SPECTRAL-LUMINESCENCE PROPERTIES AND BASICITIES OF 2-(4-PYRIDYL)-5-(4-R-PHENYL)OXAZOLES

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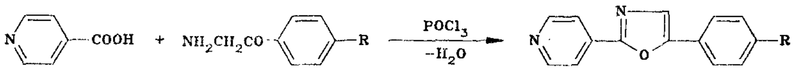
The spectral-luminescence and acid-base properties of 2-(4-pyridyl)-5-(4-R-phenyl)oxazoles were studied. Significant π-electron conjugation between the individual fragments exists in the molecules of these compounds in solutions at room temperature. Bathochromic and bathofluoric effects, which are particularly appreciable for electron-donor substituents, are observed when substituents R are introduced into the 5-phenyl ring. Ethanol solutions of the investigated compounds have high fluorescence quantum yields which, for some of them, are close to unity. Electron-donor substituents R increase the basicity of the pyridine nitrogen atom.

Previously, in a study of the character of the conjugation in heterocyclic analogs of biphenyl [1-3] by various physicochemical methods it was shown that strong π-electron intramolecular interaction (conjugation) between the heterocyclic fragments occurs in such systems. The degree of conjugation depends on the nature of the heterocyclic rings that make up the molecule, the aggregate state, the temperature, and the polarity of the solvent. The present paper is devoted to a study of the character of the conjugation in 2-(4-pyridyl)-5-(4-R-phenyl)oxazoles (I), the molecules of which are constructed in the p-terphenyl manner. With this end in mind, we obtained the electronic absorption and emission spectra and measured the fluorescence quantum yields of these compounds in solutions. In order to ascertain the direction of the shift of the electron density in the molecules we determined the pK_a values of Ia-e.



I a-e

I a R=H; b R=Cl; c $R=CH_3$; d $R=OCH_3$; e $R=C_6H_5$

Our interest in these structures is also due to the fact that 2-(4-pyridyl)-5-phenyloxazole (Ia) and its quaternary salts [4] have found application as scintillation activators [5] and effective active media of liquid lasers [6]. According to the data in [4], Ia was synthesized by condensation of isonicotinic acid chloride with ω-aminoacetophenone hydrochloride in pyridine with subsequent cyclization of the resulting acyl amide of isonicotinic acid in a mixture of 90% phosphoric acid and acetic anhydride. The method is extremely laborious, and the product is obtained in only 40% yield. We carried out the condensation of isonicotinic acid with p-substituted ω-aminoacetophenones and cyclization in one step in phosphorus oxychloride in a nitrogen atmosphere by the method in [7], which we improved, and obtained Ia-e in high yields (Table 1). The intermediate is evidently isonicotinic acid phenacylamide.

The absorption spectrum of Ia — the simplest representative of this series — is similar to the spectrum of its isoelectronic analog, viz., 2,5-diphenyloxazole (II), and has a distinctly expressed vibrational structure. Since structural changes do not have a substantial effect on the positions and intensities of the short-wave absorption bands, we restricted ourselves to an investigation of the long-wave bands responsible for conjugation and fluorescence.

The data in Table 1 make it possible to follow the effect of some substituents in the para position of the phenyl ring on the optical characteristics of I. The absorption maximum

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TABLE 1. 2-(4-Pyridyl)-5-(4-R-phenyl)oxazoles and Their Quaternary Salts (I-III)

Compound	mp, °C	λ_{max}, nm (ε or η), in ethanol		Found, %		Empirical formula	Calc., %		Yield, %
		absorption (ε · 10^{-4}, cm^2/mmole)	fluorescence (η)	Cl (N)	S		Cl (N)	S	
Ia	97—98 [4]	320 (2,33)	395 (0,74)	—	—	—	—	—	—
Ib	143—144	322 (3,74)	400 (0,69)	13,7	—	$C_{14}H_9ClN_2O$	13,8	—	56
Ic	119—120	327 (2,64)	405 (0,61)	(12,0)	—	$C_{15}H_{12}N_2O$	(11,9)	—	64
Id	110	338 (2,67)	440 (0,90)	(11,3)	—	$C_{15}H_{12}N_2O_2$	(11,1)	—	65
Ie	180—181	335 (4,40)	420 (0,55)	(9,5)	—	$C_{20}H_{14}N_2O$	(9,3)	—	53
II	71—72[12]	308 (3,18)	365 (0,51)	—	—	—	—	—	—
IIIa	228—229	375 (3,15)	480 (0,87)	—	7,6	$C_{23}H_{22}N_2O_4S$	—	7,6	59
IIIb	238—239	380 (2,48)	485 (0,72)	—	7,0	$C_{23}H_{21}ClN_2O_4S$	—	7,0	68
IIIc	202—203	390 (2,99)	500 (0,87)	—	7,3	$C_{24}H_{24}N_2O_4S$	—	7,3	76
IIId	198—199	408 (1,92)	580 (0,68)	—	7,0	$C_{24}H_{24}N_2O_5S$	—	7,1	77
IIIe	258—259	395 (3,18)	553 (0,79)	—	6,35	$C_{29}H_{26}N_2O_4S$	—	6,4	70
IIIf	240—241	385 (2,86)	485 (0,82)	10,45	—	$C_{21}H_{17}ClN_2O$	10,2	—	45
IIIg	246—247	385 (2,17)	485 (0,73)	18,6	—	$C_{21}H_{16}Cl_2N_2O$	18,6	—	67
IIIh	222—223	395 (2,34)	505 (0,76)	9,3	—	$C_{22}H_{19}ClN_2O$	9,6	—	53
IIIi	212—213	418 (2,23)	580 (0,79)	9,5	—	$C_{22}H_{19}ClN_2O_2$	9,4	—	53
IIIj	256—257	405 (2,46)	573 (0,85)	8,5	—	$C_{27}H_{21}ClN_2O$	8,4	—	54

TABLE 2. Acid–Base Properties of I and II

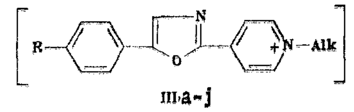
Compound	λ_{max}, nm (ε · 10^{-4} cm^2/mmole)		pK_a in 50% ethanol
	50% ethanol	ethanol + 0.1 N HCl (1 : 1)	
Ia	322 (2,38)	370 (2,30)	3,03
Ib	326 (3,80)	370 (3,68)	1,19
Ic	333 (2,72)	380 (2,60)	3,22
Id	337 (2,81)	394 (2,54)	4,07
Ie	350 (4,50)	388 (4,30)	2,59
II	310 (3,17)	310 (3,17)	—

of Ia is shifted bathochromically 15 nm as compared with its phenyl analog (II). In the fluorescence spectra of ethanol solutions of them the difference in the positions of the maxima is even greater and amounts to 30 nm. The fluorescence quantum yield of Ia is greater by a factor of approximately 1.5 than in the case of II. With respect to their spectral-luminescence properties, the chloro- and methyl-substituted compounds (Ib,c) are virtually identical to Ia.

Substantial bathochromic and bathofluoric effects are observed for Id, which contains a methoxy group; this is due to the donor-acceptor interaction of the methoxy group with the pyridine ring. However, further lengthening of the conjugation chain (Ie), although it does lead to a long-wave shift of the absorption and emission maxima, substantially decreases the fluorescence quantum yields, possibly because of an increase in the probability of nonradiating transitions.

The absorption spectra of Ia-e depend only slightly on the nature of the solvent, whereas the effect of the solvent on the spectra and the fluorescence quantum yields of some compounds is significant. The fluorescence maxima of Ia in toluene and dioxane are identical (382 nm). "Activation" of the fluorescence, which is accompanied by a bathofluoric shift of the maximum with a simultaneous increase in the quantum yield, is observed on passing to a hydroxy-containing solvent. The quantum yields in toluene and dioxane are, respectively, 0.41 and 0.54, whereas the quantum yield in ethanol is greater by a factor of about 1.5 (0.74). According to [8], the observed "activation" of the fluorescence in the case of compounds with this sort of structure is associated with inversion of the energy levels of the $S_{\pi\pi^*}$ and $T_{n\pi^*}$ states, which leads to a decrease in the probability of intercombination conversion.

The significant bathochromic shift of the long-wave absorption bands, the intense fluorescence, and the bathofluoric shift of the emission band of Ia-e as compared with II constitute a direct indication of the existence of significant conjugation between the phenyl and heterocyclic rings in the oxazole I system.



IIIa-j

III a–e Alk = C_2H_5, X = OTs; f–j Alk = $CH_2C_6H_5$, X = Cl; a, f R = H; b, g R = Cl; c, h R = CH_3; d, i R = OCH_3; e, j R = C_6H_5

Having established the existence of a significant π-electron interaction between the individual fragments in the molecules of Ia-e, we attempted to ascertain the direction of the shift of the π-electron density, i.e., to determine which of the rings — the pyridine or oxazole ring — manifests stronger electron-acceptor character. To compare the basicities of the nitrogen atoms of the oxazole and pyridine rings we studied the UV spectra of acidic solutions of Ia-e and II. It is apparent from Table 2 that a new absorption band in the long-wave region appears in the absorption spectra of the protonated forms of Ia-e. The absorption spectra of the singly charged cations of Ia-e measured in 50% aqueous ethanol at pH ~ 1 coincide with those of quaternary salts IIIa-j (Tables 1 and 2), which were obtained by treatment of Ia-e with alkylating agents.

The small bathochromic shift in the case of solutions of the quaternary salts (5-15 nm) is evidently associated with complication of the structure of the N-alkyl group. The absorption spectrum of 2,5-diphenyloxazole does not change over the pH range 12 to 1. This makes it possible to conclude that the nitrogen atom of the pyridine ring in Ia-e is quaternized first and foremost. In an investigation of the acid-base properties of Ia-e (Table 2) we observed that the pK_a values of the protonation of these compounds are considerably lower than in the case of unsubstituted pyridine (pK_a = 4.47 in 50% alcohol) [1]. The chlorine atom, which has a strong negative inductive effect, decreases the basicity of the nitrogen atom of the pyridine ring. As a result, the basicity of Ib is considerably lower than that of Ia. As expected, electron-donor methoxy and methyl groups increase the basicity of the nitrogen atom of the pyridine ring. The basicity of Ie is lower than that of Ia, but higher than that of Ib.

Thus a study of the spectral-luminescence characteristics and acid-base properties of 2-(4-pyridyl)-5-(4-R-phenyl)oxazoles showed that significant conjugation between the phenyl and pyridine rings occurs in their molecules in solutions at room temperature. It was established that the pyridine ring in this case acts as a π-electron donor and that the character of the substituent in the phenyl ring has a substantial effect on the basicity of the pyridine nitrogen atom. Consequently, the oxazole ring transmits electronic effects well, in contrast to, for example, the benzoxazole ring [9].

EXPERIMENTAL

The absorption spectra of ethanol solutions of the compounds were measured with an SF-4A spectrophotometer, and the fluorescence spectra were measured with an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical emission detector, and an M-95 microammeter. The luminescence was excited with an SVDSh lamp, from the spectrum of which light with a wavelength of 365 nm was isolated by means of a DMR-4 quartz monochromator. The absolute fluorescence quantum yields were determined by the method of equal absorption [10]. The pK_a values in 50% (by volume) ethanol were measured by spectrophotometry by the method in [11]. Hydrochloric acid served as the oxonium ion donor. The pH values of the solutions were measured directly in the cuvette of a Hitachi ESP-3T spectrophotometer with an OR-401/1 titri-pH meter with glass and calomel electrodes. In the measurement of the pH and the recording of the spectra, the solutions were thermostated at 25°C. All of the measurements of the pK_a values were made several times (five to six measurements at about 0.2 pH unit intervals). The error was ±0.1 pH unit (for Ib and Ie) and ±0.03 pH unit (for Ia and Id). Twice-distilled water was used to prepare the solutions.

The characteristics of the synthesized compounds are presented in Table 1.

2-(4-Pyridyl)-5-(4-R-phenyl)oxazoles (Ia-e). A 12.3-g (0.1 mole) sample of isonicotinic acid and 0.1 mole of the hydrochloride of the corresponding ω-amino-4-R-acetophenone were added with stirring at room temperature to 100 ml of phosphorus oxychloride, after which the mixture was heated to 125°C in the course of 20 min and maintained at this temperature for 20 min. It was then cooled and poured into ice water, and the aqueous mixture was neutralized to pH 7 with 25% ammonium hydroxide. The products obtained were purified by chromatography with a column packed with aluminum oxide by elution with heptane.

1-Ethyl-4-[5-(4-R-phenyl)oxazol-2-yl]pyridinium Toluenesulfonates (IIIa-e). A mixture of 0.1 mole of Ia-e and 0.12 mole of ethyl p-toluenesulfonate was heated at 125°C for 5 min. For purification, the products were precipitated from solutions in absolute alcohol by means of anhydrous ether.

1-Benzyl-4-[5-(4-R-phenyl)oxazol-2-yl]pyridinium Chlorides (IIIf-j). A solution of 0.1 mole of Ia-e and 0.1 mole of benzyl chloride in 150 ml of butyl alcohol was refluxed for 0.5 h, after which it was cooled, and salts IIIf-j were precipitated with anhydrous ether, removed by filtration, and dried. For purification, the products were precipitated from solutions in absolute alcohol by means of anhydrous ether.

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