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CONFIGURATION OF 2-(2-THIENYL)-5-ARYLOXAZOLES IN THEIR GROUND AND EXCITED STATES

P. B. Kurapov, L. Sh. Afanasiadi, and L. D. Patsenker

UDC 547.787.2'734'543.422.6'426:541.63

The electronic absorption and emission spectra of a series of 2-(2-thienyl)-5-aryloxazoles in solutions, vapors, and matrices (ethanol–ether, 77 K) have been studied, and the fluorescence quantum yields have been determined. The basicity constants in aqueous solutions in the ground state have been measured spectrophotometrically. The set of spectroscopic data indicate that the configuration of the 2-(2-thienyl)-5-aryloxazoles in the ground state is nearly planar and is practically independent of the temperature and the state of aggregation. Conversely, in the excited state the configuration of these molecules is generally nonplanar and depends on external factors.

We previously [1, 2] studied the influence of the temperature and phase transitions on the conjugation between the rings and the configuration of the ground (S_0) and excited (S_1) states of 2-(4-pyridyl)-5-aryloxazoles with the aid of electronic spectroscopy and mass spectrometry. It was shown that the configuration of such molecules is significantly dependent on the state of aggregation and the temperature. An analysis of the position and form of the bands in the electronic spectra of 2-(4-pyridyl)-5-aryloxazoles showed [2] that the conformations of these molecules in the S_0 and S_1 states are different in solutions and in the crystalline state; the excited state is planar, and the ground state is nonplanar, the degree of nonplanarity being dependent on the nature of the substituent in the aromatic ring. In the vapor phase the configurations of these compounds in the S_0 and S_1 are identical, and they are both essentially nonplanar.

In [3] we proposed an approach to the determination of the configuration of molecules with structures of the diphenyl type in the ground and excited states on the basis of the electronic absorption and emission spectra.

The purpose of the present investigation was to examine the configuration of 2-(2-thienyl)-5-aryloxazoles I-VI in the framework of this approach (see scheme on following page).

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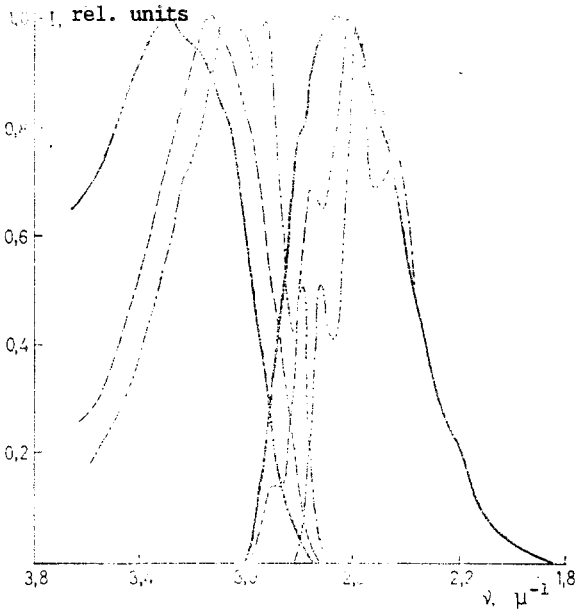
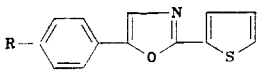


Fig. 1. Electronic absorption and emission spectra of compound I: ———) vapor (200°C); – – –) solution in hexane (20°C); –·–·–) 2:1 ethanol–ether matrix (–196°C).



I – VI

I R=H, II R=CH_3, III R=OCH_3, IV R=Cl , V R=Br, VI R=NO_2

The spectroscopic investigations were carried out in solutions at room temperature (the solvents were ethanol, toluene, and hexane), vapors, and an ethanol–ether matrix (77 K). The structural changes do not have a significant influence on the position, intensity, and form of the short-wavelength absorption bands in the UV spectra; therefore, we shall henceforth discuss only the long-wavelength bands corresponding to conjugation and fluorescence in detail.

Compounds I-VI absorb at 3.1-2.8 μ^{-1} and emit at 2.8-2.6 μ^{-1} (Table 1). The long-wavelength absorption band is highly intense in solutions ($\log \varepsilon \approx 4.5$ to 4.3) and is assigned to an allowed π-π^* transition; the oscillator strength f = 0.5 to 0.6 (Table 2). The position and form of this band are weakly dependent on the nature of the solvent (Table 2), but they undergo significant changes upon the transition from the vapor to a solution or the matrix (Table 1, Figs. 1 and 2), moving in the red direction as the temperature is lowered. Its vibrational structure, which is clearly displayed at 77 K, is obliterated in the solutions and vapors.

Compounds I-V fluoresce intensely in solutions and the matrix (Table 1). The introduction of a nitro group (compound VI) quenches the fluorescence.

The vibrational structure of the emission bands of compounds I-V is maintained upon the transition from the matrix to a solution, but it is obliterated in the vapors at a temperature of about 250°C.

An analysis of the form and position of the emission bands of compounds I-V provides evidence that the populating of the vibrational levels of the ground state is not significantly altered when the temperature is raised from –196°C to 20°C (Figs. 1 and 2). The electronic transition to the first vibrational level of the ground state is most likely. The emission spectrum of compound I at room temperature in a solution shows a "hot" transition ($\nu = 2.90\ \mu^{-1}$), which is not displayed at the low temperature. The probability of this transition increases at 200°C in the vapor (Fig. 1).

TABLE 1. Luminescence-Spectroscopic Properties of 2-(2-Thienyl)-5-aryloxazoles I-VI

R	Ethanol, 20°C		Hexane, 20°C		Toluene, 20°C		Ethanol–ether, 196°C		Vapor, 200°C	
	ν_{abs}, μ^{-1} (log ε)	ν_{fluor}, μ^{-1} (φ_f)	ν_{abs}, μ^{-1} (log ε)	ν_{fluor}, μ^{-1} (φ_f)	ν_{abs}, μ^{-1} (log ε)	ν_{fluor}, μ^{-1} (φ_f)	ν_{abs}, μ^{-1} (log ε)	ν_{fluor}, μ^{-1} (φ_f)	ν_{abs}, μ^{-1} (log ε)	ν_{fluor}, μ^{-1} (φ_f)
H	3,13 (4,51) 3,03* (4,47)	2,90 2,75 2,60 2,48 (0,33)	3,14 (4,40) 2,95* (4,33) 2,80* (3,92)	2,90 2,75 2,62 2,49 (0,33)	3,09 (4,38) 2,97* (4,32)	2,88 2,70 2,57 2,45 (0,31)	3,09 3,01 2,93 2,86* 2,78	2,72 2,59 2,45 2,31 2,17 (0,75)	3,24	2,63
CH_3	3,10 (4,44) 3,01* (4,42)	2,70 2,54 2,43 (0,29)	3,12 (4,48) 3,06 (4,47) 2,98 (4,44) 2,81* (4,01)	2,75 2,61 2,47 (0,25)	3,07 (4,39) 2,94* (4,36)	2,70 2,56 2,43 (0,32)	3,13* 3,06 2,99 2,91 2,83 2,75	2,70 2,56 2,43 2,28 2,15 (0,94)	3,18	2,58
OCH_3	3,03 (4,47) 2,74* (4,02)	2,43 (0,29)	3,06 (4,40) 2,99 (4,39) 2,93 (4,36) 2,78 (4,00)	2,72 2,57 2,44 (0,21)	3,03 (4,40) 2,90* (4,38)	2,65 2,49 2,38 (0,33)	3,00 2,92 2,86 2,78 2,70	2,64 2,50 2,36 2,22 2,08 (1,01)	3,29	2,56
Cl	3,09 (4,48)	2,70 2,56 2,45	3,16* (4,45) 3,11 (4,50) 3,03 (4,50) 2,99* (4,47) 2,82* (4,08)	2,75 2,61 2,48 (0,17)	3,07 (4,41) 2,97* (4,39)	2,70 2,61 2,44 (0,20)	3,22* 3,13* 3,07 2,99 2,91 2,83 2,75	2,72 2,58 2,45 2,43 2,31 2,17 (0,62)	3,29	2,56
Br	3,07 (4,55)	2,71 2,56 2,45 (0,19)	3,10 (4,47) 3,03 (4,47) 2,96 (4,43) 2,88 (4,25) 2,82 (4,08)	2,76 2,61 2,46 (0,22)	3,07 (4,46) 2,97* (4,44)	2,70 2,62 2,42 (0,22)	3,24* 3,15* 3,08 3,00 2,92 2,84 2,76	2,72 2,58 2,45 2,42 2,31 (0,16)	3,25	—
NO_2	2,76 (—**)	2,41 (0,1)	3,03* 2,85 2,72 2,59	— (0,1)	—	—	2,78 2,62	2,22 2,09 1,96 (0,1)	—	—

*Shoulder
**The compound is poorly soluble in ethanol, hexane, and toluene.

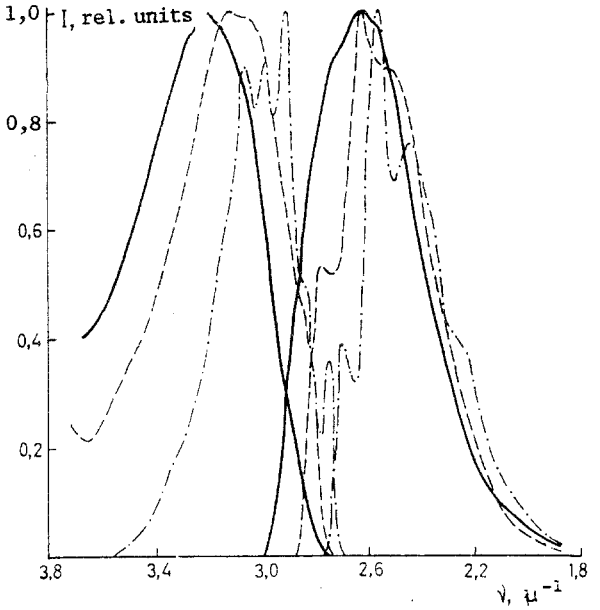


Fig. 2. Electronic absorption and emission spectra of compound II. The notation is the same as in Fig. 1.

TABLE 2. Influence of the Character of the Solvent on the Luminescence-Spectroscopic Properties of 2-(2-Thienyl)-5-phenyloxazole (I)

Solvent	Absorption			Emission	
	ν_{max}, μ^{-1}	lg ε	f	ν_{max}, μ^{-1}	φ_f
Hexane	3,14	4,40	0,58	2,90	0,33
	2,95*	4,33		2,75	
	2,80*	3,92		2,62	
				2,49	
Toluene	3,09	4,38	0,54	2,88	0,31
	2,97	4,32		2,70	
				2,57	
				2,45	
2-Propanol	3,13	4,42	0,60	2,89	0,33
				2,72	
				2,58	
				2,47	
Ethanol	3,13	4,51	0,60	2,90	0,33
	3,03*	4,47		2,75	
				2,60	
				2,48	
Methanol	3,13	4,54	0,60	2,89	0,22
				2,73	
				2,56	
				2,48	
Aceto-nitrile	3,13	4,43	0,60	2,90	0,28
				2,72	
				2,57	
				2,49	
DMSO	3,13	4,42	0,52	2,82	0,31
				2,69	
				2,53	
				2,42	

TABLE 3. Frequencies (ν_v) of Vibrational Transitions in the Electronic Absorption and Emission Spectra of Compounds I-VI

R	Transition	Ethanol–ether, –196°C		Hexane, 20°C	
		ν_v^{abs}, cm^{-1}	ν_v^{em}, cm^{-1}	ν_v^{abs}, cm^{-1}	ν_v^{em}, cm^{-1}
H	0—1	790	1340	750	1370
	1—2	760	1460	750	1240
	2—3	790	1380	680	
	3—4	750	1330		
CH_3	0—1	780	1390	840	1440
	1—2	740	1310	840	1360
	2—3	780	1440	820	1330
	3—4	730	1380	570	
OCH_3	0—1	750	1390	780	1390
	1—2	790	1350	770	1090
	2—3	670	1420	610	
	3—4	790	1390	740	
Cl	0—1	780	1330	800	1510
	1—2	740	1330	790	1290
	2—3	870	1370	630	1220
	3—4	740	1410	660	
	4—5	670		590	
	5—6	810			
Br	0—1	790	1330	650	1510
	1—2	740	1310	770	1420
	2—3	880	1390	720	
	3—4	740		660	
	4—5	770			
	5—6	820			
NO_2	0—1	—	1300	—	—
	1—2		1310		

The weak dependence of the position and form of the bands in the emission spectra of compounds I-V on the temperature and phase, as well as the significant distance between the electronic-vibrational (vibronic) bands (Table 3) in the emission spectrum, attest to the stability of the configurations of molecules I-V in the ground (S_0) state. Conversely, the position of the maximum of the long-wavelength absorption band depends on the temperature

TABLE 4. Stokes Shift of the 0-0 Band and Displacement of the Band Maxima in the Electronic Absorption and Emission Spectra of Compounds I-V

Compound	Stokes shift of the 0–0 band, μ^{-1}		Displacement of band maximum (μ^{-1}) relative to the spectrum in the matrix at −196°C			
			absorption		emission	
	ethanol–ether matrix, −196°C	solution in hexane, 20°C	solution in hexane	vapor, 200°C	solution in hexane	vapor, 200°C
I	0,06	0,10	0,21	0,31	0,03	0,04
II	0,05	0,06	0,21	0,27	0,05	0,02
III	0,06	0,06	0,20	0,33	0,08	0,07
IV	0,03	0,07	0,20	0,38	0,02	0,05
V	0,04	0,06	0,18	0,33	0,03	—

TABLE 5. Dependence of the Fluorescence Quantum Yield φ_f of Compounds I-V on the Temperature

Compound	Matrix, −196°C	Solution in toluene at various temperatures (°C)								
		18	25	38	46	64	76	86	101	110
I	0,75	0,31	0,30	0,29	0,28	0,25	0,24	0,23	0,22	0,21
II	0,94	0,32	0,32	0,32	0,32	—	0,32	0,32	0,32	—
III	1,01	0,33	0,32	—	0,31	0,27	—	—	0,26	—
IV	0,62	0,20	0,20	0,19	0,19	0,17	0,17	—	—	—
V	0,46	0,22	0,21	—	0,21	0,20	—	0,19	0,19	—

TABLE 6. Acid-Base Properties of 2-(2-Thienyl)-5-aryloxazoles in Aqueous Solution at 20°C

Compound	pK_{BH^+}	Electronic absorption spectra, ν, μ^{-1} (log ε)	
		base	cation
I	−0,03±0,03	3,10 (4,37)	2,97 (4,37)
II	0,13±0,05	3,01 (4,33)	2,94 (4,34)
III	0,99±0,10	3,01 (4,37)	2,86 (4,33)
IV	−0,19±0,05	3,05 (4,47)	2,94 (4,46)
V	−0,24±0,10	3,06 (4,52)	2,94 (4,41)
VI	−0,46±0,08	2,74 (4,36)	2,83 (4,42)
Oxazole	0,8 [5]	—	—
5-Phenyloxazole	0,26 [5]	—	—

and the phase. This band undergoes hypsochromic shifts upon the transition from the matrix (−196°C) to a solution (20°C) and the vapor (200-250°C) amounting to 0.2 and 0.3 μ^{-1}, respectively (Table 4). The analogous shifts in the emission spectra are equal to 0.02-0.08 μ^{-1}. The distance between the vibronic bands in the absorption spectra is significantly lower than that in the emission spectra (Table 3), and already at room temperature the vibrational structure of the absorption band is obliterated and is manifested only in the form of shoulders and points of inflection (Figs. 1 and 2). The magnitude of the Stokes shift of the 0-0 band ($\Delta\nu_{0-0}$) for compounds I-V also increases with increasing temperature and amounts to ~0.05 μ^{-1} at −196°C and ~0.07 μ^{-1} at 20°C (Table 4). The absorption and emission spectra do not display mirror symmetry (Figs. 1 and 2).

The fluorescence quantum yield φ_f of compounds I-V decreases appreciably as the temperature is increased (Table 5). It is maximal at −196°C, while it is close to unity in the case of compounds I-III.

Thus, the set of spectroscopic data attest to the fact that the molecules of compounds I-V are planar in the ground state, and the temperature dependence of the emission spectra indicates that the configuration of the ground state is stable and that the energy barrier to internal rotation is high.

The excited state differs in configuration from the ground state (the energies of the 0-0 transitions do not coincide, and the absorption and emission spectra do not display mirror symmetry), and the nonplanarity of the excited state increases with increasing temperature. The height of the energy barrier to internal rotation in the excited state is significantly lower than that in the ground state.

The planarity of the ground electronic state and its maintenance as the temperature is increased are indications of a significant π-electronic interaction (conjugation) between the aromatic rings in molecules I-V and the significant double-bonded character of the bonds between the rings. The localization of π electrons in the regions of the bonds between the rings causes a decrease in the electron density in the rings, which, in turn, should result in a decrease in the basicity of the nitrogen atom in the oxazole ring.

For the purpose of confirming this hypothesis, we measured the values of pK_{BH^+} for the conjugate acids of compounds I-VI in aqueous solutions at room temperature (Table 6). It is known [4] that the value of pK_{BH^+} for unsubstituted oxazole in water at 25°C is equal to 0.8 and that the value of pK_{BH^+} for 5-phenyloxazole is equal to 0.26. It would seem that the introduction of the thiophene ring, which is an electron donor with respect to oxazole [5], should increase the basicity of compounds I-VI, but this does not occur. The value of pK_{BH^+} for compound I, for example, is 0.3 pH units lower than the value for 5-phenyloxazole (Table 6). Such an experimental finding may be attributed to the displacement of π-electron density from the oxazole ring into the region of the bond between the thiophene and oxazole fragments. This is in good agreement with the conclusions regarding the significant conjugation between the rings in the molecules of 2-(2-thienyl)-5-aryloxazoles I-VI which we drew on the basis of the spectroscopic data.

The introduction of electron-donor substituents into the para position of the phenyl ring (compounds II and III) increases the basicity, while acceptor substituents (compounds IV-VI) lower the basicity of the nitrogen atom in the oxazole ring (Table 6).

Thus, the set of spectroscopic data and the results of the measurements of the basicity of the nitrogen atom of the oxazole ring point out the existence of considerable conjugation (π-electronic interaction) between the aromatic rings in the system of 2-(2-thienyl)-5-aryloxazoles I-VI in the ground state. The ground-state configuration is nearly planar and practically independent of the temperature and the state of aggregation; however, after excitation, the configurations of these molecules are generally nonplanar and significantly dependent on the external factors.

EXPERIMENTAL

The luminescence spectroscopic investigations were carried out on an Hitachi (model EPS-3T) spectrophotometer, which was equipped with a G-3 attachment. The spectrophotometer was outfitted with special devices for recording the spectra of the low-temperature matrices and vapors. The absolute fluorescence quantum yields were determined according to the equal-absorption method with the use of a solution of quinine sulfate in 0.1 N H_2SO_4 as a standard. All the emission spectra were corrected with consideration of the sensitivity of the photomultiplier. The values of pK_{BH^+} in water were measured spectrophotometrically. The donor of oxonium ions was sulfuric acid. The pH of the solutions was measured in the range from 13 to 1 directly in the cuvette of the spectrophotometer on an ÉV-74 pH-meter with glass and calomel electrodes, and solutions of sulfuric acid with a known acidity function were used in the more acidic region. Doubly distilled water was used to prepare the solutions. Compounds I-VI were synthesized and purified according to known methods [6].

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STRUCTURE AND DUAL REACTIVITY OF 2-PHENYLPEMOLINE

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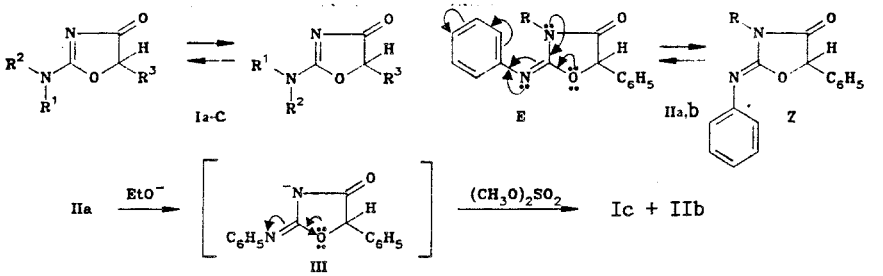
UDC 547.787.1:541.081.7'634:543.422.25

5-Phenyl-2-phenylimino-4-oxazolidinone exists in DMSO-D_6 in the form of a mixture of the E and Z isomers of the imino tautomer, but it crystallizes in the amino form. Parallelism between the basicity and nucleophilicity of the reaction centers of this mesomeric anion is observed when the alternative isomers (and the tautomers corresponding to them) differ significantly in stability. If this condition is not fulfilled, these parameters do not coincide, as is illustrated in the example of its methylation reaction.

2-Amino-4-oxazolinone (Ia) and 5-phenyl-2-amino-4-oxazolinone (pemoline, Ib) exist in solutions in the form of the amino tautomers [1, 2]. Their 2-methyl derivatives also have amino structures [3], while, the imino form predominates in the case of 5-phenyl-2-phenylimino-4-oxazolidinone (2-phenylpemoline, IIa), according to the data from UV spectroscopy in methanol [2]. The experience gained in the investigation of the structure of cyclic amidines [4] calls for the testing of this conclusion with the aid of PMR spectroscopy with the aid of model compounds Ic and IIb.



I a $R^1=R^2=R^3=H$; b $R^1=R^2=H$, $R^3=C_6H_5$; c $R^1=CH_3$, $R^2=R^3=C_6H_5$; II a R=H; b $R=CH_3$

In [1] only the singlet signal of the NH protons was discovered in the PMR spectrum of compound Ia in DMSO-D_6, but the signals of these protons were not detected at all in [2]. We found that in solutions of compounds Ia and Ib in DMSO-D_6, as in the case of 2-amino-4-thiazolinone [5], the NH protons have two signals of equal intensity, which are consistent with the amino structure and are attributable to automerization owing the hindered rotation around the partially double $C_{(2)}{=}{=}N_{(2')}$ bond [4, 5]. In the case of the thia analog, the addition of a phenyl ring to the exocyclic nitrogen atom results in "reversal" of the tautomeric equilibrium in solutions [4]. This is also true for compound IIa, as follows from a comparison of its PMR spectra in DMSO-D_6 with the spectra of methylated derivatives Ic and IIb, which simulate the amino and imino form of compound IIa, respectively.

The PMR spectrum of 2-methylphenyl derivative Ic attests to hindered rotation around the $C_{(2)}{=}{=}N_{(2')}$ bond and different populating of the conformers. The signal of the $C_{(5)}H$ proton is doubled, the low-field singlet (5.78 ppm) being approximately 5 times less intense

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 388-392, March, 1989. Original article submitted July 9, 1987; revision submitted December 14, 1987.

0009-3122/89/2503-0325 $12.50