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Fluorescence Study of the Relaxation Process in Excited Hetarylthiazole Cations

V. V. Volchkov,[1,3] S. I. Druzhinin,[1] J. A. Kossanyi,[2] and B. M. Uzhinov[1]

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The absorption and fluorescence spectra of five cations protonated at the quinolyl nitrogen atom (**I**H^+–**V**H^+) and one ethylated (**I**Et^+) cation were investigated. For these compounds (except **V**H^+) both an anomalously large fluorescence Stokes shift (up to 238 nm) and a large short-wavelength fluorescence shift (up to 145 nm) at decreasing temperatures (down to 77 K) were observed. This is not the case for unprotonated molecules. The ground-state conjugation between quinolyl and another molecular fragment was found for **II**, **I**H^+, **II**H^+, and **I**Et^+. The relaxation process of excited cations is medium viscosity and temperature dependent. The experimental results are explained in terms of excited-state structural relaxation.

KEY WORDS: Excited state; quinolyl; structural relaxation; viscosity.

INTRODUCTION

The processes of structural relaxation in excited heterocyclic compounds have received great attention in the last decade. The dual fluorescence found in acetonitrile solutions of *N*-phenyl-2,3-naphthalimide is supposed to originate from two conformers with different dihedral angles between the phenyl and the naphthalimide substituents [1]. Significant flattening was detected in the excited singlet state of the ortho analogues of POPOP molecules [2]. Solvent polarity- and viscosity-dependent rotational relaxation was revealed in the excited state of the fluorescing dye 1,1-dicyano-2-[6-(dimethylamino)-naphthalen-2-yl]propene [3]. The anomalous fluorescence Stokes shift in 2-(3′-pyridyl)oxazoles protonated cations is explained by the barrierless structural relaxation in the excited state [4]. There was no such phenomenon for ortho- and para-substituted pyridyloxazoles cations. It seems interesting to investigate the commonness of this phenomenon for metha-substituted cations of related structure.

The pronounced difference in the spectral behavior of quinolylthiazole cations in comparison with that of the uncharged molecules makes these cations a suitable model for such investigations. In this work the relaxation processes in the excited state of protonated 2-(3-quinolyl)-1,3-benzothiazole (**I**), 5-phenyl-2-(3-quinolyl)-1,3-thiazole (**II**), 2-(3-quinolyl)naphtho[1,2-*d*][1,3]thiazole (**III**), 5-phenyl-2-(3-quinolyl)-1,3-benzothiazole (**IV**), 2-(3-quinolyl)-6,7,9,10,12,13,15,16-octahydro-[1,4,7,10,13]pentaoxacyclopentadecino[2′,3′:4,5]benzo-[*d*][1,3]thiazole (**V**), and ethylated 3-(1,3-benzothiazol-2-yl)-1-ethylquinolinium 4-methyl-1-benzenesulfonate cation (**I**Et^+) (Scheme I), resulting in anomalous fluorescence Stokes shifts have been investigated.

EXPERIMENTAL

Absorption spectra were recorded using a Shimadzu-3100 spectrophotometer. Fluorescence spectra were registered by a Elyumin-2M spectrofluorimeter. The standard

[1] Department of Chemistry, Chemical Kinetics Division, Moscow State University, Vorob'evy gory, 119899, Moscow, Russia.
[2] CNRS, Laboratory des Materiaux Moleculaires, rue Henri Dunant, F-94320, Thiais, France.
[3] To whom correspondence should be addressed.

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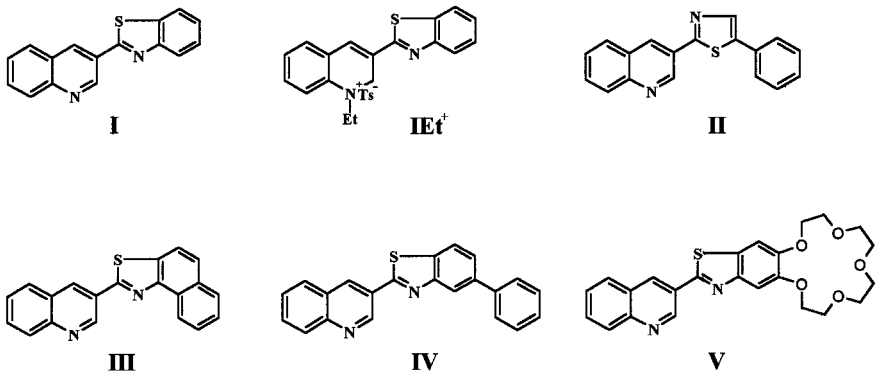

Scheme I.

quinine sulfate in 1 *N* sulfuric acid ($\varphi = 0.546$), [5] was used for fluorescence quantum yield measurements. These were performed in solvents degassed by several freeze–pump–thaw cycles. The temperature of fluorescing solutions was kept constant with a water thermostat. Variable-temperature measurements were carried out with a homemade cryostat by the adjustable flow of cooled nitrogen vapors through a microdewar. Spectral-grade sulfuric acid was used as received. Other solvents used were purified by the method described in Ref. 6. Correction of fluorescence spectra for the molar volume changes as the temperature decreased was made by standard methods [7]. Fluorescence radiative lifetimes were calculated by the Bowen–Wokes equation [8]. Compounds **I–V** and **I**Et$^+$ were synthesized according to the method already described [9] and used as received.

RESULTS AND DISCUSSION

There are two nitrogen atoms in molecules **I–V** which can accept a proton. It is known that the basicity of unsubstituted quinoline is higher than that of thiazole [10]. The absorption and fluorescence spectra of **I**Et$^+$ and **I**H$^+$ in ethanol are close to each other (Tables I and II), which points out that at a low medium acidity (up to 1 *M* H_2SO_4) the proton in the **I**H$^+$–**V**H$^+$ cations is situated at the quinolyl nitrogen atom.

Upon the addition of H_2SO_4 to solutions of compounds **I–V** in ethanol, we observed bathochromic shifts in the absorption spectra, which were noted even in 0.01 *M* sulfuric acid. The isosbestic points were observed in all five cases. Analysis of the absorption spectra using the method in Ref. 11 revealed the presence in the solution

Table I. Absorption (λ_{abs}) and Fluorescence (λ_{fl}) Band Maxima, Fluorescence Quantum Yields at 298 K (φ)[a] Basicity Constants (K_b and pK^*_b), Fluorescence Stokes Shift ($\lambda_{fl} - \lambda_{abs}$), and the Difference Between Fluorescence Band Maxima at 293 and 77 K for **I–V** and Their Protonated Cations in Ethanol [$\lambda_{fl}(293) - \lambda_{fl}(77)$]

Compound[b]	λ_{abs} (nm)	λ_{fl} (nm)	φ	K_b (M^{-1})	pK^*_b	$\lambda_{fl} - \lambda_{abs}$ (nm)	$\lambda_{fl}(293) - \lambda_{fl}(77)$ (nm)
IH$^+$	359	515	0.03	19.15 ± 0.05 (for **I**)	−6.72 (for **I**)	156	96
II	340	422	0.20	25.40 ± 0.05	−8.65	82	1
IIH$^+$	384	580	0.12	—	—	196	110
III	360	432	0.15	19.29 ± 0.02	−6.71	72	−55
IIIH$^+$	396	607	0.04	—	—	211	113
IV	318	433	0.01	11.59 ± 0.04	−9.45	115	−16
IVH$^+$	364	602	<0.01	—	—	238	145
V	361	476	0.54	20.45 ± 0.02	−7.51	115	48
VH$^+$	403	536	<0.01	—	—	133	−5

[a] For **I**H$^+$, **II**H$^+$, **III**H$^+$, and **V**H$^+$ values of φ were measured in 1 *M*, and for **IV**H$^+$ in 3 *M*, sulfuric acid solutions in ethanol.
[b] Data for compounds **I** (except K_b and pK^*_b) and **I**Et$^+$ are listed in Table II.

Table II. Absorption (λ_{abs}) and Fluorescence (λ_{fl}) Band Maxima, Extinction Coefficients at λ_{abs} (ε), Fluorescence Quantum Yields at 298 K (φ), Radiative (τ_r) and True (τ_o) Fluorescence Lifetimes, Fluorescence Stokes Shifts ($\lambda_{fl} - \lambda_{abs}$), and the Differences Between Fluorescence Maxima at 293 and 77 K for **I** and **I**Et$^+$ [$\lambda_{fl}(293) - \lambda_{fl}(77)$] in Various Solvents

	λ_{abs} (nm)		ϵ (M^1·cm)		λ_{fl} (nm)		φ		τ_r (ns)		τ_o (ns)		$\lambda_{fl} - \lambda_{abs}$ (nm)		$\lambda_{fl}(293) - \lambda_{fl}(77)$ (nm)	
Solvent	**I**	**I**Et$^+$	**I**	**I**Et$^+$	**I**	**I**Et$^+$	**I**	**I**Et$^+$	**I**	**I**Et$^+$	**I**	**I**Et$^+$	**I**	**I**Et$^+$	**I**	**I**Et$^+$
Ethanol	330	360	25,990	11,110	387	520	0.05	0.03	2.46	5.41	0.12	0.18	57	160	6	100
Butyronitrile	327	361	25,650	11,050	378	522	0.04	0.03	2.13	4.96	0.08	0.16	51	161	0	102
Water	—	355	Insol.	10,690	—	522	—	0.02	—	5.29	—	0.12	—	167	—	—
Dichloromethane	—	372	—	13,790	—	492	—	0.04	—	4.38	—	0.16	—	120	—	—
Triacetin	330	—	28,840	Insol.	384	—	0.04	—	2.11	—	0.08	—	54	—	—	—
Glycerol	—	354	Insol.	—	—	486	—	0.06	—	—	—	—	—	132	—	—

of two molecular forms for each compound: the initial one and the monoprotonated cation. Analysis of the corresponding fluorescence spectra showed the presence in the excited state of the same molecular forms which were found in the ground state. The fluorescence spectra of cations are wider than those of the initial molecules and the fluorescence quantum yields of cations are lower than those for unprotonated compounds (Fig. 1). The ground- and the excited-state basicity constants for **I–V** are shown in Table I.

The value of the fluorescence Stokes shift for all five protonated cations is anomalously large (238 nm for **IV**H$^+$ in ethanol), while the value of this shift for nonprotonated compounds is substantially lower (Tables I and II). This is an indication of some relaxation process occurring in the excited cations.

To establish the factors influencing the fluorescence Stokes shift we measured the fluorescence spectra of cations studied at different temperatures. We used 1 *M* sulfuric acid solutions in ethanol to obtain the protonated cations of **I–IV**. Solutions in ethanol, butyronitrile, and glycerol were used for **I**Et$^+$. The fluorescence spectra of each cation were measured in the range from 293 to approximately 133 K. The temperature range for **I**Et$^+$ in glycerol was from 343 to 190 K. Additional measurements were performed in ethanol solutions at 77 K. Rather large blue shifts of the fluorescence spectra accompanied by increases in fluorescence quantum yields (from 1.8

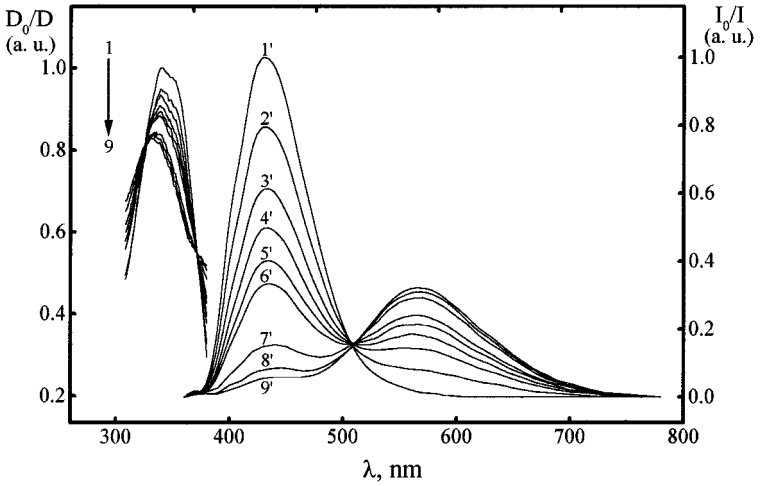

Fig. 1. The region of absorption spectra with isosbestic points (1–9) and fluorescence (1′–9′) spectra of **II** in ethanol at room temperature. The concentration of H_2SO_4 is 0 (1, 1′), 0.01 (2, 2′), 0.02 (3, 3′), 0.03 (4, 4′), 0.04 (5. 5′), 0.05 (6, 6′), 0.1 (7, 7′), 0.15 (8, 8′), and 0.2 (9, 9′) *M*.

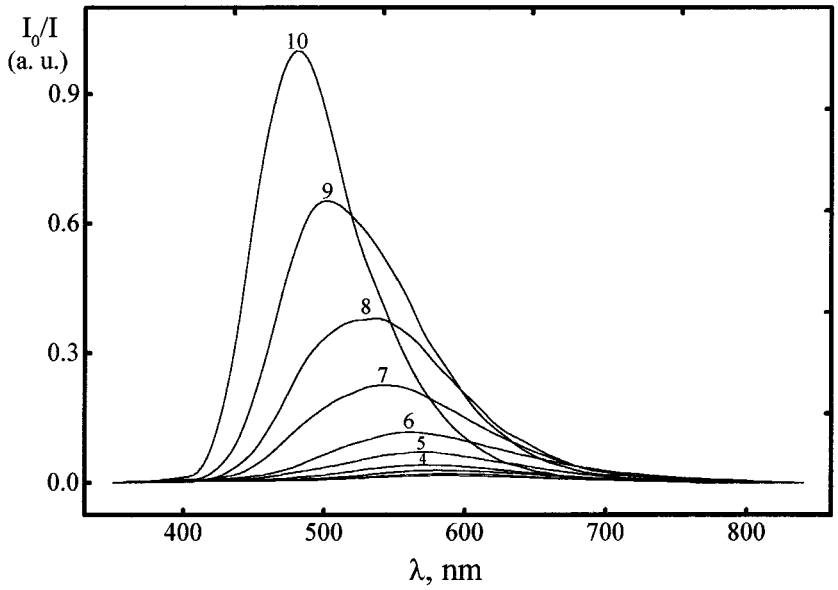

Fig. 2. The fluorescence spectra of **IV** in 1 *M* ethanolic solutions of H_2SO_4 at various temperatures: 1 (288 K), 2 (272 K), 3 (253 K), 4 (234 K), 5 (212 K), 6 (192 K), 7 (174 K), 8 (160 K), 9 (143 K), and 10 (105 K).

times for **II**H^+ to 11.5 times for **IV**H^+) as the temperature decreased were observed for all four cations (Figs. 2 and 3). At the same time the spectral width became shorter (Fig. 2). The corresponding absorption spectra measured at 77 K did not differ from those measured at 293 K. A large blue shift in the cation fluorescence spectra measured at 293 and 77 K (up to 145 nm for **IV**H^+) and small blue or red shifts in the spectra of uncharged molecules were observed (Table I).

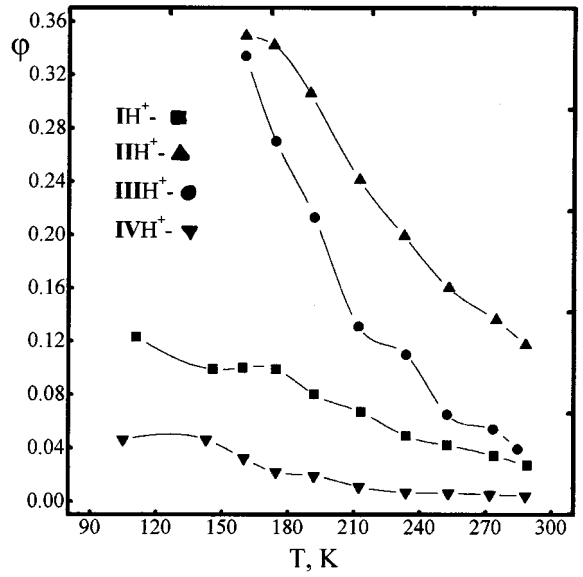

Fig. 3. The dependence of fluorescence quantum yields of four hetarylthiazole cations on temperature.

It is known that the viscosity of ethanol increases as the temperature decreases, which means that the observed blue shift of the cation fluorescence spectra is caused by the change in the solvent viscosity. Figure 2 shows the dependence of λ_{fl} of **I**H^+–**IV**H^+ on 1gη. The dependence of the fluorescence spectra maxima on the logarithm of the medium viscosity for the cations studied shows that the relaxation is supressed mainly in the range from 10 to 10^5 cP (Figs. 4 and 5). The significant deviation in the values of λ_{fl} for **I**Et^+ in ethanol and glycerol at the same medium viscosity and comparable polarity points out that the relaxation process is not only viscosity but also temperature dependent.

The long-wavelength absorption maximum of compound **I** in ethanol is close to the maximum of benzothiazole in the same solvent. The analogous values for cations **I**H^+ and **I**Et^+ are red shifted by 35 nm. The absorption maxima of quinoline and its protonated cation are situated in a shorter spectral region [12]. The difference between the long-wavelength absorption maximum of compound **II** and that of quinoline comprises 32 nm; the same parameter for **II**H^+ and protonated quinoline comprises 71 nm. Hence there is no ground-state conjugation between quinolyl and benzothiazole fragments in the ethanolic solution of **I**. On the other hand, it is present in the molecules of **II** and, also, in the cations: **I**H^+, **II**H^+, and **I**Et^+. This

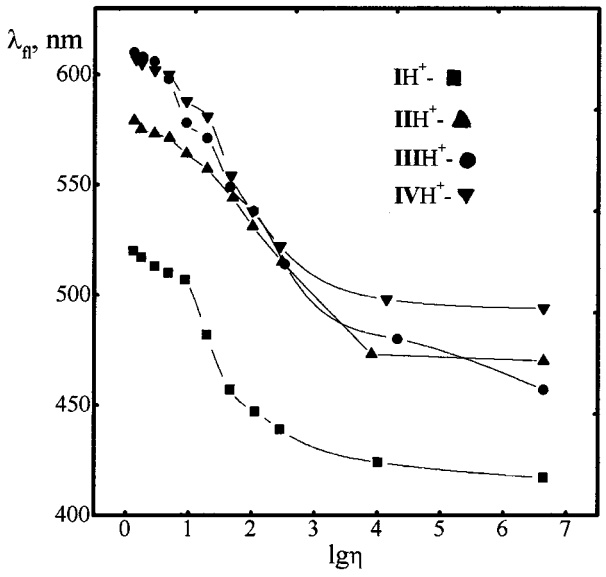

Fig. 4. The dependence of fluorescence spectra maxima of four protonated cations on the logarithm of the ethanol viscosity.

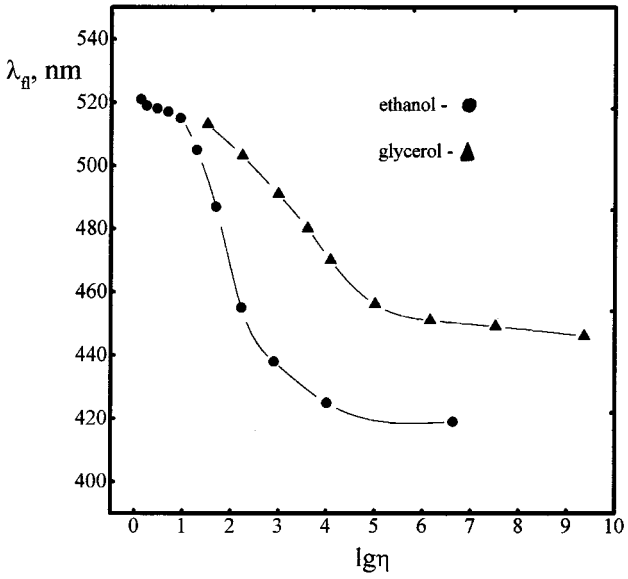

Fig. 5. The dependence of fluorescence spectra maxima of the **I**Et$^+$ cation on the logarithm of the ethanol and glycerol viscosity.

conjunction points to a zero or small value of the dihedral angle between the corresponding molecular fragments in the ground state.

Comparison of the spectral characteristics of **I** and **I**Et$^+$ in different solvents was performed to determine the influence of the medium polarity on the relaxation process (Table II). The difference between the parameter $\tilde{\nu}_{abs} - \tilde{\nu}_{fl}$ in ethanol and that in triacetin for compound **I** is relatively small (232 cm^{-1}). The fluorescence Stokes shift of the cation **I**Et$^+$ depends much more on the solvent polarity parameter—the difference between the value of $\tilde{\nu}_{abs} - \tilde{\nu}_{fl}$ in water and that in 1,2-dichloromethane is 2420 cm^{-1}. Thus, the anomalously large fluorescence Stokes shift observed cannot be explained solely by the variation in the solvation energy during excitation.

The most probable type of relaxation under study is the structural one, which consists of torsion motion of the quinolyl fragment relative to the other heterocyclic moiety of the cation. At a low medium viscosity it takes place within a time interval that is significantly shorter than the lifetime of the excited fluorophore.

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