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CONFIGURATION OF 2-(4-PYRIDYL)-5-ARYLOXAZOLE MOLECULES IN VARIOUS STATES OF AGGREGATION

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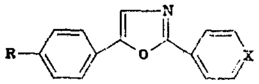
The electronic absorption and emission spectra in the crystals, solutions, vapor, and ethanol—ether (77°K) were investigated for the series of 2-(4-pyridyl)-5-aryl-substituted oxazoles at various temperatures. The conjugation between the rings of the system was investigated by mass spectrometry. The combination of spectral data shows that the configurations of such molecules both in the ground state and in the excited state depends substantially on the state of aggregation and on the temperature.

Earlier [1-3] we studied the effect of the state of aggregation and temperature on the configuration and on the conjugation between the rings in heterosystems with structures of the biphenyl type in the ground and excited states. Using a set of independent physical methods (electronic and vibrational spectroscopy, dielectric constant measurement, mass spectrometry, photoionization, and x-ray crystallography) and considering the reactivity of such compounds, we came to the conclusion that the conjugation in this case does not in fact depend on the angle of rotation (θ) of the rings forming the bis-system when $\theta < 60°$.

The aim of the present investigation was to examine the more complex system of 2-(4-pyridyl)-5-aryloxazoles in terms of the above-mentioned problems. We undertook spectral-luminescence and mass-spectrometric studies of the molecules of a series of 2-(4-pyridyl)-5-aryloxazoles (I-IV) and of the model compound 2,5-diphenyloxazole (V).



I-V

I—IV X=N, V X=CH; I, V R=H, II $R=CH_3$, III R=Cl, IV $R=OCH_3$,

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TABLE 1. Luminescence-Spectral Characteristics of 2-Pyridyl-5-aryloxazoles I-V

Compound	Electronic spectra							
	crystal		solution		vapor		ethanol-ether matrix, 77°K	
	absorption, ν_{max}, cm^{-1}	emission, ν_{max}, cm^{-1}, (φ, %)*	absorption ν_{max}, cm^{-1}	emission, ν_{max}, cm^{-1} (f)	Absorption ν_{max}, cm^{-1}	emission ν_{max}, cm^{-1}	Absorption ν_{max}, cm^{-1}	emission ν_{max}, cm^{-1}
I	31300 29400 (sh)	24400 (127) 22200 (sh)	31250	25300 (0,74)	33700 33000 30700 28900	29150 28100	33900 31100 29900 28400	27500 26300
II	29800 (sh) 28100	25000 (129) 23800	30600	24700 (0,61)	33900 32680 (sh) 29400 (sh)	28700 27600	30700 29400 27900	26300 25600 24300
III	33300 27500	24100 (125) 23300 (sh)	31050	25000 (0,69)	33300 (sh) 30900 28600 (sh)	28900 27800	31300 29900 28300	27500 26300 25000
IV	29400 27800 (sh)	28600 (149) 27500 24400	29600	22700 (0,90)	30000	29800 (sh) 28250 27000 (sh)	29900 28400 27000	25600 24400 23300
V	31750 30500 28700	25900 —	32500	27400 (0,51)	34500 28700 (sh)	29400 28100	34000 32700 31950 31150 30500 29500	29000 27600 26100 25000

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*The percentages in relation to 1,3,5-triphenylpyrazoline as standard are given.

TABLE 2. Stokes' Shifts ($\Delta\nu$) of Compounds I-V

Compound	Magnitude of Stokes' shift $\Delta\nu$, cm^{-1} *		
	ethanol-ether, 77°K	crystal, 293°K	solution in ethanol, 293°K
I	900	3400	6000
II	1600	3100	5900
III	800	3400	6100
IV	1100	5000	5800
V	500	2600	5100

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*For the vapor of compounds I-V $\Delta\nu = 0$.

TABLE 3. Barriers to Internal Rotation and Lifetimes of the Conformers of Biphenyl at Various Temperatures

T, K	$\Delta E^{\neq}$, kcal/mole (according to published data [1])	τ, sec
100	8,8	$\sim 10^{5}$
300	5,4	$\sim 10^{-10}$
343	3,1	$\sim 10^{-12}$
450	1,8	$\sim 10^{-13}$

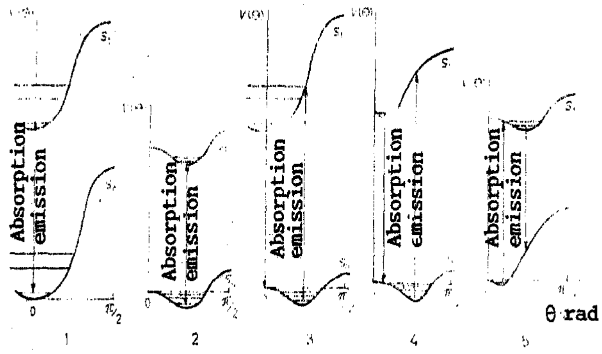

Fig. 1. Cut-out form of the internal rotation potential function for the analogs of diphenyl in ground (S_0) and excited (S_1) states.

TABLE 4. Mass Spectra of Compounds I-V

Compound	m/z value (J)*									
	$[M+1]^+$	M^+	A	B	$[B-H]^+$	M^{2+}	$[M-RC_6H_4CO]^+$	$[RC_6H_4CO]^+$	$[RC_6H_4]^+$	W_M
I	223 (16)	222 (100)	194 (15)	167 (71)	166 (15)	111 (11)	117 (12)	105 (24)	77 (60)	(17,8)
II	237 (17)	236 (100)	208 (11)	181 (30)	180 (24)	118 (14)	117 (10)	118 (14)	91 (41)	(18,3)
III	257 (18)	$\frac{258}{256}\left(\frac{33}{100}\right)$	228 (12)	$\frac{203}{201}\left(\frac{11}{33}\right)$	200 (10)	128 (10)	117 (19)	$\frac{141}{139}\left(\frac{12}{36}\right)$	$\frac{113}{111}\left(\frac{16}{47}\right)$	(17,2)
IV	253 (17)	252 (100)	224 (10)	197 (16)	196 (10)	126 (10)	116 (10)	135 (19)	107 (10)	(17,2)
V	222 (17)	221 (100)	193 (10)	166 (15)	165 (29)	110,5 (11)	116 (18)	105 (17)	77 (35)	(25,3)

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*The intensities of the ions ⩾10% of J_{max} in the mass spectrum are given.

TABLE 5. Shift of the Emission Bands of Compounds I-V during the Phase Transitions (in relation to the emission band of the crystal)

Compound	Hammett σ_p	$\nu - \nu_0$, cm^{-1}		
		matrix (77 K)	solution (293 K)	vapor (550 K)
I	0,00	1860	930	4760
II	−0,170	640	−310	3740
III	0,227	2150	900	4810
IV	−0,268	0	−1660	3860

The spectroscopic investigations were carried out in various states of aggregation (crystal, solution, vapor, and ethanol—ether matrix) (Table 1). The structural changes do not significantly affect the position and intensity of the short-wave absorption bands in the UV spectra. We therefore restricted ourselves to discussion of the long-wave bands corresponding to the conjugation and fluorescence. As seen from Table 1, the position and form of these bands in the electronic spectra change during the phase transitions.

The absorption and emission bands of the crystals of compounds I-V are shifted toward the red region compared with the solutions, and their vibrational structure appears in the form of shoulders and inflections (Table 1). Compound (I-V) luminesce well in the crystal

(Table 1). The Stokes' shift ($\Delta\nu$) amounts to 3000-5000 cm^{-1} (Table 2). It is usually considered [4] that the presence of strong luminescence presupposes planarity in the excited state of the molecules of I-V in the crystal, while a significant Stokes' shift indicates a difference between the configurations of the ground and excited states.

In solution the position of the bands in the electronic spectra is intermediate between the crystal and the vapor. The $\Delta\nu$ value is maximum for the investigated compounds, and they fluoresce well in ethanol solution. The quantum yields of fluorescence (φf) amount to 0.5-0.9. The fluorescence spectrum contains structure (Tables 1 and 2).

In the vapor at about 250°C the bands observed in the absorption and emission spectra were shifted toward the blue region by 50-70 nm compared with the crystal and the solution, and the form of the bands also changed. There was no Stokes' shift (Tables 1 and 2).

In the ethanol—ether matrix at 77°K the vibrational structure of the bands shows up clearly in the electron absorption and emission spectra of compounds I-V, and the bands for compounds I-IV are mirror-symmetric (Table 1). In contrast to this the spectra of (V) are devoid of mirror symmetry. The emission bands of the investigated molecules of I-V at 77°K are shifted toward the blue region compared with the spectra of the crystals and the solutions, while the absorption bands conversely undergo a bathochromic shift with decrease in temperature. The $\Delta\nu$ values for all the investigated compounds are small (500-1600 cm^{-1}) (Table 2).

It is correct to discuss the obtained experimental data in terms of the potential functions for internal rotation, i.e., the dependence of the energy of the molecule on the angle of rotation of the rings (θ). 2-(4-Pyridyl)-5-aryloxazoles can be regarded as conformational analogs of biphenyl which only represent a system consisting of three independent tops having two rotation axes and, accordingly, two angles of rotation for the nuclei θ and ψ.

Thus, whereas the potential function of internal rotation $V(\theta)$ for a molecule of the biphenyl type looks like a curve on a plane, the $V(\theta,\psi)$ function looks like a potential surface in three-dimensional space. However, there are no fundamental differences between these two functions, and for simplicity and clarity in our subsequent discussions we therefore restricted ourselves to discussion of one of them $V(\theta)$.

According to Bellman's classification [5], the molecules of such a structure can be divided arbitrarily into five classes according to their configurations in the ground and excited states. In Fig. 1 we have represented the internal rotation potential functions (IRPF) for these five classes in cut-out form. It is seen that the molecules for which the two states belonging to classes 1 and 2 respectively are simultaneously planar or nonplanar have a small Stokes' shift. (The energies of the 0—0 transitions are similar). In these cases the electronic absorption and emission spectra will be mirror-symmetric, since the S_0 and S_1 states have identical configurations. The deeper the potential well, the more structure the electronic spectrum contains. With a deeper potential well the amplitude of the torsional vibrations in the excited state decreases, and the probability on nonradiative transitions is reduced. This is turn leads to an increase in the quantum yield of fluorescence. Consequently, compounds belonging to classes 1 and 3 must luminesce well, and there will be clearly defined vibrational structure in their luminescence spectra, in contrast to compounds belonging to the second class, which as a rule do not luminesce. Compounds belonging to classes 4 and 5 can be regarded as intermediate between classes 1-3.

By analyzing the position and the form of the bands in the electronic spectra of compounds I-V (Table 1), we came to the conclusion that the conformations of the ground and excited states show the maximum difference in ethanol solution and in the crystal; the S_1 state is planar, while the S_0 state is clearly nonplanar. Consequently, compounds I-V must be assigned to class 3 in Bellman's classification (Fig. 1), but the degree of nonplanarity will differ for each investigated compound in the S_0 state. In the vapor the configuration of the molecules I-V is identical both in the ground state and in the excited state, and they are both substantially nonplanar.

On the basis of published data [1] on the sizes of the barriers to internal rotation we calculated the lifetimes of the conformers of biphenyl at various temperatures (τ) (Table 3). The τ values given in Table 3 were determined by means of the formula taken from [6], where A was taken as equal to 10^{14} sec^{-1}:

$$1/\tau = k = A\exp(-\Delta E/RT).$$

On the other hand, the lifetime of the excited state τ_R amounts to approximately 10^{-8}-10^{-9} sec [4, 7]. As follows from the data in Table 3, at low temperatures the lifetime of the excited state of the molecules with structures of the biphenyl type (τ_R) is shorter than the lifetime of the conformer (τ), and such a molecule (being in the excited state) consequently does not succeed in changing its conformation. At room temperature the τ and τ_R values are approximately the same, while at elevated temperatures in the excited state the benzene rings can rotate several tens of times about the central bond during the lifetime of the excited state (τ_R).

After analysis of the electronic spectra of compounds I-V it can be concluded that in the S_1 state and 77°K the conformation of the molecules I-III does not succeed in changing, and the fluorescence emission takes place from the nonequilibrium nonplanar vibrational state. In contrast to this, in compound V at 77°K the conformation of the S_0 and S_1 states is different, since the absorption and emission spectra are not mirror-symmetric. For compound (IV) the position and the form of the emission bands in the crystal, solution, and matrix at 77°K coincide. Consequently, in the above-mentioned states of aggregation the molecule of IV is planar in the S^1 state.

While examining the electronic spectra of compounds I-V (Table 1) in the gas phase, we concluded that the aromatic fragments of these molecules are in free rotation, and it can be assumed that the conformations of the ground and excited states are identical. (This case was not classified by Bellman.)

The maximum-intensity molecular ion peak is recorded in the mass spectra of compounds I-V (Table 4). Dissociation processes involving the direct elimination of the aryl or pyridine fragment from M^+ were not observed. (This was demonstrated by recording the mass spectra of the metastable ions by the DADI technique.)

The mass-spectrometric data (Table 4) indicate significant conjugation between the rings in the molecules of I-V. Apart from the absence of cleavage of the bond between the rings, the presence of conjugation in the system is confirmed by the high stability of the compounds I-V to electron impact (W_M lies in the range of 17-25% of the total ion current) and by the significant intensity of the doubly charged molecular ion ($M^{2+} \sim 10\%$) [2, 5].

In addition to the above-mentioned ions, the following fragments were observed in the mass spectra (Table 4): $[M - CO]^+$ (A) (for compound I, found 194.0868, $C_{13}H_{10}N_2$, calculated 194.0843); $[A - HCN]^+$ (B) (for I found 167.0744, $C_{12}H_9N$, calculated 167.0735); $[B - H]^+$ (for I found 166.0646, $C_{12}H_8N$, calculated 166.0657); $[M - RC_6H_4CO]^+$; $[RC_6H_4CO]^+$. The ejection of the CO particle from M^+ presupposes migration of the aryl radical to position 4 of the oxazole ring. The analogous process has been observed and discussed for 2-phenyl-substituted indoles [8]. The appearance of the last two ions presupposes strong π-electronic interaction between the aryl and oxazole rings compared with the substituent at position 2.

The suggestions made on the basis of the mass spectra are closely confirmed during examination of the electronic effects of the substituents in the phenyl ring on the position of the emission bands. Earlier, while studying the acid-base characteristics of compounds I-IV, we established [9] that the pyridine ring behaves as a π-electron donor. The introduction of electron-donating substituents into the benzene ring must in turn increase the π-electron density in the region of the bonds between the rings, i.e., increase the conjugation and promote stabilization of the planar conformer. The shifts of the emission bands in the vapor, solution, and matrix in comparison with the crystal are given in Table 5. From this table it follows that the magnitude of this shift correlates with the electronic characteristics of the substituents in the benzene ring. The electron-donating groups $-OCH_3$ and CH_3 reduce this quantity. This is particularly noticeable for the matrix and solution. In the vapor this shift also changes in line with the electronic characteristics of the substituents, but the effect of the substituents in this case is not so substantial, since the effect of the substituents is leveled out in the vapor on account of free rotation of the rings.

Our study of the luminescence-spectral characteristics of compounds of the 2-(4-pyridyl)-5-aryloxazole series has shown that the phase transitions and temperature changes are reflected significantly in the spectral characteristics and, consequently, affect the degree of conjugation and the conformation in the investigated molecules.

EXPERIMENTAL

The luminescence-spectral investigations were carried out on a Hitachi EPS-3T spectrophotometer fitted with a G-3 fluorescence attachment. The spectrophotometer was provided with special devices for recording the spectra of low-temperature matrices and vapor. The absorption spectra of the crystals were obtained in tablets with potassium chloride. The luminescence spectra of the crystals were obtained on apparatus consisting of a mirror-type ZMR-3 monochromator, an FEU-18 optical detector, and an M-95 microammeter. The photoluminescence was excited with a SVDSh-500 lamp, from the spectrum of which the λ_{exc} 365 nm line was isolated by means of a DRM-4 quartz monochromator. The absolute quantum yields of fluoresence were determined by the method of equal absorption with 1,3,5-triphenylpyrazoline as standard. All the emission spectra were corrected with allowance for the sensitivity of the FEU instrument. The low- and high-resolution mass spectra were obtained on a Varian MAT-311A instrument. The recording conditions were standard: accelerating potential 3 kV; cathode emission current 1000 μA; ionizing potential 70 eV; evaporation temperature for samples of (I-V) in the ion source from 140°C. Compounds (I-V) were obtained by known methods [9]. The purity of the compounds was monitored by chromatography.

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