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Spectrophotometric Characteristics of New Pyridylindolizine Derivatives Solutions

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Abstract Three new pyridylindolizine derivatives, 1, 2, 3-tricarbometoxi-7-(4-pyridyl)-pyrrolo[1, 2-a]pyridine (**I**), 1,2-dicarboethoxy-3-(4-bromobenzoyl)-7-(4-pyridyl)-pyrrolo[1,2-a]pyridine (**II**) and its isomer 1,2-dicarboethoxy-3- (4-bromobenzoyl) -5- (2-pyridyl) -pyrrolo[1, 2-a]pyridine (**III**) have been investigated in different solutions by UV-VIS absorption, steady-state, and time-resolved fluorescence methods. The effects of the substituent and solvent on the spectroscopic properties have been demonstrated. The fluorescence decay data could be fitted to a single-exponential function. The lifetime values are higher in protic polar than in aprotic apolar solvents for compound **I**. In the case of compounds **II** and **III** the fluorescence intensities and lifetimes are very low, with the exception of **III** in aprotic solvents. The absorption and fluorescence properties of the compounds showed a solvent dependence.

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Introduction

Heterocycles form one of the most important and well investigated classes of organic compounds owing to their occurrence in living organisms and a wide range of biological activity. Beside their practical applications, their optical properties present interesting scientific features. UV-VIS absorption properties of heterocycles are very sensitive to substituent and solvent, which is mainly due to the hydrogen bond. Some of them emit an intense fluorescence. The fluorescence properties of aromatic hydrocarbons generally depend on the substituent nature and position. For the five atoms heterocycles the substituent position is critical [1]. Indole (2,3-benzopyrrole) is fluorescent, whereas pyrrole is not fluorescent [2, 3]. Changing the substituent in a heterocycle molecule, a large scale of compounds could be obtained with different properties; positions and intensities of both absorption and fluorescence bands are modified, and therefore a large number of applications could be envisaged. In this sense, in the series of "pyrrolo-fused conjugated systems," a number of very important advancements have been observed over the last few years. Thus ranging from their biological activity, to components for organic-based electroluminescent devices, new research horizons have been opened [4–11].

Indolizine is the simplest heteroaromatic planar molecule containing both a π–excessive pyrrole and a π–deficient pyridine ring with one bridgehead nitrogen, the whole system being isomeric with indole. This has had an impact on the

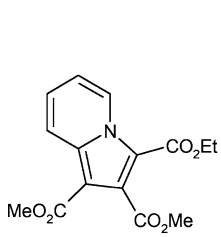
development of the indolizine chemistry which attempts to obtain biologically active structures that mimic indole derivatives [12, 13]. Indolizines are widely distributed in nature, in plants and in many animals. It is an important class of heterocyclic compounds since many alkaloids contain in their structure indolizine moiety [14]. The development of general methods for the synthesis of indolizine derivatives remains an area of active investigation [15]. Esters of indolizinic compounds exhibit a profound inhibition of lipid peroxidation *in vitro*, probably by an electron donation mechanism, and compounds with antioxidant properties have great therapeutic potential [5]. Recently, indolizines have been used as fluorescent moiety in modified β–cyclodextrines, and thus applied as chemical sensor for volatile organic compounds [16, 17].

There are however only a few works devoted to the substituents influence on the optical properties of indolizines [10, 15, 18].

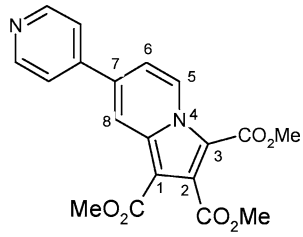
The physico-chemical characterization of new indolizinic compounds is important in view of their applications. In order to obtain compounds with high fluorescence quantum yield (with practical applications such as markers, scintillators, or as organic electroluminescent thin-film devices), the investigation of the relationship between optical properties and substituent position or expansion of the π–π conjugated system of indolizine is conducted. Three new indolizine derivatives **I–III** bearing a pyridine moiety in positions 7 and 5: 1,2,3-tricarbomethoxy-7-(4-pyridyl)-pyrrolo[1,2-a]pyridine (**I**), 1,2-dicarboethoxy-3-(4-bromobenzoyl)-7-(4-pyridyl)-pyrrolo[1,2-a]pyridine (**II**) and its isomer 1,2-dicarboethoxy-3-(4-bromobenzoyl)-5-(2-pyridyl)-pyrrolo[1,2-a]pyridine (**III**) have been synthesized, selected and prepared with a view to evidence the importance of both the position of the pyridyl substituent and the nature of the substituent at C(3). The influence of the solvent nature on the optical properties of the compounds is interesting in order to find out if the compounds present solvatochromic properties, and to evidence the effect of bromide atom on the fluorescence intensity and of the stereochemistry of the two isomers on the absorption and fluorescence function of solvent. It is worth mentioning that the compounds are very fluorescent in solid-state and for this reason their photochemical study helps elucidate their special fluorescence properties.

Experimental

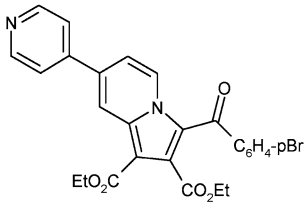
The three new pyridylindolizine derivatives have the molecular structures **I–III**, confirmed by elemental analysis and NMR spectroscopy.



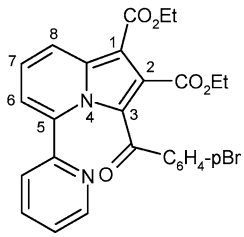
A



I



II



III

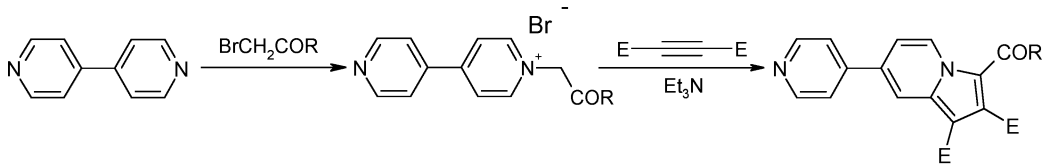
The photochemical properties of the compound **A,** investigated by Cheng, Ma and Wudl in [10], are useful for a comparison, and thus to evidence the effect of the pyridyl substituent in the present paper analyzed compounds.

Materials and solutions

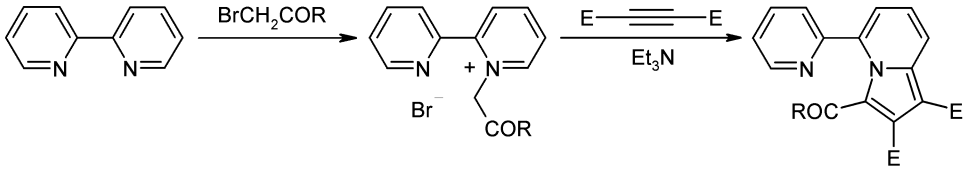
The compounds were prepared by 1,3 dipolar cycloaddition reactions between pyridinium *N*-ylides with activated alkynes according to procedure described for pyrrolo[1,2-b]pyridine or close analogues [19–22]. Initially, 2,2′-dipyridine and 4,4′-dipyridine were alkylated at the nitrogen atom with halide derivatives to obtain the corresponding cycloimmonium bromides [23]. Then, treatment of the appropriate dipyridine bromide with activated alkynes (dimethyl or diethyl acetylenedicarboxylate) in the presence of triethylamine yielded the indolizines **I–III** (Scheme 1).

General procedure for the synthesis of pyridylindolizines **I–III**

5 Mmol of bipyridine salt were suspended in 25 mL of dichloromethane and then 5.5 mmol of dimethyl (or diethyl) acethylenedicarboxylate were added. Under vigorous stirring, 0.7 mL (5 mmol) of triethylamine (dissolved in 5 mL of methylene chloride) were added dropwise. After 20 min the reaction mixture was washed twice with 50 mL of water and the solvent evaporated. The residue was treated with 20 mL ethanol and the product was isolated by filtration.



I,II



III

I: R = OMe, E = CO_2Me

II, III: R = 4-BrC_6H_4, E = CO_2Et;

Scheme 1

Trimethyl 7-(4-pyridyl)indolizine-1, 2,3-tricarboxylate (**I**)

The product was recrystallized from toluene and yellow crystals were obtained. Yield 49%, m.p. 193-4°C. Anal. $C_{19}H_{16}N_2O_6$. Calcd. C 61.96, H 4.38, N 7.61. Found C 62.32, H 4.70, N 7.92. ^{1}H-NMR ($CDCl_3$, δ, ppm, J, Hz): 3.92 (2s, 6H, 2 Me); 4.02 (s, 3H, Me); 7.32 (dd, 1H, 7.5, 1.8, H-6); 7.61-7.63 (m, 2H, H-10, H-13); 8.62-8.63 (m, 1H, H-8); 8.74-8.76 (m, 2H, H-11, H-12); 9.56 (dd, 1H, 7.5, 1.8, H-5). ^{13}C-NMR ($CDCl_3$, δ, ppm): 51.7, 52.1, 52.9 (3 Me); 104.1 (C-1); 112.1, 130.8, 135.9, 137.5 (C-2, C-3, C-7, C-8a); 113.8 (C-6); 117.5 (C-8); 121.0 (C-10, C-13); 128.2 (C-5); 144.7 (C-9); 150.6 (C-11, C-12); 160.2, 163.0, 165.8 (3 CO_2Me).

Diethyl 3-(4-bromobenzoyl)-7-(4-pyridyl) indolizine-1,2-dicarboxylate (**II**)

The product was recrystallized from nitromethane and yellow crystals were obtained. Yield 61%, m.p. 210-2°C. Anal. $C_{26}H_{21}BrN_2O_5$. Calcd. C 59.90, H 4.06, Br 15.33, N 5.37. Found C 60.19, H 4.21, Br 15.64, N 5.59. ^{1}H-NMR ($CDCl_3$, δ, ppm, J, Hz): 1.09 (t, 3H, 7.2, Me); 1.36 (t, 3H, 7.2, Me); 3.75 (q, 2H, 7.2, CH_2); 4.36 (q, 2H, 7.2, CH_2); 7.37 (dd, 1H, 7.5, 1.8, H-6); 7.59 (s, 4H, H-15, H-16, H-18, H-19, system A_2); 7.63-7.65 (m, 2H, H-10, H-13); 8.74-8.77 (m, 3H, H-8, H-11, H-12); 9.65 (dd, 7.4, 1.0, H-5). ^{13}C-NMR ($CDCl_3$, δ, ppm): 13.6, 14.2 (2 Me); 60.7, 61.9 (2 CH_2); 105.6 (C-1); 114.4 (C-6); 117.5 (C-8); 120.4, 132.0, 137.3, 138.0, 138.3 (C-2, C-3, C-7, C-8a, C-14); 121.1 (C-10, C-13); 126.9 (C-17); 128.8 (C-5); 130.3, 131.3 (C-15, C-16, C-18, C-19); 144.8 (C-9); 150.6 (C-11, C-12); 162.7, 164.5 (2 CO_2Et); 185.4 (COAr).

Diethyl 3-(4-bromobenzoyl)-5-(2-pyridyl) indolizine-1,2-dicarboxylate (**III**)

The product was recrystallized from ethanol and yellow crystals were obtained. Yield 54%, m.p. 170-2°C. Anal. $C_{26}H_{21}BrN_2O_5$. Calcd. C 59.90, H 4.06, Br 15.33, N 5.37. Found C 60.22, H 4.29, Br 15.61, N 5.69. ^{1}H-NMR ($CDCl_3$, δ, ppm, J, Hz): 1.08 (t, 3H, 7.1, Me); 1.36 (t, 3H, 7.1, Me); 3.81 (q, 2H, 7.1, CH_2); 4.36 (q, 2H, 7.1, CH_2); 7.06 (dd, 1H, 7.0, 1.2, H-6); 7.11 (ddd, 7.2, 5.0, 1.0, H-12); 7.45 (dd, 1H, 9.0, 7.0, H-7); 7.54, 7.64 (2d, 4H, H-15, H-16, H-18, H-19); 7.60 (dt, 1H, 7.9, 1.0, H-10); 7.80 (td, 1H, 7.9, 1.8, H-11); 8.03 (ddd, 5.0, 1.8, 1.0, H-13); 8.48 (dd, 9.0, 1.2, H-8). ^{13}C-NMR ($CDCl_3$, δ, ppm): 13.6, 14.2 (2 Me); 60.3, 61.5 (2 CH_2); 103.2 (C-1); 118.0 (C-6); 120.4 (C-8); 122.1 (C-10); 124.0 (C-12); 124.2, 128.9, 136.4, 138.1, 138.3 (C-2, C-3, C-5, C-8a, C-17); 126.2 (C-7); 127.6 (C-17); 131.1, 131.3 (C-15, C-16, C-18, C-19); 138.2 (C-11); 148.6 (C-13); 154.5 (C-9); 163.1, 165.2 (2 CO_2Et); 184.7 (COAr).

Solutions preparation

Solvents (spectroscopic grade) from Merck have been used without further purification. Because of the higher solubility

of the compounds in ethanol, a fresh stock ethanolic solution (ca. 1 mM) was prepared for each derivative. Appropriate amounts of stock solutions were transferred into a volumetric flask and the ethanol evaporated under a stream of nitrogen, then the different solvents were added. The concentrations of the solutions were in the 10^{-5} M–5×10^{-5} M range.

The UV-VIS absorption, steady state, and time-resolved fluorescence measurements have been done both in different protic solvents, methanol, ethanol, *n*-propanol, *n*-butanol, *n*-pentanol, and in a series of aprotic solvents as acetonitrile, DMSO, dioxane, cyclohexane and *n*-hexane.

Methods

Absorption spectra were recorded with a Shimadzu UV-VIS 2501 PC spectrophotometer, at 23°C, with a 0.2 nm increment.

The fluorescence spectra (emission and excitation) were recorded with Spex spectrofluorimeter, at 23°C. The emission and excitation spectra were corrected. The relative fluorescence quantum yield values were determined by comparison to diluted quinine bisulfate solution in 0.1 N H_2SO_4, with 0.55 absolute quantum yield [24]. The fluorescence lifetime of the samples were measured, at 21°C, on an Edinburgh Instruments single photon counting apparatus. The excitation setup uses a mode - locked Nd-YAG laser (Spectra Physics Model 379.344S) and a dye-laser. The excitation wavelength was 300 nm. The experimental method is described in [25]. Data were fitted by a monoexponential function: $F(t) = a \exp(-t/\tau)$.

Steady-state spectra of pyridyl-pyrrolo[1,2-a]pyridine compounds (**I-III**) in ethanol and cyclohexane

The effect of substitution on the photochemical properties of compounds (**I-III**) in ethanol and cyclohexane is presented comparatively.

The UV-VIS absorption spectra of compounds in the spectral range 240–440 nm exhibit two electronic bands (Fig. 1). The difference of the compounds structure, as one can expect, is reflected in the shape of the spectra. The differences were observed even in the case of compounds **II** and **III**, which are isomers. By the substitution at C(3) of carbomethoxy group (in **I**) with 4-bromobenzoyl group (in **II** and **III**) the effects are the extension of the hyperconjugation of the pyrrolo-pyridinic π-electrons by bromobenzoyl with a bathochromic shift of $\Delta_{max} = 24$ nm (in ethanol) and $\Delta_{max} = 35.5$ nm (in cyclohexane) and $\Delta_{max} = 21$ nm (in cyclohexane for **III** comparatively with **I**) and a modification of the molar extinction coefficients, ε for low-energy band. The influence of the substitution position in the case of the pyridyl group (in 5 or 7 position) in compounds **II** and **III** can been observed by comparison of the optical properties. Pyridyl in 5 position reduces

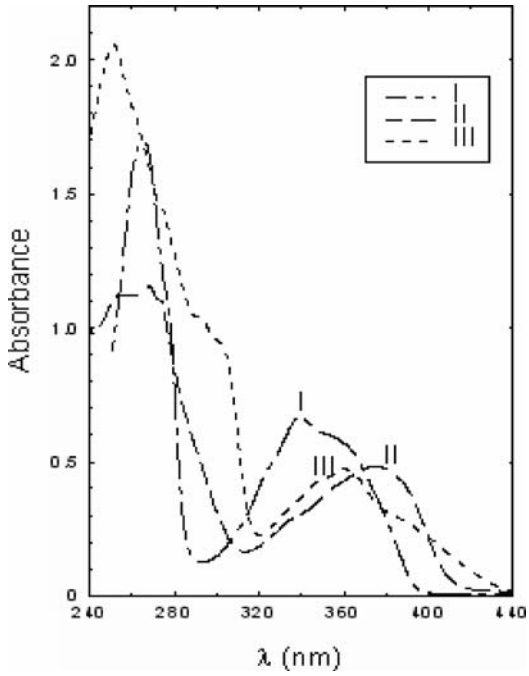


Fig. 1 The absorption spectra of the compounds **I–III** cyclohexane

the extension of hyperconjugation, and the shift of the long wavelength absorption band, from 379.6 nm (**II**) to 355.6 nm (**III**) in ethanol can be observed. The reduction of the hyperconjugation in the case of **III** can be explained by differences in geometrical structure of the molecules compared with **II**, in which case the coplanar pyridyl- indolizine system is conjugated with the benzoyl group. This structure was confirmed by [26]. In the case of **III** the steric interactions between the substituents at positions 1,2,3 and 5 lead to rotation of the benzoyl ring plane at position 3 and respectively pyridyl ring at position 5 with respect to the plane of the indolizine system. This interpretation is based on X-ray crystallographic investigation conducted on similar compounds [27]. On the other hand, in the case of compound **III** the planes of the pyridyl and ethoxycarbonyl are inclined with respect to the indolizine plane, probably due to the steric repulsion from the 4-Br-benzoyl group. X-ray studies on similar compounds have even lead to the conclusion of the absence of the π–π conjugation between pyrrolo[1,2-a]isochinoline system and ethoxycarbonyl and phenyl substituents with inclined planes with respect to the pyrrolo[1,2-a]isochinoline plane [28]. The ε values are also modified. The outlines of the absorption spectra illustrate the presence of some shoulders due to the overlapping of the vibrational bands. High energy bands for **II** and **III** are extensively broadened relative to the high energy band in the spectrum of compound **I**.

The normalized emission spectra of the compounds in ethanol are shown in Fig. 2. The spectra are obtained by the excitation at 365 nm, and were normalized to the same height to emphasize the spectral shifts. One can observe

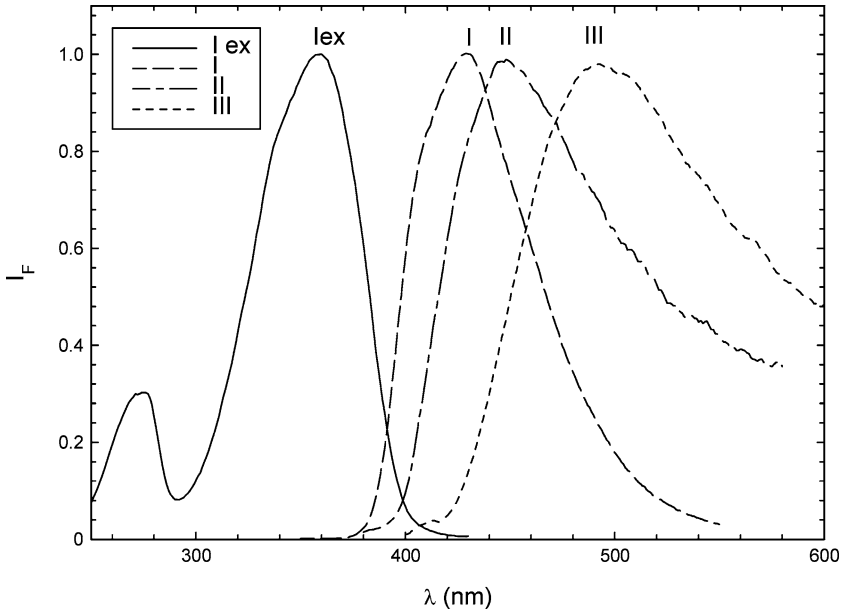


Fig. 2 The normalized emission spectra of compounds **I–III** in ethanol, excitation wavelength is $\lambda_{ex} = 365$ nm, and normalized excitation spectrum of **I** in ethanol measured at $\lambda_{em} = 430$ nm, emission wavelength

the bathochromic shift of the emission band for compounds **II** and **III** relative to the spectrum of the compound **I**. In the case of **I**, the fluorescence quantum yield, $\phi = 0.134$, is much higher than for the others two (for **II** the fluorescence intensity is extremely small, and for **III** $\phi = 0.0013$). The presence of Br decreases the fluorescence because of the internal heavy atom quenching effect; this effect is greater for **II**, which has a more planar structure compared with **III**. Figure 2 shows the normalized excitation spectrum of the compound **I**, measured at $\lambda_{em} = 430$ nm. The positions of the excitation bands are practically the same as the positions of the absorption bands, but the long wavelength absorption band is more efficient for fluorescence excitation. The fluorescence emission and excitation spectra of compounds in cyclohexane are shown in Figs. 3 and 4, respectively. It is known that molecules dissolved in cyclohexane generally show sharper vibrational structure than in ethanol. Compared with **I**, the effects of the substitution are bathochromic shifts of fluorescence band (103.4 nm for **III**, and 25.7 nm for **II**) and a weaker defined vibronic structure for **II** and **III**, greater in case of the compound **III,** indicating a non-planar molecule. Fluorescence quantum yield is higher in cyclohexane than in ethanol: 0.463 for **I** and 0.015 for **III**.

In order to explain the effects of the molecular structure and solvent-solute interactions on absorption and emission spectroscopic properties, the compounds were investigated

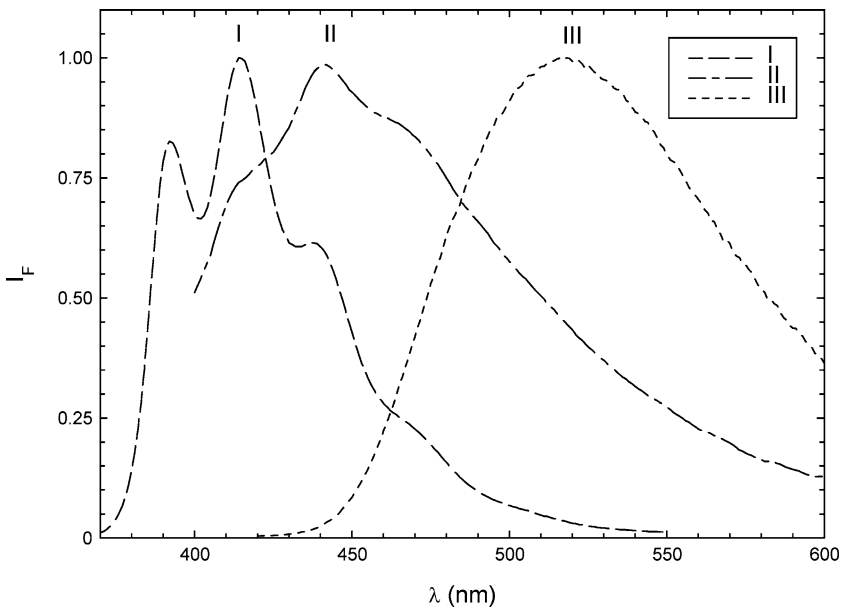


Fig. 3 The normalized emission spectra of compounds **I–III** in cyclohexane, excitation at $\lambda_{ex} = 365$ nm

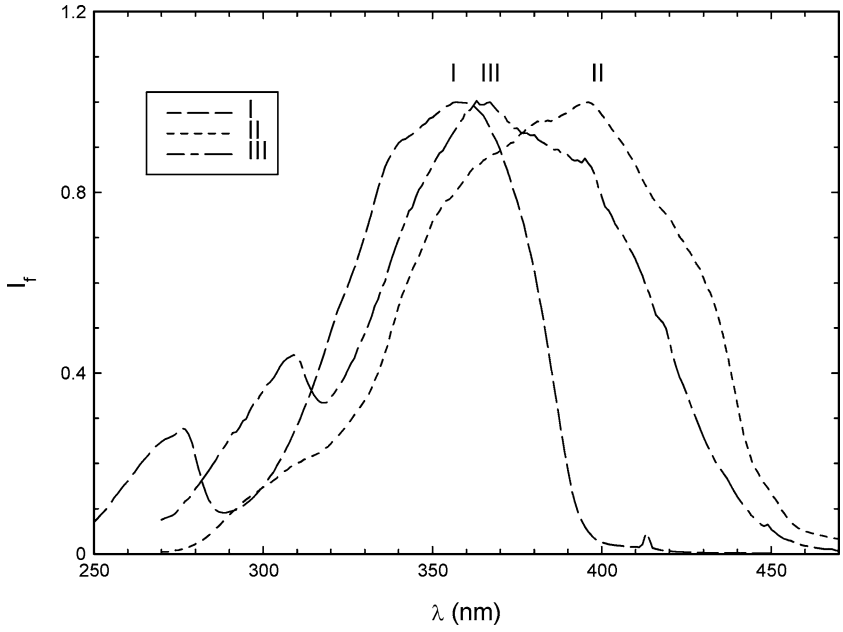


Fig. 4 The normalized excitation spectra of compounds **I–III** in cyclohexane, monitored at $\lambda_{em} = 420$ nm (for **I**), 440 nm (for **II**) and 520 nm (for **III**)

in different solvents. It is important to underline that all three compounds exhibit strong fluorescence in the condensed state. The results will be published elsewhere.

Steady-state spectra of 1,2,3-tricarbomethoxy-7-(4-pyridyl)-pyrrolo[1,2-a]pyridine (**I**) in various solvents

Absorption spectra

Representative solvents have been selected for this investigation. Table 1 shows the absorption band maxima wavelengths in the 240-450 nm range and the corresponding absorbances for **I** in methanol (MeOH), ethanol (EtOH), n-propanol (PrOH), n-butanol (BuOH), n-pentanol (PeOH), acetonitrile (AN), dimethylsulfoxide (DMSO), dioxane (Diox), cyclohexane (Chx), and n-hexane (Hex).The data in Table 1 demonstrate the effect of the nature of solvent, polar protic vs. polar aprotic, on the shape and intensity of the absorption spectra. In protic solvents one can observe a band with maximum at aprox. 353 nm, probably due to the hydrogen bond with carbonylic oxygen atom.

Fluorescence spectra

Table 1 also shows the positions of the emission maxima (λ_{mem}) in fluorescence spectra of compound **I** and the fluorescence relative intensity. The fluorescence intensity in cyclohexane was arbitrarily considered 100. The intensity values are low in alcohols, the smallest intensity is in MeOH, which interact stronger by hydrogen bonds with estheric carbonyl in compound **I**.

The difference between the maxima of absorption and fluorescence spectra, Stokes' shift, ΔS, is affected by dynamic properties of the solvent, namely by the solvent reorganization free energy. The solvent polarity influences the

Table 1 Maxima Wavelengths, λ_{max}, and molar extinction coefficients, log ε, for the main absorption bands, the fluorescence emission maxima, λ_{mem}, relative intensities, I_f , lifetimes, τ, and Stokes shift, ΔS, for the compound **I** in various solvents

Solvent	λ_{max} (nm) [log ε] (l mol^{-1} cm^{-1})				λ_{mem} (nm)	I_f	τ (ns)	ΔS cm^{-1}
MeOH	228.0 [4.345]	265.0 [4.593]	340.4 [4.206]	353.0 [4.203]	433.0	35.5	4.68	5234
EtOH	228.8 [4.331]	265.2 [4.589]	341.2 [4.201]	351.4 [4.198]	428.5	42.4	4.87	5121
PrOH	—	267.0 [4.687]	336.2 [4.249]	353.0 [4.225]	429.0	40.5	4.76	5019
BuOH	—	267.4 s[4.680]	339.4 [4.234]	354.4 [4.228]	429.4	41.2	4.77	4961
PeOH	—	267.2 [4.628]	340.6 [4.218]	354.4 [4.217]	430.5	40.8	4.76	4988
AN	228.4 [4.343]	262.2 [4.599]	340.0 [4.243]	—	426.4	40.4	4.74	5960
DMSO	—	267.8 [4.594]	342.8 [4.250]	—	432.0	46.9	4.95	6092
Diox	—	267.4 [4.621]	340.6 [4.621]	—	431.0	28.6	3.19	6158
Chx	—	265.2 [4.530]	338.8 [4.125]	—	414	100	3.87	—
Hex	—	264.8 [4.454]	339.0 [4.049]	—	413	88	3.86	—

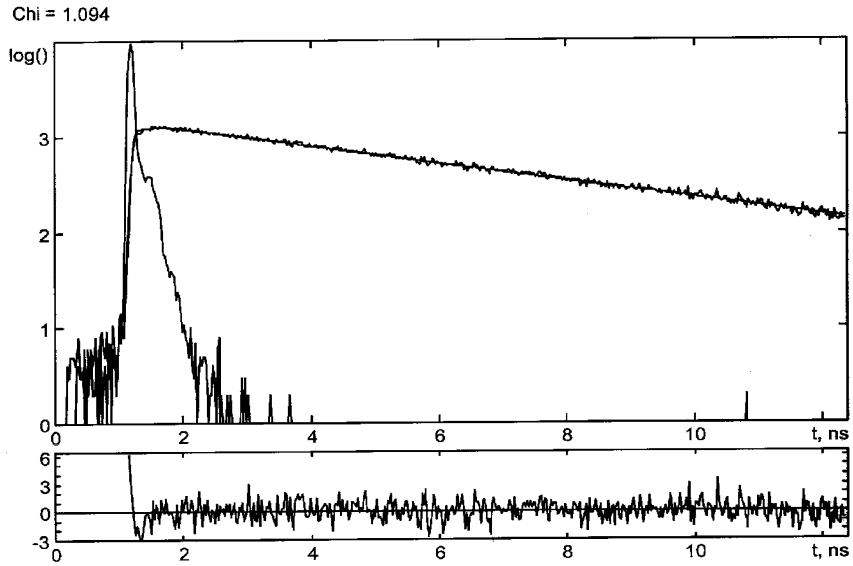


Fig. 5 The fluorescence decay curve ($\lambda_{em} = 430$ nm) of **I** in ethanol and random distribution of weighted residuals ($r(t_i)$)

electronic density redistribution upon the electronic transition. One can observe (Table 1) that in aprotic polar solvents the ΔS values are higher, but the values change only slightly with the polarity of the solvent. In polar protic solvents a decreasing trend of ΔS is observed.

For compound **A**, the absorption maxima in n-hexane are 315 nm, 328 nm, and the emission maxima 370 nm with the fluorescence quantum yield 0.17 [10]. By comparison with A, the effect of pyridyl is the bathochromic shift of absorption and emission spectra (Table 1) and an increase of the quantum yield to 0.41.

Time-resolved fluorescence spectra of 1,2,3-tricarbomethoxy-7-(4-pyridyl)-pyrrolo[1,2-a]pyridine (**I**)

The fluorescence decay of **I** in all investigated solvents is measured on the nanosecond time scale, and values are presented in Table 1. After deconvolution, a monoexponential decay curve is obtained. Figure 5 shows as an example the fluorescence decay curve ($\lambda_{em} = 430$ nm) of **I** in ethanol and random distribution of weighted residuals ($r(t_i)$). The measured values are almost constant, but in aprotic apolar

Table 2 Wavelengths, λ_{max}, and molar extinction coefficients, log ε, for the main absorption bands of **II** and **III** pyridyl-pyrrolo [1,2-a]pyridine bromobenzoyl derivatives in various solvents

Compound	Solvent	λ_{max} [logε] (nm) (l mol^{-1} cm^{-1})			
II	MeOH		254.4 [4.473]	—	379.0 [4.261]
	EtOH	—	255.0 [4.455]	—	379.6 [4.266]
	PrOH	—	255.2 [4.535] 267.2 [4.529]	—	379.4 [4.287]
	BuOH	—	254.6 [4.496] 269.2 [4.486]	—	379.4 [4.314]
	PeOH	—	255.4 [4.464] 269.4 [4.454]	—	379.8 [4.285]
	AN	—	254.0 [4.493]	—	378.4 [4.276]
	DMSO	—	—	—	381.6 [4.338]
	Diox	—	—	—	379.4 [4.280]
	Chx	—	255.6 [4.351] 267.8 [4.363]	—	373.8 [3.984]
	Hex	—	253.6 [4.171] 267.2 [4.176]	—	372.4 [3.750]
III	MeOH	—	244.8 [4.528] 266.6 [4.467]	335.0 [3.987]	355.2 [4.000]
	EtOH	225.6 [4.338]	246.4 [4.449]	—	355.6 [4.024]
	PrOH	—	247.4 [4.457]	—	357.0 [4.013]
	BuOH	—	248.2 [4.472]	—	357.4 [4.024]
	PeOH	—	248.2 [4.488]	—	357.6 [4.039]
	AN	—	247.4 [4.452]	—	356.2 [3.987]
	DMSO	—	—	333.6 [4.069]	356.2 [4.002]
	Diox	—	—		359.8 [3.994]
	Chx	—	251.8 [4.614]	—	359.8 [3.975]
	Hex	—	251.8 [4.732]	273.0 [4.652]	359.8 [3.971]

Table 3 Fluorescence parameters: λmem, relative intensity and lifetime, τ, of compound **II** and **III** in various solvents; ΔS is Stokes' shifts

Compound	Solvent	λ_{mem} (nm)	If	τ (ns)	ΔS cm^{-1}
II	EtOH	450.6	14	—	4151
	AN	568	16	—	8822
	DMSO	524	24	—	7161
	Diox	514	43	—	6940
	Chx	440	100	—	
	Hex	437	69	—	—
III	EtOH	497	3	—	8017
	PrOH	547		—	10710
	PeOH	556	40	—	9946
	AN	537	70	0.93	10383
	DMSO	533	118	1.81	9327
	Diox	528	16	2.02	8839
	Chx	518	100	5.88	
	Hex	520	91	—	

solvents: dioxane, hexane and cyclohexane the values are lower.

Absorption and fluorescence spectra of 1,2-dicarboethoxy-3-(4-bromobenzoyl)-7-(4-pyridyl)-pyrrolo[1,2-a]pyridine (**II**) and 1,2-dicarboethoxy-3-(4-bromobenzoyl)-5-(2-pyridyl)-pyrrolo[1,2-a]pyridine (**III**) in various solvents

In the case of compound **II** one can observe in the Table 2 the hipsochromic shift of the bands 372.4 nm in hexane and 373.8 in cyclohexane as compared with the other solvents.

An extension of hyperconjugation in the case of **II** is observed as compared with **III** due to the structural differences, as is the substitution of 4-pyridyl in 7 position. As an example, the 379 nm and 254.4 bands in methanol in the case of **II** are situated at 355 nm and 244.8, respectively, in the case of **III** with 4-pyridyl in 5 position. The spectra of compound **III** show a weak bathochromic shift with the decreasing of the solvent polarity.

From the Table 3 one can observe the solvent dependence of fluorescence parameters. The fluorescence intensities of compounds **II** and **III** are very low, especially in polar solvents (Table 3). Also, the fluorescence lifetime values are much lower than in case of compound **I,** except **III** in aprotic apolar solvents. Figure 6 shows the fluorescence decay curve ($\lambda_{em} = 430$ nm) of **III** in DMSO and random distribution of weighted residuals (r(t_i)). The Stokes' shift values depend on solvent and generally are higher than in the case of compound **I,** due to the greater shift of the fluorescence bands.

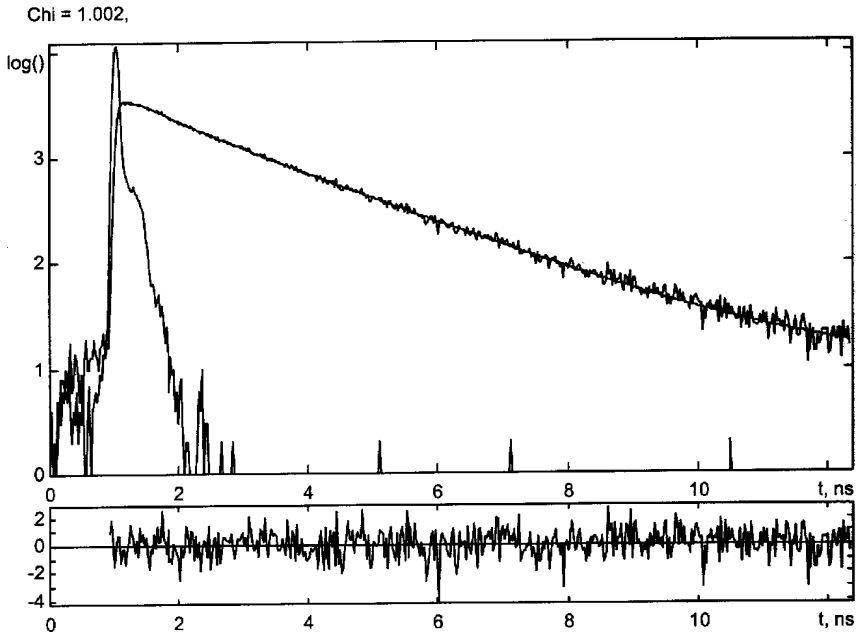


Fig. 6 The fluorescence decay curve ($\lambda_{em} = 530$ nm) of **III** in DMSO and random distribution of weighted residuals ($r(t_i)$)

Conclusions

The absorption spectra and steady-state and time-resolved fluorescence of three new pyridylindolizines derivatives in different solvents have been measured.

- The positions of the absorption bands and the values of the molar extinction coefficient values evidence the influence of the substituent and of the solvent nature. By the substitution of carbomethoxy groups (in **I**) with 4-bromobenzoyl and carboethoxy groups (in **II**) a bathochromic shift of the spectra is observed. The position of the substituent is reflected by the shape modification of absorption spectra of the compounds **II** and **III**.
- The fluorescence spectra present the same behavior. In the case of derivatives **II** and **III**, the bathochromic shift of the spectra, compared with **I** is due to the modification of the substituent. Because of the Br presence in **II** and **III,** their fluorescence is much lower, especially in polar solvents. The fluorescence quantum yield is about a hundred times greater in the case of **I** in ethanol compared with **III** and 30-times greater in cyclohexane. The fluorescence lifetime values are almost constant in the case **I:** 4.68-4.95 ns in polar solvents and 3.19-3.87 ns in aprotic apolar investigated solvents. The fluorescence lifetime values are much lower in case of compounds **II** and **III,** except **III** in cyclohexane.

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