Photophysical Properties of Some Quindoline Bases and their Salts

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The title compounds are used as sensitizers in electrophotography. The dependence of their absorption and luminescence characteristics on the substituent, medium and temperature is investigated. The influence of various factors on the equilibrium base – salt in solution is elucidated. On the basis of changes in the absorption spectra with concentration the equilibrium constants K_q are determined.

I. Introduction

10-Alkylquindolines (I) and their salts (II) (Fig. 1) are used as sensitizers in electrophotographic layers based on poly(N-epoxypropylcarbazole) [1, 2].

However, in the literature there are no data about the spectral properties of this type of compounds. As it was shown recently for compounds with similar application [3–5], the photophysical properties are important for understanding their sensitizing ability. Therefore the aim of this work is to study in detail the absorption and luminescence characteristics of this class of compounds in dependence of the substituent, medium and temperature. In the course of the investigations it became possible to use their absorption properties to determine the salt-base equilibrium constants in solution.

The substituents R1, R2, R3 and the counterion X- are specified in Table 1.

II. Experimental

The synthesis of the investigated compounds **1**–**9** is described in [1, 2]. The absorption spectra were taken on a Specord M-40 spectrophotometer (Carl Zeiss, Jena) at concentrations less than 10^{-4} mol l^{-1}. The corrected luminescence and excitation spectra at room temperature and 77 K were recorded on a spectrofluorimeter Perkin Elmer MPF 44 B, 3-aminophthalimide ($Q_f = 0.6$ in ethanol [6]) was used as a standard for the determination of the relative fluorescence quantum yield Q_f. The low-temperature luminescence measurements were performed at 77 K using the standard phosphorescence accessory to the MPF 44 B. The natural lifetime was measured on a nanosecond spectrofluorimeter PRA 2000. The solvents used were of fluorescence grade. The solutions of the salts were stabilized by adding an approximately 1 vol.% $HClO_4$ to a 10^{-4} M solution.

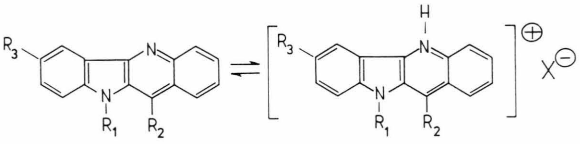

Fig. 1. Structures investigated.

Table 1. Substituents R1, R2, R3 and counterion X$^-$.

	R1	R2	R3	X$^-$
1	$CH_2-\underset{\substack{\vert \\ OH}}{C}H-CH_2$	H	H	–
2	CH_3	$COOCH_3$	H	–
3	CH_3	$COOCH_3$	Br	–
4	$CH_2CH=CH_2$	H	H	–
5	$CH_2(CH_2)_2CH_3$	H	Br	–
6	CH_3	$COOCH_3$	Br	Br
7	CH_3	$COOCH_3$	H	ClO_4
8	$CH_2(CH_2)_2CH_3$	H	Br	BrF_4
9	$CH_2C_6H_5$	H	H	Cl

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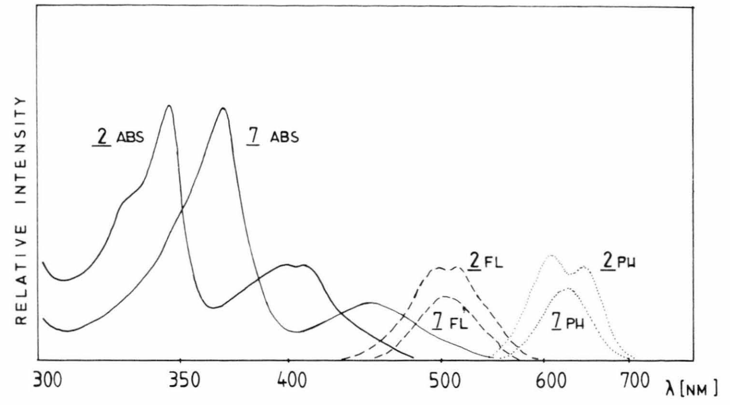

Fig. 2. Absorption (——), fluorescence (- - -) and phosphorescence (...) spectra of the base **2** and the corresponding salt **7** in ethanol.

Table 2. Experimental spectral characteristics of the compounds in ethanol. λ (A) absorption maximum (nm); ε molar absorptivity (l mol^{-1} cm^{-1}); λ (fl) fluorescence maximum (nm); Q_f fluorescence quantum yield; λ (ph) phosphorescence maximum (nm); I (f)/I (ph) fluorescence vs. phosphorescence intensity at 77 K, $\lambda_{ex} = 400$ nm.

	λ (A)	ε	λ (f)	Q_f	λ (ph)	$\frac{I\text{ (f)}}{I\text{ (ph)}}$ (77 K)
1	345.405	18 540.3100	445	0.27	545.505	9
2	347.406	10 880.3280	501	0.11	555.610	8
3	348.412	16 480.4250	490	0.013	570	0.8
4	344.406	18 260.3820	432	0.19	542.590	20
5	346.399	21 730.3750	462	0.42	560.580	2
6	377.440	27 880.2700	490	0.001	650	3
7	375.452	49 630.5950	518	0.003	640	100
8	367.433	44 810.3570	537	0.008	630	3
9	368.434	31 810.3520	530	0.05	620	100

III. Results and Discussion

In Table 2 the absorption and luminescence characteristics of the investigated compounds in ethanol at 293 K and 77 K are given. Figure 2 shows the absorption, fluorescence and phosphorescence spectrum of base **2** and the corresponding salt **7**.

III. A) Absorption

The absorption spectra of the bases are similar to those of the corresponding salts, characterized by two well defined bands (Figure 2). For the bases they are about 350 nm and 450 nm, while for the absorption spectra of the salts the two bands are bathochromically shifted by about 30 nm relative to the corresponding bases (compare compounds **2**–**7**, **3**–**6**, **5**–**8**). The salts (**6**, **7**, **8**, **9**, Table 2) have a higher molar absorptivity of the shorter-wavelength transition (340–380 nm).

III. B) Luminescence

The fluorescence maxima of the compounds studied are in the region 430–540 nm (Table 2). The energy of the fluorescence transition (unlike that of the absorption one) depends on the substituent both in the bases and the salts. Consequently, the substituents influence the electron density redistribution in the excited singlet $\pi\pi^*$ state to a greater extent than in the ground one. The data in Table 2 show no direct relation between the energy of the fluorescent FC transition and the fluorescence ability of the studied compounds.

10-Alkylquindolines may be regarded as conjugated systems composed of two main structural fragments: indole and quinoline; in both fragments the lowest-lying singlet $\eta\pi^*$ level is below 310 nm [7, 8]. According to [9] the energy of the $\eta\pi^*$ state is practically independent of the length of the conjugated system: consequently the lowest-lying singlet state of the investigated compounds, which is around 450 nm, is of $\pi\pi^*$ character and is about 10 000 cm^{-1} below the $\eta\pi^*$ level. The radiationless deactivation via the $\eta\pi^*$ state in similar structures is of low effectiveness [10], which together with the fixed planar structure of I determines the relatively high fluorescence quantum yields of the bases **1**–**5**.

The only exception is compound **3**, $Q_f = 0.013$ in ethanol, 293 K. The low fluorescence ability of this compound may result from the presence of a heavy atom (Br), which leads to an effective ISC. The experimental data in Table 2 show that the phosphorescence intensity of **3** in a frozen ethanol solution (77 K) is higher than the fluorescence intensity under the same conditions.

The comparison of the data for compounds **2** and **3**, which differ only in the R3 substituent, shows that the decrease of Q_f (293 K) of **3** relative to that of **2** (about 1 order of magnitude) is accompanied by an enhancement of the phosphorescence intensity (77 K) of **3** relative to that of **2** in practically the same ratio. It should be noted that a heavy Br atom in position R3 not always quenches the fluorescence of the investigated compounds, e.g. Q_f of **5** in solution is high ($Q_f = 0.42$). The difference in the luminescence characteristics of **3** and **5** obviously results from the specific effect of the substituents R1 and R2.

Q_f of the salts **6**–**9** is about 2 orders lower than that of the corresponding bases (solution, 293 K) – compare e.g. **2**–**7**, **3**–**6**, **5**–**8** in Table 2, the fluorescence FC transition being bathochromically shifted. These data show that upon changing from base to salt a significant change in the electron density distribution in the fluorescence S1 ($\pi\pi^*$) state occurs.

The frozen ethanol solutions (77 K) of all compounds studied exhibit intense phosphorescence and a well defined heavy atom effect. The intensity of the phosphorescence band of **3** is even higher than that of the fluorescence band under the same conditions (77 K, $\lambda_{exc} = 400$ nm). The triplet state lifetime is of the order of milliseconds.

The decay curve of the fluorescence intensity in ethanol at room temperature is fitted with a good precision to a monoexponential function. The computed natural lifetime of the fluorescent S1 ($\pi\pi^*$) state, the radiative and nonradiative lifetimes τ_f and τ_{nf} and the corresponding rate constants K_f and K_{nf} for some of the studied compounds are given in Table 3.

The measured natural lifetimes are about 10 ns, the radiative lifetimes are in the range 50–150 ns, the characteristics of the nonradiative transitions are of the same order of magnitude. In our opinion, the relatively delayed processes of radiative and intramolecular nonradiative deactivation of the first singlet excited state account for the high effectiveness of the studied compounds as sensitizers [1, 2].

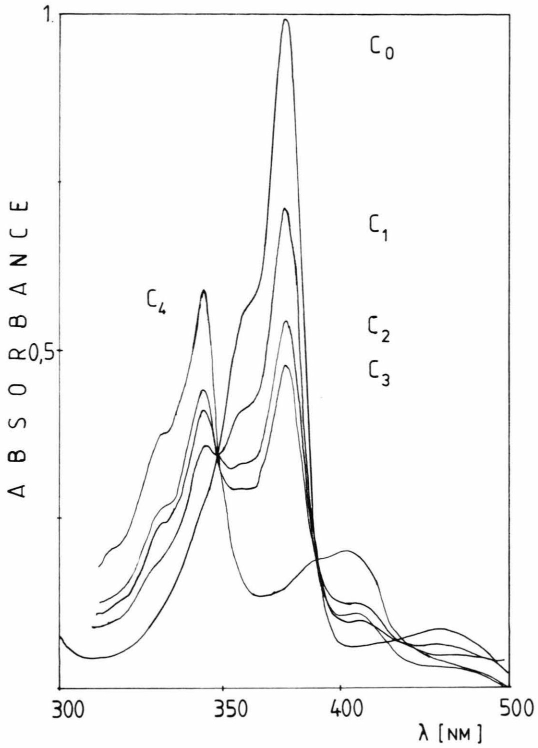

Fig. 3. Concentration dependence of **7** in CH_3CN; for all solutions $C * L = \text{const}$, where L is the path length. Concentrations: **1** 2.16×10^{-4}; **2** 1.08×10^{-4}; **3** 5.4×10^{-5}; **4** 2.7×10^{-5}; **5** 5.4×10^{-6} mol l^{-1}.

Table 3. Natural lifetime (τ), radiative (τ_f) and nonradiative (τ_{nf}) lifetime and corresponding constants of radiative (K_f) and nonradiative (K_{nf}) transitions, calculated from τ and Q_f in ethanol at 293 K. τ is calculated from the fluorescence decay curve, fitted to a monoexponential linear function $I(t) = A \cdot \exp(-t/\tau)$. For all cases $\chi^2 \leq 1.2$.

	τ (ns)	τ_f (ns)	τ_{nf} (ns)	K_f (ns^{-1})	K_{nf} (ns^{-1})
1	12.4	44.4	17.0	0.022	0.059
2	7.1	66.7	8.1	0.015	0.123
4	10.8	55.6	13.2	0.018	0.076
5	21.9	52.6	37.0	0.019	0.027
9	8.9	166.7	9.4	0.006	0.106

III. C) Characteristics of the Equilibrium Base-Salt

The absorption spectra of I and II in ethanol without adding acid are very similar, while only for **7** the bands at 345 nm and 400 nm, typical for the free base, and the bands at 370 nm and 440 nm, typical for the corresponding salt, are observed simultaneously. Therefore **7** was used for the evaluation of different factors influencing base-salt equilibrium: pH of the medium, concentration, solvent polarity, addition of surfactants, etc.

The adding of water in ethanol solution of **7** causes an increase of the band intensity which corresponds to the free base, and a decrease of the bands at 370 nm and 440 nm. The absorption spectra of the same compound in CH_3CN and CH_2Cl_2 are strongly dependent on the concentration (Figure 3). When the concentration increases, the relative intensity of the peaks, corresponding to the salt, increases. The opposite is true on dilution for all the compounds (**6**–**9**) investigated. In all cases, when a small amount of acid (H^+) is added to an alcoholic solution of the base or to its corresponding salt, a strong shift of the absorption bands towards the peaks corresponding to the salt is observed. If a surface active agent (SAA) is added to the ethanol solution of **7**, it causes an apparent shift towards the spectrum of the free base.

All these experimental data allow us to suggest that the following equilibrium is taking place:

$$BH^+ \underset{C,\,H^+}{\overset{SAA,\,H_2O}{\rightleftarrows}} B + H^+, \tag{1}$$

where BH^+ and B are the conjugated acid and its free base and:

$$K_{eq} = \frac{(B) * (H^+)}{(BH^+)} \tag{2}$$

Following the well known transformation and assuming that the total concentration C_t of the salt is:

$$C_t = C_{BH^+} + C_B + C_{H^+}, \tag{3}$$

where during solvation

$$C_B = C_{H^+}, \tag{4}$$

and introducing the molar part α:

$$\alpha = C_{BH^+}/C_t, \tag{5}$$

then the equilibrium constant K_{eq} is

$$K_{eq} = \frac{C_t(1-\alpha)^2}{4\alpha} \tag{6}$$

If the absorption and fluorescence of both forms B and BH^+ is different, it is possible to investigate quantitatively all factors affecting this equilibrium, using (7) and (8):

$$\alpha = \frac{\varepsilon_{OBS}(\lambda_1) - \varepsilon_B(\lambda_1)}{\varepsilon_{BH^+}(\lambda_1) - \varepsilon_B(\lambda_1)}, \tag{7}$$

$$\alpha = \frac{\varepsilon_B(\lambda_2) - \varepsilon_{OBS}(\lambda_2)}{\varepsilon_B(\lambda_2) - \varepsilon_{BH^+}(\lambda_2)}, \tag{8}$$

where λ_1 and λ_2 are the wavelengths were the forms BH^+ and B are dominating: $\varepsilon_{OBS}(\lambda_i)$, $\varepsilon_B(\lambda_i)$ and $\varepsilon_{BH^+}(\lambda_i)$ are the molar absorptivities of the observed solution, free base and its conjugation acid, respectively at appropriate wavelengths λ_i.

From the (6) it is evident that when the total concentration C_t is increased, the value of α, respectively the molar part of BH^+, also increases and the equilibrium (1) is shifted towards the conjugated acid BH^+. The influence of H^+, SAA and H_2O could also easily be interpreted using the equilibrium (1) and the effect of solvolysis in the salts II.

Using (7) and (8) the values of K_{eq} for **7** in CH_3CN and CH_2Cl_2 were determined, the mean values being $5.02 \pm 1.17 \times 10^{-6}$ mol l^{-1} and $2.16 \pm 0.86 \times 10^{-7}$ mol l^{-1}. In ethanol the value of K_{eq} was estimated to approximately 7.5×10^{-4} mol l^{-1}, while adding of water causes shift of the equilibrium to the free base B, i.e. α approaches zero. These experimental data show that the polarity of the solvents is also an important factor for this equilibrium. The observed tendency is that at high concentrations and in low polar solvents the amount of BH^+ increases, while at lower concentrations and in polar solvents the free base B is dominating.

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