$).

For the present it is difficult to say reliably which sort of intramolecular motion is responsible for the relaxation coordinate of the molecules. On the one hand, the observed charge transfer supports the ring flattening under excitation. In the orthogonal position of π systems the CT state is weakly allowed. On the other hand, due to more pronounced sp^3 hybridization character of pyridinium nitrogen in CT state, there is a tendency of the bent structure

formation [3,9]. TRES data obtained support rather both possibilities. In the recent study of time-resolved emission spectra of pyridyloxazoles and quinolythiazoles cations [8] we did not find an appearance both the longwavelength shoulder and the separate longwavelength band at similar experimental conditions. It is worth to emphasize, that the carbon atom, which is situated at the acceptor fragment in these cations in a position of the nitrogen one in **I–III** has much lower sp^3 hybridization tendency.

CONCLUSIONS

Thus, the excited state relaxation process of the cations **I–III** has the viscosity-dependent, activation character. It is consistent with the two-state model: $A \rightarrow A^* \leftrightarrow B^*$, where A^* belongs to the local excited mainly orthogonal and B^* apparently to more planar, bent conformer.

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