Protonation of 2-quinolylthiazoles in the ground and excited states in ethanol

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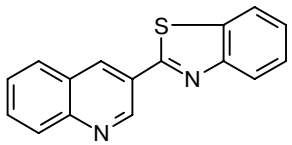
The protonation of some 2-quinolylthiazoles by trichloroacetic, trifluoroacetic, and sulfuric acids in the ground and excited states was studied in ethanol. The formation of the cations was found in the reaction with sulfuric acid. The formation of a mixture of cations and ionic pairs was found in the reactions with trichloroacetic and trifluoroacetic acids. The spectral-luminescence parameters of the reaction products obtained and the kinetic characteristics of the processes were determined.

Key words: 2-quinolylthiazoles, ionic pair, cation, fluorescence, kinetics, protonation.

2-Quinolyloxazoles are weak bases, whose basicity increases on excitation. The reaction of 2- and 4-quinolyloxazoles with acetic acid in ethanol affords complexes with a hydrogen bond in the excited state.[1] The reactions of these fluorophores with sulfuric acid give cations.[1] 2-Quinolylthiazoles are weaker bases than 2-quinolyloxazoles[2]; therefore, mechanisms of their protonation can differ.

This work is aimed at studying the mechanism of the reaction of 2-quinolylthiazoles with proton donors of different strengths in the ground and excited states. We studied the processes occurring in the reactions of 2-(3-quinolyl)-1,3-benzothiazole (**1**), 5-phenyl-2-(3-quinolyl)-1,3-thiazole (**2**), 2-(3-quinolyl)naphtho[1,2-*d*][1,3]thiazole (**3**), and 5-phenyl-2-(3-quinolyl)-1,3-benzothiazole (**4**) with acetic, trichloroacetic, trifluoroacetic, and sulfuric acids in ethanol in the ground and excited states.



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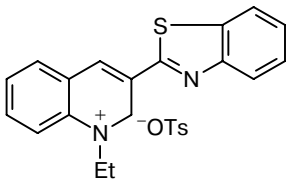

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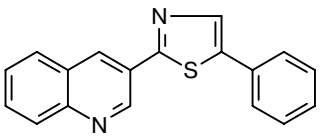

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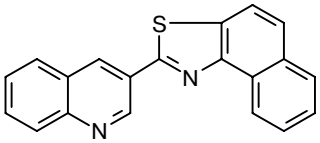

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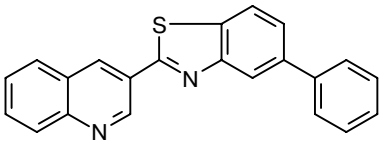

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Experimental

Absorption and fluorescence spectra were measured on a Shimadzu-3100 spectrophotometer and an Elyumin-2M spectrofluorimeter. Quantum yields of fluorescence (φ) were calculated by comparing the surface areas under corrected fluorescence spectra of fluorophores in ethanol and solutions of quinine bisulfate in 1 *N* H_2SO_4 (φ = 0.546).[3] Basicity constants of the initial compounds in the ground state and wavelengths of absorption maxima of the products were calculated by the home-generated software EQUILI program based on multidimensional nonlinear least-squares method,[4] using absorbances of nine solutions with different acid concentrations at 39 values of wavelength. Basicity constants of the compounds in the excited state were obtained using Förster's method.[5] The fluorescence kinetics in solutions was measured on an SP-70 nanosecond spectrometer with a channel width of 54 ps by a single-proton counting technique. Acetic, trichloroacetic, and trifluoroacetic acids were purified by distillation, ethanol was distilled above CaH_2, and H_2SO_4 (special purity grade) was used as received. Compounds **1—4** and **1a** were synthesized by

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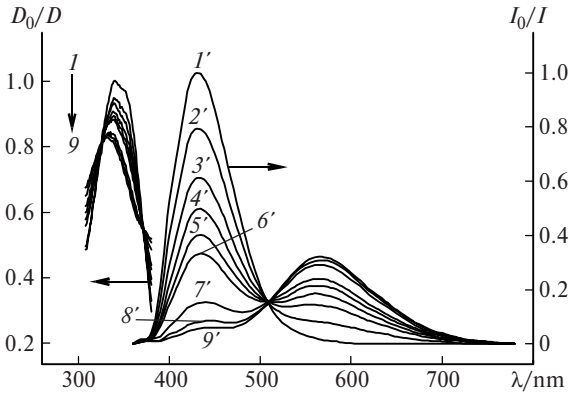


Fig. 1. Region of absorption spectra with isosbestic points (*1*—*9*) and fluorescence spectra (*1′*—*9′*) of compound **2** in ethanol at 20 °C: $[H_2SO_4]$ = 0 (*1*, *1′*), 0.01 (*2*, *2′*), 0.02 (*3*, *3′*), 0.03 (*4*, *4′*), 0.04 (*5*, *5′*), 0.05 (*6*, *6′*), 0.1 (*7*, *7′*), 0.15 (*8*, *8′*), and 0.2 mol L^{-1} (*9*, *9′*).

a previously described procedure.[6] All measurements were carried out at 20 °C.

Results and Discussion

The addition of sulfuric (to 0.2 mol L^{-1}) or trichloroacetic and trifluoroacetic acids (to 1 mol L^{-1}) to solutions of compounds **1—4** in ethanol results in the long-wave shift of their absorption and fluorescence spectra (Fig. 1). Analysis of the spectral series by the Wallace—Katz method[7] revealed, that two molecular forms (initial and monoprotonated) of each compounds are present in both the ground and excited states. The quantum yields of fluorescence of the photoprotonation products are lower than the corresponding values for the initial compounds. The addition of acetic acid to solutions of **1—4** in ethanol did not result in the appearance of shifts in either absorption or fluorescence spectra. The spectra are only broadened at a high (>3 mol L^{-1}) concentration of acetic acid.

The $-\log K_a$ values for solutions of quinoline and 1,3-benzothiazole in ethanol are 4.58 and 1.41, respectively.[2] The maxima in the absorption and fluorescence spectra of an ethanolic solution of **1a** are close to those in the spectra of compound **1** protonated with sulfuric acid. This suggests that in a moderately acidic medium the protonation of **1—4** occurs only at the N atom of the quinoline fragment.

The $\log K_b$ values of all four compounds in the ground state are close (Table 1). The increase in the $-\log K_b$ value, depending on the type of the acid used, corresponds to the decrease in $-\log K_a$ for CCl_3COOH, CF_3COOH, and H_2SO_4 in ethanol at 20 °C (5.7,[8] 5.24,[9] and 1.42,[9] respectively). The same dependence for $-\log K_b$* has a similar character, except for the reaction of compounds **1**, **2**, and **4** with CF_3COOH: these values are lower than the expected values. Weaker acetic acid ($-\log K_a$ = 10.4)[8] does not form with compounds **1—4** any products in either the ground or excited state.

Table 1. Maxima of absorption (λ_{abs}) and fluorescence (λ_{fl}) spectra, quantum yields of fluorescence (φ) of compounds **1—4** and products of their protonation in EtOH, and basicity parameters of compounds **1—4** in the ground state ($\log K_b$)

Compound	Reactant	λ_{abs} / nm	λ_{fl} / nm	φ (φ_∞')*	$\log K_b$
1	—	330	387	0.05	—
	CCl_3COOH	361	497	(0.03)	0.22
	CF_3COOH	355	501	(0.04)	0.49
	H_2SO_4	359	515	(0.03)	1.28
2	—	340	422	0.20	—
	CCl_3COOH	383	574	(0.12)	0.49
	CF_3COOH	374	576	(0.11)	0.61
	H_2SO_4	384	580	(0.13)	1.40
3	—	360	432	0.15	—
	CCl_3COOH	394	588	(0.05)	0.41
	CF_3COOH	394	601	(0.04)	0.52
	H_2SO_4	396	607	(0.05)	1.29
4	—	318	433	0.01	—
	CCl_3COOH	366	575	(0.005)	0.24
	CF_3COOH	358	597	(0.003)	0.48
	H_2SO_4	364	602	(0.003)	1.06

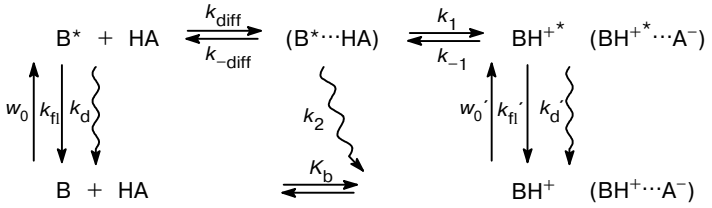
* Limiting quantum yields of fluorescence at the acid concentration $\to \infty$. All measurements were performed at 20 °C.

The substantial long-wave shift in the absorption spectra of **1—4** induced by the addition of acids allows the exclusion of a complex formation with the hydrogen bond between a base and acid in the ground state. The consecutive long-wave shift of the maximum in the fluorescence spectrum observed for compounds **1—4** on going from trichloroacetic to sulfuric acid (see Table 1) suggests that predominantly ionic pairs with a hydrogen bond are formed between the protonated N atom of quinolyl and the CCl_3COO^- anion in the reaction with weaker trichloroacetic acid. In the reaction of stronger trifluoroacetic acid, the contribution of ionic pairs becomes lower, and the fluorescence of only the protonated cation is observed for the reaction with sulfuric acid. The identity of positions of the maxima in the fluorescence spectra for the **1**—EtOH—3*M* H_2SO_4, **1a**—EtOH—3*M* CCl_3COOH, and **1a**—EtOH—3*M* H_2SO_4 systems and the short-wave shift of the maximum in the fluorescence spectra for **1**—EtOH—3*M* CF_3COOH and **1**—EtOH—3*M* CCl_3COOH as compared to the fluorescence spectrum of the cation confirm the above assumption. Ionic pairs are poorly solvated than cations, which explains their shorter-wave emission. The quantum yields of fluorescence of the ionic pair and cation are approximately equal.

The processes that occur in the systems under study can be described by the kinetic scheme (Scheme 1), excitation occurring in the isosbestic point.

In Scheme 1 (B*···HA) is the encounter complex between compound B and proton donor HA; τ_0 is the fluorescence lifetime of the initial compound; k_{diff} and k_{-diff} are the rates constants of formation and dissocia-

Scheme 1



tion of the encounter complex, respectively; k_1 and k_2 are the rate constants of formation of the excited product and nonradiative deactivation induced by the photoprotonation reaction; and k_{-1} is the rate constant of the back photoreaction. The k_{diff} and k_{-diff} values were calculated from the equations[10—12]

$$k_{diff} = 4\pi r_c(D_B + D_{HA})N_A\delta/(e^{\delta} - 1), \quad (1)$$

$$k_{-diff} = k_{diff}\delta/[V_c(1 - e^{-\delta})], \quad (2)$$

$$\delta = Z_B Z_{HA} e^2 N_A/(\varepsilon r_c RT), \quad (3)$$

where r_c and V_c are the radius and volume of the (B*···HA) encounter complex, D_B and D_{HA} are the diffusion coefficients of B* and HA, Z_B and Z_{HA} are the charges of compounds B and HA, and ε is the dielectric constant of the solvent.

The molar ratio of nondissociated CCl_3COOH (CF_3COOH) molecules and solvated $EtOH_2^+$ protons in 1 *M* solutions of acids is 180 : 1 and 104 : 1, respectively. Therefore, the nondissociated acid molecules should be considered as prevailing, although weaker protonating agents compared to the $EtOH_2^+$ cations and the D_B and the D_{HA} values for these systems should be calculated from the equation[13]

$$D_{B(HA)} = 1.4 \cdot 10^{-4}/(V^{0.6}\eta_s), \quad (4)$$

where *V* is the molar volume of B (HA), and η_s is the viscosity of the solvent at 20 °C. Sulfuric acid dissociates to a great extent in ethanol by the first step (the molar ratio for the nondissociated molecules and solvated protons for a 1 *M* solution is ~1 : 1.1), and its dissociation by the second step at 20 °C is negligible ($-\log K_a^{II} = 6.7$).[9] For solutions of H_2SO_4 the diffusion coefficient of the solvated proton is calculated from the equation

$$D_H = \lambda_+ RT/F^2, \quad (5)$$

where λ_+ is the limiting proton conductivity of the solvent, and *F* is the Faraday constant.

According to this scheme, the relative quantum yield of fluorescence of the initial form can be expressed by the equality

$$\varphi_0/\varphi = (1 + K_b[HA])(1 + k_q\tau_0[HA]), \quad (6)$$

where φ_0 and φ are the quantum yields of fluorescence of the initial form in the absence and presence of a quencher, respectively; and k_q is the effective rate constant for fluorescence quenching of B:

$$k_q = \frac{k_{diff}[k_1 + k_2(1 + k_{-1}\tau_0')] - k_{-diff}k_{-1}(\tau_0'/\tau_0)K_b}{k_1 + (k_2 + k_{-diff})(1 + k_{-1}\tau_0') + k_{-diff}k_{-1}\tau_0'K_b[HA]}, \quad (7)$$

where τ_0' is the fluorescence lifetime of the protonation product when it is excited from the ground state. Under the condition $k_{-1} \ll k_1$, the photodissociation of the product can be neglected

$$k_q = k_{diff}(k_1 + k_2)/(k_1 + k_2 + k_{-diff})$$

or

$$k_1 + k_2 = k_q k_{-diff}/(k_{diff} - k_q). \quad (8)$$

In the case of comparable k_1 and k_{-1} values at $k_2 \to 0$, the following equality is valid:

$$k_q = \frac{k_{diff}k_1 - k_{-diff}k_{-1}(\tau_0'/\tau_0)K_b}{k_1 + k_{-diff}[1 + k_{-1}\tau_0'(1 + K_b[HA])]}. \quad (9)$$

Evidently, the k_q value is independent of the quencher concentration at $k_{-1} \to 0$. Taking into account that in the 2-quinolyloxazoles—EtOH—AcOH systems[1] related to the studied systems, k_{-1} is negligible compared to k_1, the k_q and $k_1 + k_2$ values can be obtained from Eqs. (6) and (8) (Table 2). This assumption was also confirmed by calculations from Eqs. (6) and (7).

Consideration of Scheme 1 without the intermediate reaction of formation of the (B···HA) complex under the condition $k_{-1} \to 0$ results in the following expression that describes the time dependence of the concentration of the excited protonation product BH^+ ($BH^+\cdots A^-$) under pulse excitation:

$$[BH^{+*}] = C_1\exp(-t/\tau_0') + C_2\exp\{-t[(1/\tau_0) + (k_1' + k_2')[HA]]\}. \quad (10)$$

Here τ_0, τ_0' are the fluorescence lifetimes of B and BH^+ in the absence of any reactions in the excited state, C_1 and C_2 are the parameters determined from the initial excitation conditions. The biexponential fluorescence kinetics of the BH^+ product obtained in the spectral region where fluorescence of the initial compound B is negligible allows the use of Eq. (10) for its description. The absence of significant changes in the experimental τ_0' values for the (**1**—**4**)—EtOH—H_2SO_4 systems with an increase in the H_2SO_4 concentration from 1 to 1.5 mol L^{-1} confirms the assumption on negligible values of the photodissociation rate constants in these

Table 2. Kinetic parameters of proton transfer (k_{diff}, k_q, $k_1 + k_2$), basicity parameters in the excited state ($\log K_b^*$), and lifetimes of fluorescence of compounds **1—4** in EtOH at 20 °C

Compound	$\log K_b^*$			τ_0 /ns	$k_{diff} \cdot 10^{-9}$			$k_q \cdot 10^{-9}$			$(k_1 + k_2) \cdot 10^{-9}$		
					L mol^{-1} s^{-1}						/s^{-1}		
	I[a]	II[b]	III[c]		I[a]	II[b]	H_{solv}[d]	I[a]	II[b]	III[c]	I[a]	II[b]	III[c]
1	5.77	5.04	6.50	0.3	9.1	9.5	13.5	1.0	0.2	11.1	0.4	0.1	27.6
2	7.53	6.31	8.59	0.6	9.1	9.4	14.4	3.9	1.1	14.9	2.4	0.5	—
3	5.52	5.63	6.67	0.7	9.1	9.4	14.3	1.0	1.3	12.7	0.4	0.6	44.6
4	9.03	7.97	9.54	0.5	9.0	9.4	13.4	0.3	0.3	8.3	0.1	0.1	8.4

Protonating agents: [a] CCl_3COOH, [b] CF_3COOH, [c] H_2SO_4.
[d] Solvated proton.

reactions. The τ_0' values for $\mathbf{1}H^+$, $\mathbf{2}H^+$, $\mathbf{3}H^+$, and $\mathbf{4}H^+$ in EtOH are 1.4, 2.1, 1.0, and 0.1 ns, respectively.

The experimental k_q values do not correlate with the corresponding k_{diff}; moreover, for solutions of H_2SO_4 the k_q values are close to k_{diff}. The main role in changing k_q and $k_1 + k_2$ on going from trichloroacetic to sulfuric acid is played by the $\log K_b^*$ value: the constant for fluorescence quenching of the studied compounds increases with an increase in their basicity in the excited state (except for the **4**—EtOH—CF_3COOH system) (see Table 2).

Thus, 2-quinolylthiazoles react with trichloroacetic and trifluoroacetic acids to form in the ground and excited states mainly ionic pairs with a minor fraction of cations, and the reaction with sulfuric acid affords only cations. This is also confirmed by the fact that the calculated φ_0/φ values for all studied fluorophores in the reactions with CCl_3COOH and CF_3COOH agree more poorly with the experimentally determined values than those in the reaction with sulfuric acid.

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