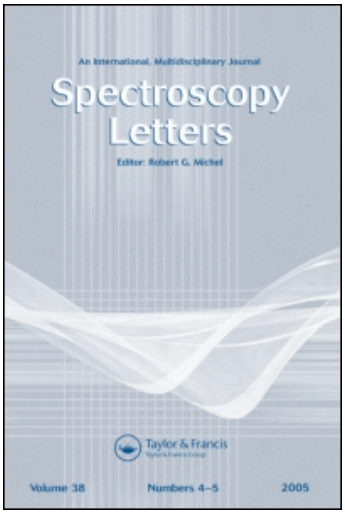

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Fluorescence Characteristics of Schiff Bases Derived from Amino- and Aminoalkylpyridines

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FLUORESCENCE CHARACTERISTICS OF SCHIFF BASES DERIVED FROM AMINO- AND AMINOALKYLPYRIDINES

Key words: aminopyridines, aminoalkylpyridines, fluorescence quantum efficiency, salicylaldehyde, Schiff base

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ABSTRACT

The fluorescence characteristics of the Schiff bases 2-(3-pyridylmethyliminomethyl)phenol (**1**), 2-(2-pyridyliminomethyl)phenol (**2**), N,N'-bis(salicylidene)-2,3-pyridinediamine (**3**), N,N'-bis(salicylidene)-2,6-pyridinediamine (**4**) and 2-(2-amino-4-methoxymethyl-6-methyl-3-pyridylmethyliminomethyl)phenol (**5**) were studied in various solvents at different pH values. Corresponding quantum efficiencies were determined. Compound **1**, which showed a tendency towards tautomeric interconversion to ketoamine in polar protic solvents, was not fluorescent at pH < 8. The fluorescence of other compounds was very sensitive to solvent polarity and the pH of the medium. Compounds **2** - **4**, preferably present as enolimines in all solvents, were not fluorescent in non-polar and moderately polar solvents, whereas weak emission was observed in polar solvents, like methanol, dimethylformamide and dioxane/water 1/1 ($0.001 < Q < 0.072$). A significant increase in Stokes shifts and in quantum efficiencies was noted as a result of increasing polarity of dioxane/water mixtures, indicating specific

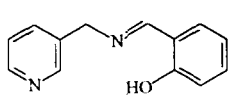
interactions with polar water molecules. The emission was promoted at acidic pH values where a pyridinium cation was formed ($0.061 < Q < 0.519$, in dioxane/water 1/1 at pH 3.4). Compound **5**, which was a tautomeric mixture of enolimine and cyclic diamine in all solvents, was fluorescent in polar as well as in non-polar media. The quantum efficiency varied dependent on the solvent and pH ($0.023 < Q < 0.435$). The cyclic diamine, i. e. the more rigid structure was supposed to be responsible for the fluorescence in non-polar and aprotic solvents as well as at neutral, and weakly basic pH values.

INTRODUCTION

The interest in the spectral characteristics of Schiff bases is associated with their role in biochemical equilibria, as well as with their analytical applications. The luminescence properties of Schiff bases are useful for recognizing biochemically relevant details and can be a basis for the development of new, highly sensitive analytical methods. Additionally, luminescence properties are important for investigations of photochromism and thermochromism. These facts have motivated a number of works about fluorescent aromatic Schiff bases [1-9].

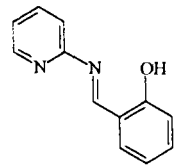
However, there are limited data on the luminescence of heteroaromatic Schiff bases, although they might be very attractive compounds, particularly for analytical applications [10-12]. Holzbecher measured the fluorescence intensity of 2-(2-pyridyliminomethyl)phenol in a dioxane/water mixture. He noted a significant increase in emission intensity when going from neutral to alkaline or acidic medium, as well as in the presence of some metal ions [11]. Valcarcel utilized the fluorescence properties of salicylaldehyde picolinoylhydrazone to develop Al(III) sensitive sensors [12].

We have systematically studied the fluorescence properties of a series of recently prepared [13-16] Schiff bases derived from amino- or aminoalkylpyridines and salicylaldehyde, some of which possess promising characteristics for analytical applications (Scheme 1) [17]. Here, we report on the quantum efficiencies of this group of Schiff bases in pure solvents of different polarity, in mixtures of dioxane and water as well as at various pH values.



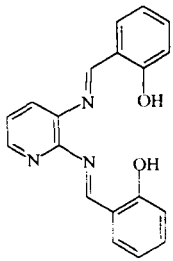
2-(3-pyridylmethyliminomethyl)phenol

1



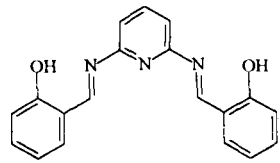
2-(2-pyridyliminomethyl)phenol

2



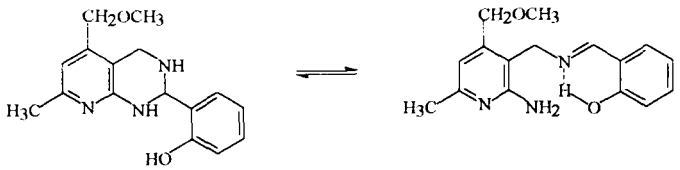
N,N'-bis(salicylidene)-2,3- pyridinediamine

3



N,N'-bis(salicylidene)-2,6-pyridinediamine

4



2-(2-amino-4-methoxymethyl-6-methyl-3-pyridylmethyliminomethyl)phenol

5

Scheme 1

EXPERIMENTAL

General procedures for the preparation of Schiff bases of amino- and aminoalkylpyridines have already been reported [13-16]. All other chemicals were of p.a. purity grade. All solutions were prepared with solvents of spectroscopic grade (additionally purified when necessary) and doubly deionized water that was free from carbon dioxide.

Stock solutions of Schiff bases were prepared in an appropriate organic solvent. The concentrations in working solutions were $1.0 \cdot 10^{-4}$ M or $5.0 \cdot 10^{-5}$ M for UV-vis absorption measurements and $1.0 \cdot 10^{-5}$ M or $5.0 \cdot 10^{-6}$ M for fluorescence measurements. Dilution of working solution for fluorescence measurements was sufficient (absorbance < 0.1) to consider self-absorption negligible. The pH was adjusted with standard buffers (acetic acid - sodium acetate buffer and universal buffer mixture consisting of acetic, phosphoric and boric acid and their sodium salts). Quenching by oxygen was avoided by bubbling each solution with N_2 for 2-3 minutes before fluorescence measurement.

UV-vis absorption spectral data were obtained on a Varian Cary 3 spectrometer. Fluorescence measurements, correction of spectra and integration of the corrected spectra area were performed on a Perkin Elmer LS 50 fluorescence spectrometer. Conventional quartz cells (10 x 10 mm) were used throughout.

The samples were thermostated during the measurements at 20 °C. Spectra were always recorded within the first three minutes following the preparation of the solution, as hydrolysis of Schiff bases may take place in solvents containing water.

The excitation source (a xenon lamp) was calibrated using the high absorbance solution method [18] and rodamin B ($1.0 \cdot 10^{-5}$ M solution in deionized water) as a quantum counter ($\lambda_{em} = 581$ nm).

Relative fluorescence quantum efficiencies were calculated by the method of Parker and Rees [19] from the equation:

$$Q_s = Q_r \cdot \frac{A_r(\lambda_r)}{A_s(\lambda_s)} \cdot \frac{I(\lambda_r)}{I(\lambda_s)} \cdot \frac{n_s^2}{n_r^2} \cdot \frac{D_s}{D_r}$$

where , Q: quantum efficiency;

$A(\lambda)$: absorbance of the solution at excitation wavelength;

$I(\lambda)$: relative intensity of the exciting light at wavelength λ;

D: integrated area under the corrected emission spectrum;

n: refractive index;

subscripts r and s relate to the reference material and sample, respectively.

Quinine sulfate solution (1.0 ppm solution in 1.0 M sulfuric acid) was used as a reference standard. Refractive indexes of solvents were measured on a differential Brice-Phoenix refractometer, Model BP-2000-v.

Fluorescence sensitivities were calculated as follows:

$$F.S. = Q \cdot \varepsilon$$

where ε is molar absorption coefficient.

For pH measurements a Radiometer pH/mV meter, Model pHM 85 with a Radiometer combined glass-calomel electrode GK2401 C was used. The pH meter was calibrated with standard aqueous buffer solutions. Factors, U_H, of van Uitert and Haas [20] for conversion of the pH measured in dioxane/water 1/1 (mol % of water, x = 0.83%) to H^+ concentrations, log m_H, amount to $-0.1 < \log U_H < 0.1$ by applied ionic strengths.

RESULTS AND DISCUSSION

Equilibria in the Solution

It has been shown recently [15, 21] that in the ground state, in non-polar solvents compounds **1** - **4** were in the enolimino form with a strong hydrogen bond between the imino nitrogen and the proton of the hydroxylic group. A tendency of interconversion to ketoamine was noted in polar, protic solvents and was significant only in the case of compound **1**. Accordingly, the tautomeric constant, K_t (K_t = [ketoamine]/[enolimine]) of compound **1** in methanol amounted to 0.1, whereas K_t of compounds **2**, **3** and **4** in the same solvent was 0.01, 0.08 and 0.02, respectively. It was also shown [13] that compound **5** was a mixture of cyclic diamine and enolimine in most solvents. The enolimino form was preferably present in polar, protic solvents, like alcohols. A cyclic form was prefered in less polar or aprotic solvents, like diethyl ether, chloroform, dioxane and dimethylformamide.

UV-vis Spectroscopic Characteristics

The absorption and emission characteristics of compounds **1** - **5** in different solvent systems are listed in Table 1. The long wave UV absorption maxima were in the region

TABLE 1

Absorption and Emission Characteristics of Compounds **1** - **5** in Different Solvents

Compound	Solvent	λ_{abs} nm	λ_{ex} nm	λ_{em} nm	$\varepsilon \cdot 10^{-4}$ $mol^{-1}\ dm^3\ cm^{-1}$	Q
1	Dioxane/H_2O 1/1[a]	316	-	-	0.37	-
	Dimethylformamide	317	-	-	0.42	-
	Methanol[a]	317	-	-	0.42	-
	Dioxane	318	-	-	0.46	-
2	Dioxane/H_2O 1/1[a]	305	304	365	1.08	0.072
	Dimethylformamide	306	309	341	1.30	0.001
	Methanol[a]	304	306	339	1.33	0.001
	Dioxane	305	306	339	1.33	0.001
3	Dioxane/H_2O 1/1[a]	338	338	381	1.78	0.001
	Dimethylformamide	338	412	507	2.03	0.024
	Methanol[a]	339	339	381	2.01	0.001
	Dioxane	339	-	-	2.16	-
4	Dioxane/H_2O 1/1[a]	331	331	387	1.42	0.053
	Dimethylformamide	371	422	507	2.43	0.002
	Methanol[a]	367	367	387	2.45	0.001
	Dioxane	372	-	-	2.48	-
5	Dioxane/H_2O 1/1[b]	312	312	376	0.75	0.295
	Dimethylformamide[b]	311	313	372	0.61	0.435
	Methanol[b]	311	312	372	0.75	0.064
	Dioxane[b]	310	310	364	0.79	0.203

[a] A weak additional absorption band of the ketoamino form is observable above 400 nm.

[b] Absorption maximum is due to the absorption of both, enolimino and cyclic forms.

305 - 372 nm. These maxima corresponded to the enolimino form and were assigned to $\pi^* \leftarrow \pi$ transition extending over the entire molecule [7, 22]. In the case of compounds **1** - **4** in polar protic solvents, an additional absorption band of ketoamine appeared above 400 nm (e.g. 403 nm, comp. **1**; 442 nm, comp. **2**; 466 nm, comp. **3**; 452 nm, comp. **4**). Whereas this band of compound **1** was always perceptible in polar solvents, the ketoamine band of compounds **2** - **4** was very weak, growing noticeable only at increased concentrations. The band was missing in the spectrum of compound **5**. In the case of compound **5**, only one band was present in the long wave region. The intensity of this band (310 nm < λ_{max} < 312 nm) changed with changes in the ratio of cyclic diamine and

enolimine, revealing that both forms had the same absorption maximum, but different molar absorption coefficients.

The emission caused by excitation at the absorption maximum of enolimine (cyclic diamine) depended strongly on solvent properties. Compound **1** was not fluorescent in the investigated solvents at pH < 8. Compounds **2** - **4** were not fluorescent in non-polar and moderately polar solvents, like hexan, diethyl ether and chloroform, whereas weak emission was observed in polar solvents, like methanol, dimethylformamide and dioxane/water 1/1. Inspection of Table 1 reveals the differences between the wavelengths of absorption and the excitation maxima of compounds **3** and **4** in dimethylformamide. Such differences appear when more forms with different absorption and emission characteristics are in the equilibria. In solvents bearing atoms that can behave as Lewis bases, like dimethylformamide, the weak emission at 507 nm may be due to the presence of ionized or deprotonated forms (e.g. phenolate anion).

Compound **5** exhibited fluorescence in polar as well as in non-polar solvents. The strong emission in non-polar and aprotic solvents was ascribed to the cyclic form, preferably present in such medium. Cyclic diamine was more rigid than enolimine, giving rise to a decrease in the efficiency of non-radiative decay.

Fluorescence in Dioxane/Water System

The fluorescent characteristics of all compounds were studied in detail in the system dioxane/water of various volume ratios.

The corrected fluorescence spectra of compound **2** in various dioxane/water mixtures are shown in Fig. 1. The spectra are characterized by a small, solvent induced red shift and by a large increase in the fluorescence intensity through water addition in the more polar region.

Fig. 2 shows a plot of the Stokes shifts of compound **2** against the molar fraction of water and Fig. 3 a plot of the Stokes shifts against polarity of dioxane/water mixture. Since the dioxane/water mixture does not behave like ideal solvent mixture, polarity is expressed as empirical polarity parameter, D [23].

Stokes shifts exceeded the value of 5000 cm^{-1} after the addition of 0.7 mol % of H_2O (D > 30). Corresponding results have been obtained with compounds **3** and **4** as well. The value of the shift is a measure of the energy difference between the absorption wavelength

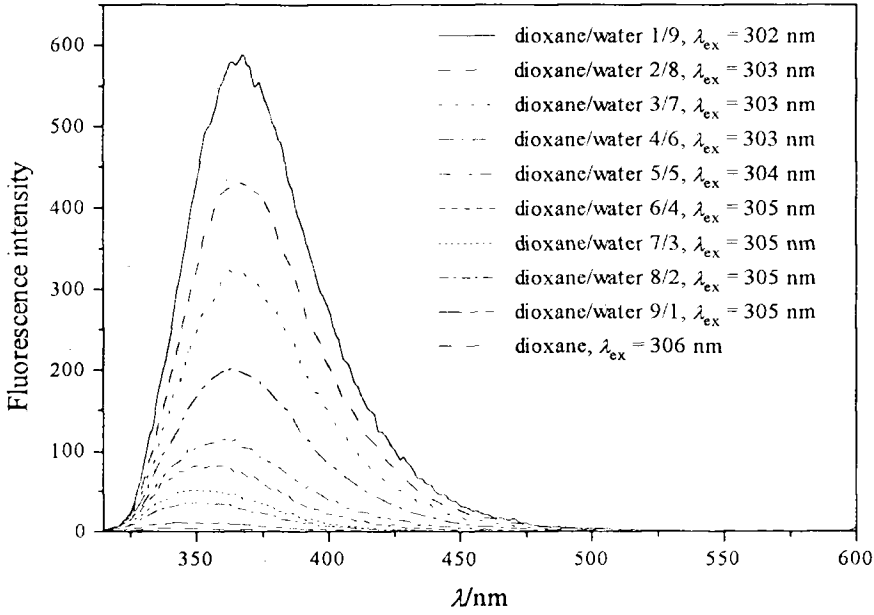


FIG. 1 The corrected emission spectra of compound **2** in dioxane/water mixtures.

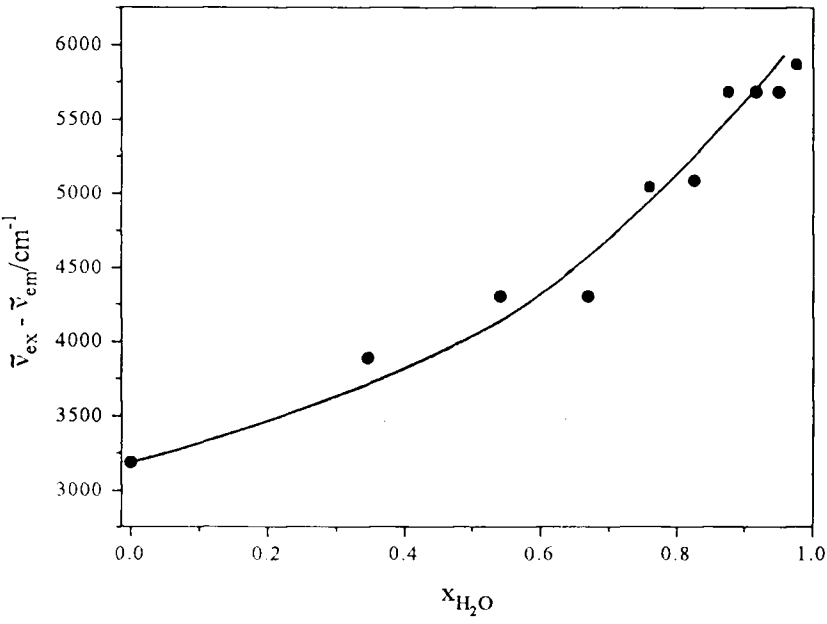


FIG. 2 Dependence of Stokes shifts of compound **2** on molar fraction of water in dioxane/water mixtures.

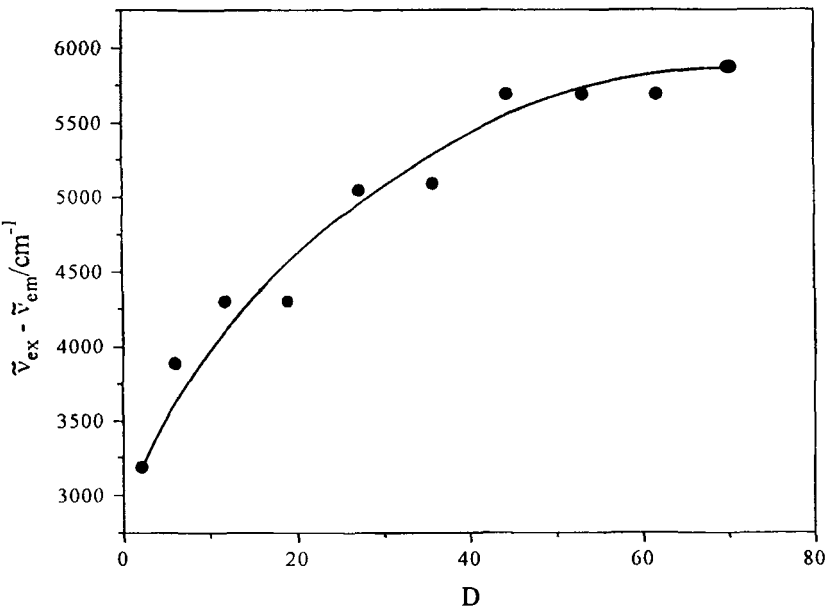


FIG. 3 Dependence of Stokes shifts of compound **2** on empirical polarity parameter [23] of dioxane/water mixtures.

and the fluorescence wavelength. For molecules in which no reaction occurs in the excited state, the Stokes shifts are mostly in the region of 2000 - 5000 cm^{-1}. A shift greater than this can be regarded as indicative of a reaction occurring when the molecule is in the excited state. The reaction robs the excited molecule of some of its absorbed energy and less is available for emission. Emission occurs from a new species formed during the reaction. The new species can be an ion, as the result of excited state ionization [24], or ketoimine formed during transition by proton transfer from the hydroxy group toward the nitrogen along the H bond [7], or most probably a complex between the enolimine in its excited state and the polar solvent molecule [25]. Figure 4 shows an increase in the quantum yield of compound **2** following increase in polarity parameter, D of dioxane/water mixture. In the region where D > 30 (above 0.7 mol % water), a significant increase in quantum efficiency was noted, indicating that transition was followed by the formation of a new species.

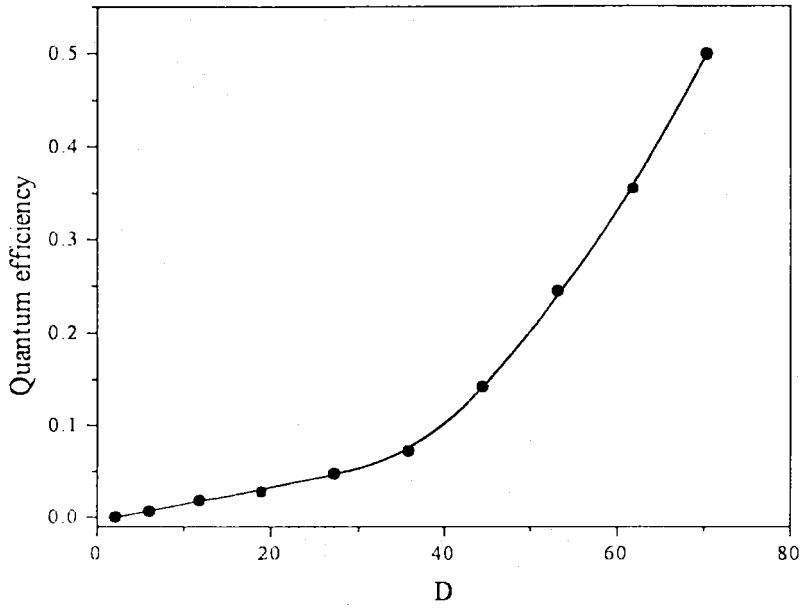


FIG. 4 Dependence of quantum efficiencies of compound **2** on polarity parameter [23] of dioxane/water mixtures.

Although also strongly dependent on the composition of dioxane/water mixtures, fluorescent properties of compound **5** were different compared with those of compounds **2** - **4**. Figure 5 shows dependence of quantum efficiency on the empirical polarity parameter, D. Quantum efficiency increased in the region $0 < D < 30$ but decreased with a further increase in solvent polarity. Stokes shifts varied in the range 5000 - 6000 cm^{-1}. Such characteristics of compound **5** can be explained by its tendencies towards ring - chain tautomerism. In less polar solutions, where the cyclic form was predominantly present, higher values of quantum efficiency were obtained than in strong polar protic solutions, where enolimine was prefered. A more detailed correlation between the solvent properties, tautomeric equilibria of compound **5** and its fluorescence characteristics will be the object of our further investigations.

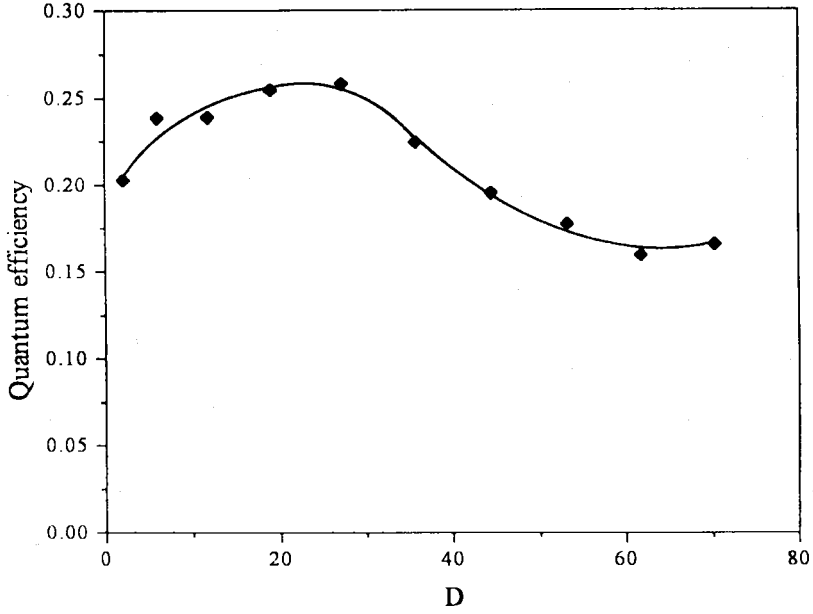


FIG. 5 Dependence of quantum efficiencies of compound **5** on polarity parameter [23] of dioxane/water mixtures. Dioxane/water 1/9, λ_{ex} = 311 nm, λ_{em} = 368 nm; dioxane/water 2/8, λ_{ex} = 312 nm, λ_{em} = 370 nm; dioxane/water 3/7, λ_{ex} = 312 nm, λ_{em} = 373 nm; dioxane/water 4/6, λ_{ex} = 312 nm, λ_{em} = 373 nm; dioxane/water 5/5, λ_{ex} = 312 nm, λ_{em} = 376 nm; dioxane/water 6/4, λ_{ex} = 311 nm, λ_{em} = 375 nm; dioxane/water 7/3, λ_{ex} = 311 nm, λ_{em} = 373 nm; dioxane/water 8/2, λ_{ex} = 311 nm, λ_{em} = 373 nm; dioxane/water 9/1, λ_{ex} = 310 nm, λ_{em} = 371 nm; dioxane, λ_{ex} = 310 nm, λ_{em} = 367 nm.

Dependence of Fluorescence Characteristics on pH

The quantum efficiency values of Schiff bases in dioxane/water 1/1 (mol % of water, x = 0.83%) at different pH values are listed in Table 2. Fig. 6. shows the dependence of the fluorescence sensitivities on pH. The fluorescence sensitivity, expressed as a product of the molar absorption coefficient and fluorescence quantum yield for a specific wavelength, is a measure of fluorescence intensity, suitable for comparing various compounds studied under identical conditions.

Compound **1** exhibited weak fluorescence at pH > 8 with maximum emission at 489 - 495 nm, when excited at 390 nm, the wavelength corresponding to the maximum

TABLE 2

Influence of pH on the Fluorescence Characteristics of Compounds **1** - **5** in Buffered Dioxane /Water 1/1 Solutions

Compound	pH	λ_{ex} nm	λ_{em} nm	Q
1[a]	11.6	391	489	0.045
	12.9	392	495	0.041
2	3.4	299	368	0.519
	5.7	299	366	0.415
	7.8	295	353	0.054
	9.5	295	351	0.026
	11.6	295	351	0.071
	12.5	295	351	0.096
3[a]	3.4	326	405	0.061
	5.8	334	405	0.010
	7.8	338	405	0.001
	9.6	336	381	0.001
	11.7	381	486	0.003
	12.9	392	493	0.005
4	3.4	336	385	0.406
	5.8	334	386	0.349
	7.8	313	363	0.066
	9.8	313	359	0.023
	11.7	310	359	0.067
	12.8	305	357	0.318
5	3.4	316	380	0.138
	5.8	313	371	0.217
	8.0	313	371	0.274
	9.8	313	372	0.297
	11.6	311	372	0.172
	13.0	308	363	0.023

[a] The excitation maximum of compounds **1** and **3** at pH > 10 corresponds to the absorption maximum of phenolate anion.

absorption of phenolate anion. Compounds **2** - **5** emitted in the whole pH range but their fluorescence characteristics depended strongly on pH (Table 2, Fig. 6). Emission of compounds **2** - **4** was weak at neutral and moderately alkaline pH values and increased significantly at pH < 7, where a pyridinium cation was formed [21]. The effect of increase in the fluorescence quantum efficiencies with a shift of the equilibria from the neutral to the protonated form was striking in the case of compounds **2** and **4** prefering a planar structure [14, 16].

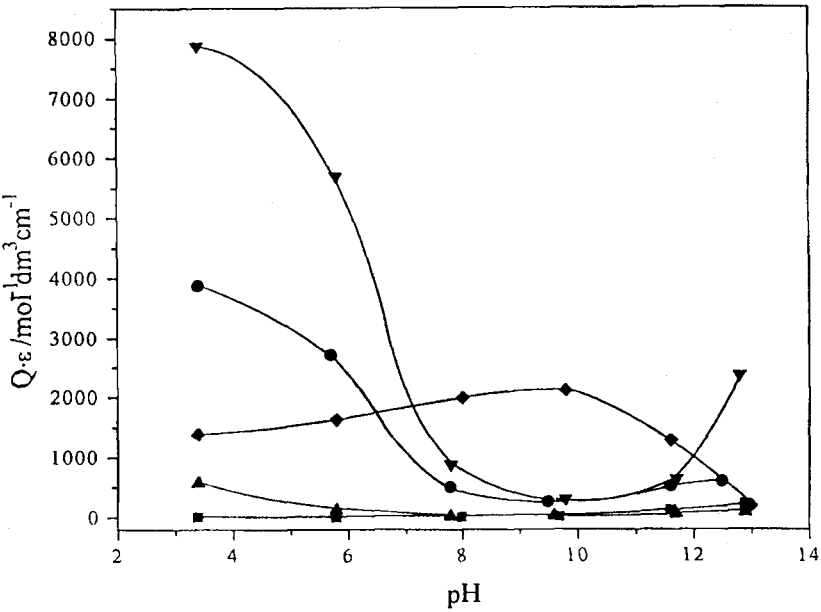


FIG. 6 Dependence of the fluorescence sensitivities of compounds **1** - **5** in buffered dioxane/water 1/1 mixtures on pH. ■ Compound **1**, ● Compound **2**, ▲ Compound **3**, ▼ Compound **4**, ◆ Compound **5**.

The fluorescence of compound **5** was strongest in the neutral and weakly alkaline pH regions, probably because of the presence of the cyclic form. The quantum efficiency decreased at strong alkaline and acidic pH values, where tendency towards cyclization was diminished.

CONCLUSION

In conclusion, it was shown that the fluorescence of Schiff bases derived from amino- and aminomethylpyridines was dependent on their structural characteristics, tautomeric equilibria, pH and solvent.

According to the obtained data, some fluorescence characteristics of the Schiff bases studied can be applied in analytical chemistry. A particularly promising characteristic is

the high sensitivity of compounds **2** - **5** to pH and to solvent polarity in polar, protic solvents, which opens attractive applications in optical sensors.

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