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Intramolecular structural relaxation in excited hetarylazole cations

Valery V. Volchkov,[1]* Gaston Hui Bon Hoa,[2] Jean A. Kossanyi,[2] Sergey P. Gromov,[3] Mikhail V. Alfimov[3] and Boris M. Uzhinov[1]

[1]Department of Chemistry, Chemical Kinetics Division, Moscow State University, Leninskie gory 1/3, 119899 Moscow, Russia
[2]CNRS, Laboratoire des Matériaux Moléculaires, rue Henri Dunant, F-94320 Thiais, France
[3]Center of Photochemistry, Russian Academy of Sciences, ul. Novatorov 7a, 117421 Moscow, Russia

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ABSTRACT: Neutral quinolyl-and pyridyl-substituted hetarylazoles and their protonated (ethylated) cations with anomalously high Stokes shifts were investigated. Fluorescence measurements at different temperatures and pressures confirmed the viscosity-dependent activation relaxation of the latter. Fluorescence kinetic analyses at various temperatures showed that in the range 293–77 K, the $\bar{k}_f$ values of cations increase 2–8-fold whereas those of neutral molecules change only 0.3–1.5-fold. The low-temperature time-resolved emission spectra of **1a**, **1H**$^+$ and **5a** were found to be consistent with the model: $A \rightarrow A^* \leftrightarrow B^*$, where A* is the local excited planar and B* is the relaxed twisted state of the molecule. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: intramolecular structural relaxation; pressure; hetarylazole cations

INTRODUCTION

Aryl, hetaryl and benzoannelated derivatives are important heterocycles used for the production of luminophores, as ligands in transition metal complexes and in liquid crystal materials.[1,2] Therefore, the determination of the spectral and luminescence characteristics and the study of the photochemical behavior of hetarylazoles and their derivatives are of great interest. The protonated and ethylated cations of some hetarylazoles were chosen for this investigation.

The anomalously high fluorescence Stokes shifts of hetarylthiazole cations, including **1H**$^+$–**4H**$^+$ and **1a** in ethanol and glycerol, are reduced significantly as the temperature decreases (as the solvent viscosity increases). This reduction was considered to be an indication of the existence of an effective intramolecular relaxation process in their excited state.[3] The spectral behavior of 12-(9-anthroyloxy)stearic acid[4] was explained by a structural relaxation process consisting of the mutual rotation of the excited molecular fragments. Nowadays there are two main hypotheses for treating the intramolecular relaxation phenomenon, the TICT[5–7] and PICT[8,9] models. According to the former, the relaxation is accompanied by full perpendicular twisting of both molecular fragments with a more forbidden emissive nature for the twisted structure. The latter is a state reversal model. It postulates a planarized structure of the charge transfer (CT) state. The aim of the present work was to establish the intramolecular relaxation mechanism for protonated and ethylated hetarylazole cations by steady-state fluorescence measurements at various pressures and fluorescence kinetic measurements in the temperature range 293–77 K.

EXPERIMENTAL

2-(3-Quinolyl)-1,3-benzothiazole (**1**), 3-(1,3-benzothiazol-2-yl)-1-ethylquinolinium 4-methyl-1-benzenesulfonate (**1a**), 5-phenyl-2-(3-quinolyl)-1,3-thiazole (**2**), 2-(3-quinolyl)naphtha[1,2-*d*][1,3]thiazole (**3**) and 5-phenyl-2-(3-quinolyl)-1,3-benzothiazole (**4**) were prepared by known methods[10] and used as received. The protonated cations **1H**$^+$–**4H**$^+$ were prepared by the addition of spectral-grade sulfuric acid to ethanolic solutions of **1**–**4** up to concentrations of 1–3 M. 3-(5-Phenyloxazol-2-yl)pyridine (**5**),[11,12] 4-(5-phenyloxazol-2-yl)pyridine (**6**), 1-ethyl-3-(5-phenyloxazol-2-yl)pyridinium 4-methyl-1-benzenesulfonate (**5a**) and 1-ethyl-4-(5-phenyloxazol-2-yl)pyridinium 4-methyl-1-benzenesulfonate (**6a**) were used as received.[13] Benzene, toluene, ethyl acetate, dichloromethane, 2-propanol, *n*-butanol, glycerol, butyronitrile, ethanol and acetonitrile were of spectroscopic

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**Correspondence to:* V. V. Volchkov, Department of Chemistry, Chemical Kinetics Division, Moscow State University, Leninskie gory 1/3, 119899 Moscow, Russia.
E-mail: volchkov@light.chem.msu.ru
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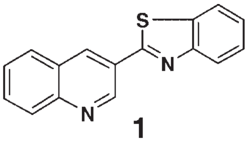
grade. Ethanol was dried by distillation from CaH_2 prior use.



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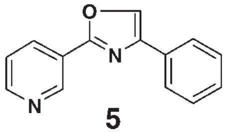

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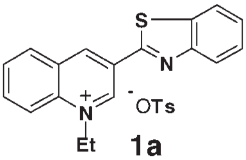
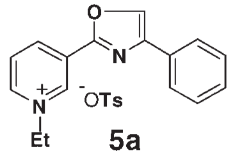
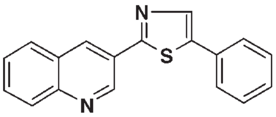


1a



5a



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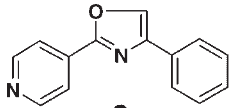

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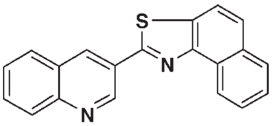

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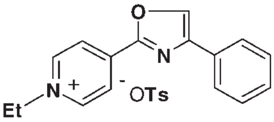
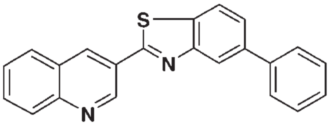


6a



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The absorption and fluorescence spectra were recorded on a UV-3100 spectrophotometer and an Elyumin-2M spectrofluorimeter. Absorption and fluorescence measurements at low temperatures were carried out using a laboratory-made cryostat with an adjustable flow of cooled nitrogen vapor through a spectroscopic Dewar vessel. Standard quinine bisulfate solution in 1 N sulfuric acid ($\Phi_0 = 0.546$)[14] was used for fluorescence quantum yield measurement. The fluorescence quantum yields at low temperatures were calculated considering the absorption spectra recorded at the same temperatures as the corresponding fluorescence spectra by the equation

$$\Phi_i = \Phi_0 \frac{S_i(1 - 10^{-D_0})}{S_0(1 - 10^{-D_i})} \tag{1}$$

where Φ_i and Φ_0 are the fluorescence quantum yields of the compounds, S_i and S_0 are the squares of corrected fluorescence spectra and D_i and D_0 are the optical densities at the excitation wavelength at T_i and 293 K, respectively.

Registration of the fluorescence spectra at high pressures at 293 K was carried out as described earlier.[15] A correction for the absorption spectral changes with increase in pressure was not carried out. The fluorescence kinetics were recorded with 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 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. Measurements of fluorescence kinetics at low temperatures were performed using the same spectroscopic Dewar vessel. The accumulation of the signal was carried out at the wavelengths corresponding to the steady-state emission spectra maxima, recorded at the same temperatures. Time-resolved emission spectra (TRES) were calculated from the set of fluorescence kinetic curves obtained at different wavelengths at equal accumulation times and constant temperature (173 K).

RESULTS AND DISCUSSION

The fluorescence Stokes shifts ($\Delta\tilde{\nu}_{a,f}$) of all cations studied except **6a** are anomalously large in all solvents used and significantly exceed the corresponding values for neutral molecules (Table 1). The fluorescence spectra of cations in ethanol are shifted to short wavelengths as the temperature decreases.[3] The above effects were explained by the existence of an excited-state relaxation process inhibited either by the increasing solvent viscosity due to the temperature decrease or by the temperature decrease itself, or both effects simultaneously.[3] The fluorescence quantum yields (Φ_f) of the protonated $\mathbf{1H^+}$–$\mathbf{4H^+}$ and the ethylated cations **1a** and **5a** are less than those for the uncharged molecules. As the temperature decreases to 77 K, Φ_f of $\mathbf{1H^+}$, $\mathbf{3H^+}$, $\mathbf{4H^+}$, **1a** and **5a** in ethanol increase many times more than the Φ_f of **1**–**6**. The Φ_f of the cations $\mathbf{2H^+}$ and **6a** at 77 K are less than those at 293 K.

The fluorescence spectra of the uncharged molecules **1**–**6**, the monoprotonated $\mathbf{2H^+}$–$\mathbf{4H^+}$ and the monoethylated cations **1a**, **5a** and **6a** at 293 K are red shifted as the solvent polarity increases. Their Stokes shifts ($\Delta\tilde{\nu}_{a,f}$) also increase. For 12 compounds, the dependence of $\Delta\tilde{\nu}_{a,f}$ on the solvent polarity parameter Δf shows a linear correlation (Fig. 1), which allows one to use the Lippert function for the evaluation of their dipole moment changes on excitation[16] (Table 1):

$$\begin{aligned}\Delta\tilde{\nu}_{a,f} &= \frac{2(\mu_e - \mu_g)^2}{hca^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) + \text{constant} \\ &= \frac{2(\mu_e - \mu_g)^2}{hca^3}\Delta f + \text{constant}\end{aligned} \tag{2}$$

where μ_g and μ_e are the dipole moments of the ground and excited states of the molecule, respectively, h is Planck's constant, c is the velocity of light, a is the radius of the Onsager cavity which fits the molecule, ε is the dielectric constant and n is the refractive index. From the differences in the slopes of the lines it is obvious that solvatochromism of the cations is slightly more

Table 1. Fluorescence Stokes shifts ($\Delta\tilde{\nu}_{a,f}$), quantum yields (Φ_f), fluorescence lifetimes (τ) and averaged fluorescence radiative rate constants ($\bar{k}_f$) at 293 and 77 K in ethanol and dipole moment changes ($\Delta\mu = \mu_e - \mu_g$) of **1**–**6** and their protonated or ethylated cations[a]

		Φ_f		τ (ns)		$\bar{k}_f \times 10^{-7}$ (s^{-1})		
No.	$\Delta\tilde{\nu}_{a,f}$, (cm^{-1})	293 K	77 K	293 K	77 K	293 K	77 K	$\Delta\mu$ (D)
1	4530	0.05	0.11	0.1	1.0	41.7	10.9	4.8
1H$^+$	6920	0.04	0.21	1.1	0.8	3.6	26.3	—
1a	9360	0.03	0.11	1.8	0.7	1.9	15.7	5.0
2	5930	0.20	0.36	0.6	1.0	41.7	37.0	6.2
2H$^+$	9280	0.12	0.10	2.9	1.3	4.3	7.7	6.9
3	4940	0.15	0.30	0.9	1.2	17.2	26.0	3.8
3H$^+$	8860	0.04	0.39	1.2	5.3	2.9	7.4	5.0
4	7280	0.01	0.14	0.2	0.5	6.4	3.0	5.6
4H$^+$	11000	0.004	0.067	0.8	2.7	0.5	2.5	7.6
5	6190	0.63	0.67	1.5	1.1	44.7	60.9	3.1
5a	11700	0.15	0.94	3.3	3.0	4.5	31.0	3.8
6	6160	0.81	0.63	1.5	1.7	54.0	37.1	6.7
6a	6000	1.00	0.85	2.4	1.9	41.7	44.6	5.6

[a] The data for **1H$^+$** are in glycerol.

pronounced than that of the corresponding uncharged molecules.

To clarify the reasons why the fluorescence Stokes shift decreases with decreasing temperature, the effect of pressure on the fluorescence spectrum at room temperature was measured in glycerol. The viscosity increases significantly as the pressure increases. An increase in Φ_f of **1a** in glycerol, accompanied by a small blue shift of the fluorescence maximum, is observed as the pressure increases from 1 bar to 4.5 kbar (Fig. 2). The same pressure increase does not influence the fluorescence spectrum position of **1**, where the Stokes shift is normal. In the range from 1 bar to 4.5 kbar, the analogous spectra of **1**, **1H$^+$**, **3H$^+$** and **1a** in ethanol are also not shifted, since the ethanol viscosity is changed slightly at the pressure increases. These results confirm the suggestion that the relaxation rate decreases as the viscosity of the medium increases.[3] A variation of log η for **1a** in glycerol only from 3.15 to 4.35 with increasing pressure results in a blue shift of the fluorescence maximum by 10 nm. The same variation of log η of glycerol solution of **1a** with decreasing temperature at normal pressure results in a short-wavelength shift of 23 nm. This indicates that the relaxation of **1a** has an energy barrier. In contrast, the small growth of the solvent dielectric constant as the temperature decreases and also as the pressure increases (from 23.2 to 29.3 for ethanol and from 42.8 to 49.7 for glycerol at 303 K)[17] must favor the stabilization of the relaxed state. The fluorescence maximum of **5a** in glycerol at 293 K ($\eta = 1412$ cP) coincides with λ_f^{max} of **5a** in ethanol at 170 K where the solution viscosity is 64 cP. It also indicates the activation character of the process in this case. Examples of the influence of pressure on the fluorescence spectra of organic compounds are known in the literature.[18–20] The decrease in the fluorescence Stokes shift with pressure increase has been observed for solutions of 4-[4-(dimethylamino)phenyl]pyridine (4-DAPP) in solvents of a different polarity.[21] The results were explained by lowering of the efficiency of the formation of the excited planar relaxed conformer.

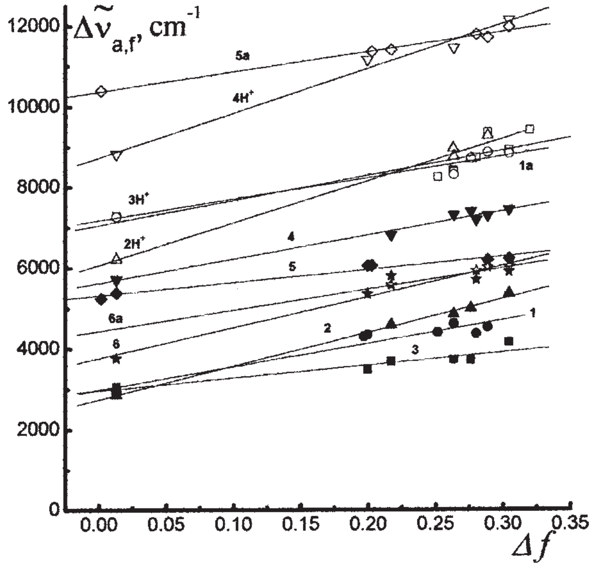

Figure 1. Dependence of fluorescence Stokes shift, $\Delta\tilde{\nu}_{a,f}$, on the solvent polarity parameter Δf for compounds **1**–**6**, **1a**, **2H$^+$**–**4H$^+$**, **5a** and **6a** at 293 K

The relaxation under study can be caused either by the intramolecular rotation of fluorophore molecular fragments followed by the solvent orientational relaxation (structural relaxation) or by the solvent orientational relaxation only. Important information about relaxation mechanisms can be obtained from the dependence of the fluorescence rate constant (k_f) on temperature. If the relaxation process is associated with fluorophore molecular fragment rotation resulting in different molecular

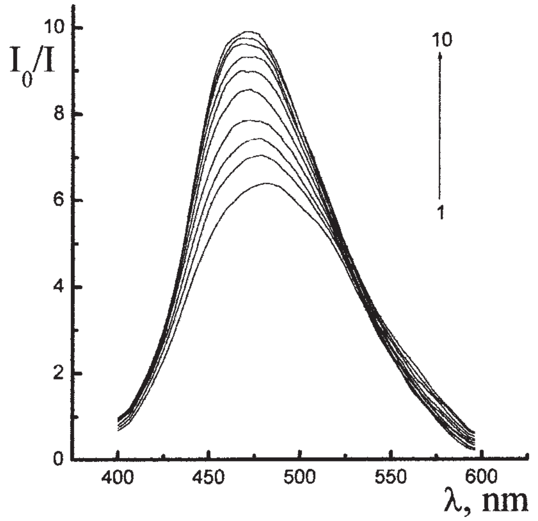

Figure 2. Fluorescence spectra of **1a** in glycerol at increasing pressure: (1) 0.001; (2) 0.5; (3) 1.0; (4) 1.5; (5) 2.0; (6) 2.5; (7) 3.0; (8) 3.5; (9) 4.0; (10) 4.5 kbar. $T = 293$ K; $\lambda_{exc} = 360$ nm

structures, then the k_f of relaxed and non-relaxed states should differ significantly. Through solvent relaxation the molecular structure is not changed significantly, therefore in this case the k_f of relaxed and non-relaxed states should differ less or remain the same. The fluorescence quantum yields and the fluorescence kinetics of uncharged compounds and cation **6a** were measured at 293 and 77 K. Φ_f and the kinetics of cations **1a**, **5a**, **2H**$^+$ and **3H**$^+$ were measured at different temperatures in the range 293–77 K. Φ_f and τ measured at corresponding temperatures enabled us to calculate the radiative rate constants of the compounds: $\bar{k}_f = \Phi_f/\tau$ (Fig. 3). The values of $\bar{k}_f$ in the 293–77 K temperature range are effective values. They characterize the averaged-out emission rate from relaxed and partially relaxed states. Since at 77 K $\bar{k}_f$ does not demonstrate an asymptotic character, the relaxation process at this temperature is not suppressed completely. In the above-mentioned range the $\bar{k}_f$ of cations having $\Delta\tilde{\nu}_{a,f} > 8000\,\text{cm}^{-1}$ increase 2–8-fold, whereas the $\bar{k}_f$ of uncharged molecules change only 0.3–1.5-fold (Table 1). The distinguishing feature of **6a** with the lowest $\Delta\tilde{\nu}_{a,f}$ among cations is the smallest change of its $\bar{k}_f$ with the temperature.

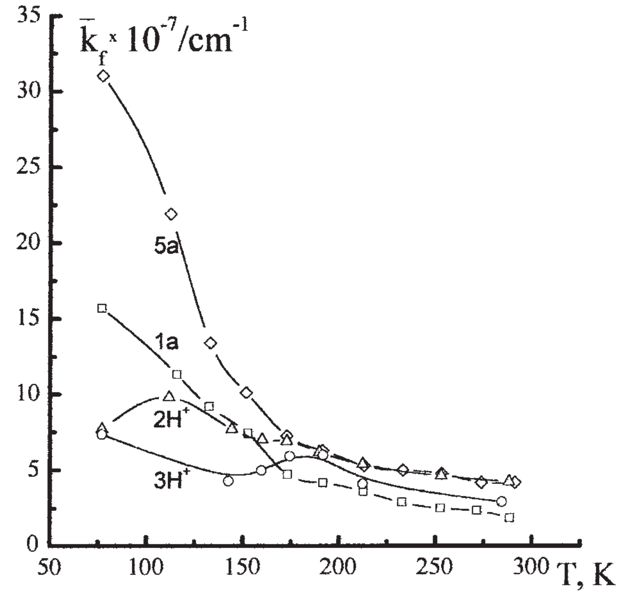

Figure 3. Averaged radiative rate constants $\bar{k}_f$ of compounds **1a**, **2H**$^+$, **3H**$^+$ and **5a** in ethanol at various temperatures in the range 293–77 K

The data obtained support the assumption that the relaxation observed in the cations **1a**, **5a**, **2H**$^+$ and **3H**$^+$ is structural. The fact that $\bar{k}_f$ of **1a** and **5a** increase strongly, may be caused by the substantial increase in their torsional barrier crossing probability, since the temperature takes significant values. The weaker increase in $\bar{k}_f$ for **2H**$^+$–**4H**$^+$ is assumed to be connected either with higher barriers between the local excited and relaxed molecular forms or with their small torsional angle differences. Analogous experiments with 2-(4-hexoxy-2-methoxyphenyl)-4,6-bis(2,4,6-trimethylphenyl)-1,3,5-triazine (**H-MeO-Ms**) in EPA showed an approximately twofold increase in its $\bar{k}_f$ in the range 293–77 K.[22] This was explained by the decrease in the TICT state formation efficiency with an orthogonal position of resorcinyl and triazine groups. The fluorescence kinetics of the cations, registered at 77 K at the blue and red sides of the spectrum, gives additional information about the degree of inhibition of its relaxation process. The fluorescence lifetimes of non-protonated species (τ) vary from 0 to 0.3 ns and the corresponding τ of cations **1a**, **1H**$^+$, **2H**$^+$ and **3H**$^+$ increase from 0.4 to 2.7 ns. The differences $\tau(520\,\text{nm}) - \tau(430\,\text{nm})$ for **5a** and **6a** are 0.44 and 0.41 ns, respectively. This indicates that the influence of the solvent on the fluorescence kinetics of the compounds under study exists even in a low-temperature glassy medium.

Detailed information about the relaxation dynamics could be obtained by means of the time-resolved fluorescence spectra measurements. The viscosity region where the fluorophore lifetime is close to its relaxation time is the most convenient for the observation of such dynamics. Figure 4 demonstrates the red fluorescence shift of **5a** with the subsequent appearance of a second long-wavelength band. The maximum of this band is close to the corresponding steady-state fluorescence maximum of **5a** at 293 K. TRES measurements of **1H**$^+$ and **1a** at the same conditions showed a similar behavior. This indicates that two molecular forms, initial and relaxed, exist mainly in the excited **1H**$^+$, **1a** and **5a** (two-step model). We assume that the short-and long-wavelength TRES bands belong to the emission from the planar and twisted conformers, respectively. The ground state of **1H**$^+$ and **1a** is planar or quasi-planar.[3] The time-resolved emission spectroscopy of 4-*N*,*N*-dimethylaminobenzonitrile (DMABN) in acetonitrile and 1,4-dioxane

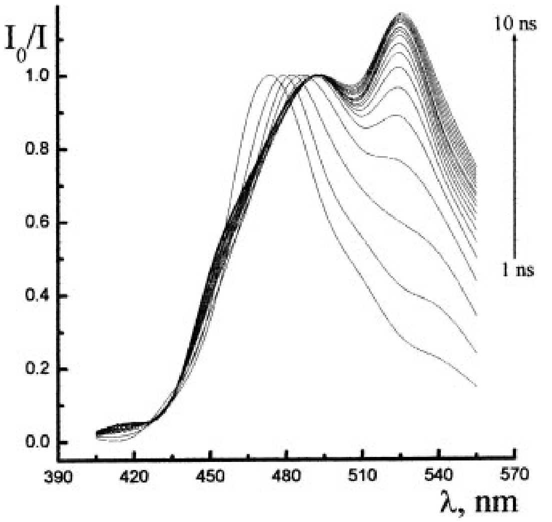

Figure 4. Time-resolved emission spectra of **5a** in ethanol at 173 K. The time interval after excitation is changed from 1 to 10 ns. The increment is equal to 0.5 ns

at 293 K reveals analogous behavior on a time-scale from 0 to 0.1 ns. There are only two emissive species.[23]

The rate constants of the formation of the excited twisted product (k_1) and back reaction (k_{-1}) of **5a** in EtOH at 173 K were estimated according to the equation

$$\frac{S_i}{S_i'} = \frac{k_f}{k_f'}\left[\frac{\frac{k_{-1}}{k_1} + e^{-(k_1+k_{-1})t}}{1 - e^{-(k_1+k_{-1})t}}\right] \tag{3}$$

where S_i and S_i' are the squares under the short-and long-wavelength TRES bands, fitted as single Gaussian functions at time delays t_i and k_f and k_f' are the emission rate constants of planar and twisted conformer at given temperature. The values k_1 and k_{-1} are 9.6×10^8 and $2.3 \times 10^7\,s^{-1}$, respectively. Considering that the viscosity of ethanol at 173 K is equal to that of glycerol at 336 K, the values obtained are of the order of the rate constants for the excited-state flattening reaction of 1,2-bis(5-phenyloxazol-2-yl)benzene, 2-(5-phenyl-1,3,4-oxadiazol-2-yl)benzene and 2-[5-(2-furyl)-1,3,4-oxadiazol-2-yl]benzene in glycerol.[24]

Hence the excited-state relaxation process of the cations **$1H^+$**, **1a** and **5a** shows a viscosity-dependent activation barrier. This is consistent with the two-state model: $A \rightarrow A^* \leftrightarrow B^*$, where A^* belongs to the local excited planar conformer and B^* to the twisted one.

Acknowledgement

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