According to the results given in [4], the phase of $(Y, Yb, Er)_3OCl_7$ has a much smoother thermal dependence for the intensities of both luminescences — where the maxima are situated close to the value of the room temperature — than is the case for $(Y, Yb, Er)OCl_7$. Therefore, from the point of view of practicality, it is advantageous to use phosphors based on (Y, Yb, $Er)_3OCl_7$. However, one should emphasize that known synthesis techniques allow one to obtain uniform, single-phase samples only on the basis of the gadolinium matrix.

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SPECTRAL-LUMINESCENT AND LASING PROPERTIES OF PYRIDYLARYLOXAZOLES

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Pyridine analogs of 2,5-diaryloxazoles are known as effective lasing compounds in the blue-green and yellow regions of the spectrum [1-4]. The introduction into the 2,5-diaryloxazole molecule of an N-heterocycle instead of an aromatic radical leads to increase in the fluorescence quantum yield and causes an appreciable bathofloric effect. 2,5-Pyridylaryloxazoles are more readily soluble in ethanol, and their quaternary salts, obtained by the quaternization of the nitrogen atom of the N-heterocycle, are also readily soluble in water, which with respect to the thermophysical properties is one of the best solvents for the lasing compounds.

In the present work, we studied the spectral-luminescent and lasing properties of several new 2-(4-pyridyl)-5-aryloxazoles with a varying substituent in the 5-phenyl radical (I) and their quaternary salts (II):



In contrast with what has been described in [1], compounds I were obtained by a one-step method by heating isonicotinic acid with substituted α -aminoaryl methyl ketones in a phosphorus oxychloride medium. The synthesis of the quaternary salts II was carried out by heating 2-(4-pyridyl)-5-aryloxazoles I with a small excess of alkylating agents (benzyl chloride, ethyl p-toluenesulfonate) at 125°C for 5 min [5].

The spectral-luminescent properties of the compounds synthesized were investigated by using a SF-4A spectrophotometer and a fluorescent apparatus, based on the ZMR-3 monochromator

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Com- pound	Ri	Ru	X	vmax abs cm ⁻¹	$\varepsilon \cdot 10^{-4}$, liter/ mole.cm	v max, abs; cm ^{_1}	η	$\Delta v \cdot 10^{-1}$ cm ⁻¹
Ia	Н		_	31250	2,33	25320	0,74	5,93
Ib	CI	- 1	-	31060	3,74	25000	0,69	6,05
Ic	C_6H_5	-	-	29850	4,40	23810	0,55	6,04
Id	CH₃O	- 1	-	29590	2,67	22730	0,90	6,86
IIa	Н	C ₂ H ₅	PTS	40000 26670	1,78 3,15	20830	0,87	5,84
ПÞ	н	$CH_2-C_6H_5$	CI	40000 25970	$1,62 \\ 2,86$	20620	0,82	5,35
IIc	Cl	C_2H_3	PTS	39220 26320	1,54 2,48	20620	0,72	5,70
ΪIđ	CJ	$CH_2 - C_6H_3$	C!	39220 25970	1,50 2,17	20620	0,73	5,35
Ile	C ₆ H ₅	C ₂ H ₅	PTS	35090 25320	2,34 3,18	18020	0,79	7,30
Ηf	C ₆ H ₅	CH ⁵ -C ⁶ H ²	CI	35090 24690	2,06 2,46	17390	0,85	7,30
IIg	CH₃O	CH3	PTS	38460 24390	$1,70 \\ 2,26$	17540	0,56	6,85
IIh	CH3O	C ₂ H ₅	PTS	38460 24390	$1,52 \\ 1,92$	17240	0,68	7,15
IIi	CH3O	CH ₂ -C ₆ H ₅	CI	37740 23810	$1,88 \\ 2,23$	17240	0,78	6,57
	PPO		}	32890	2,70	27620	0,51	5,27

TABLE 1. Spectral-Luminescent Characterístics of Ethanol Solutions of Compounds I, II

TABLE 2. Spectral-Luminescent Characterístics of Aqueous Solutions of Compounds I and II

Compound	Per-volume content of acetic acid, %	$\gamma_{abs}^{max}, cm^{-1}$	E·10 ⁻⁴ . liter/ mole·cm	$\gamma_{fl}^{max}, cm^{-1}$	ŋ
Ia	5	27170	2,05	21050	0,85
١b	5	26460	1,60	20620	0,86
Ic	60	25770	2,86	17700	0,44
Iq	5	25640	2,10	17240	0,28
Ha	0	26670	2,35	20620	0,81
Пр	0	26320	1,98	20620	0,81
IIc	0 5 50	26740 26670 26460	1,14	20160 20120 20080	0,81 0,84 0,93
11q	5	264 60	2,51	20410	0,85
II.e	0 5 50	25640 25640 25320	$2,60 \\ 2,82 \\ 2,96$	18020 17860 17860	0,39 0,39 0,65
IIf	0 5 50	25320 25130 24940	2,12	18180 18080 17990	0,38 0,38 0,53
IIg	0	25380	1,79		·
llh	0	25000	2,17	17240	0,44
Πī	0	24810	1,87	17090	0,24

with photoelectric recording. The absolute fluorescence quantum yields were determined by the equal absorption method [6].

The absorption spectra of compounds I in 96% ethanol are not different in their character from an absorption spectrum of an unsubstituted 2,5-diphenyloxazole (PPO). Using the data shown in Table 1, it is possible to trace the influence of substituents in the paraposition of the 5-phenyl radical on the spectral-luminescent properties of compounds I. Com-

Compound	Solvent	v_1, cm^{-1}	KTr ^{max} , %
Ia	Ethanol Water (5%)	25320—25710 20450—21650	$4 \\ 20$
IÞ	Ethanol Water (5%)	Does not lase 19880—19190	14
Ic	Ethanol	23260—23700	2
	Water (60%)	16000—16950	14
Id	Ethano1 Water (5%)	Does not lase 16810-17790	15
IIa	Ethanol	19840—20240	16
	Water	19570—20330	20
Пр	Ethanol	19460—20040	14
	Water	19310—20080	16
llc	Ethanol	19160—19610	13
	Water	18980—19610	14
Πq	Ethanol	18660—18900	<1
	Water (5%)	18830—19650	16
Ile	Water Water (5%) Water (50%)	$\begin{array}{c} 16340 - 16840 \\ 16290 - 16950 \\ 16290 - 16950 \end{array}$	3 7 15
IIf	Water	16290—16920	3
	Water (5%)	16130—16950	8
	Water (50%)	16130—16950	21
IIg	Water	16720—17610	15
	Water(5%)	16720—17610	20
	Water(50%)	16720—17610	24
II b	Water	16670—17760	16
	Ethanol	16720—17890	28
Ili	Ethanol	16720—17210	6
	Water	16670—17540	9

TABLE 3. Lasing Characteristics of Solutions of Compounds I and II

pared with the aromatic analog (PPO), the absorption and luminescence spectra of pyridylaryloxazoles are shifted to the long-wave region and have a considerably larger Stokes shift ($\Delta \nu$). The highest values of the shifts are observed in the methoxy-substituted compound, which is due to the coordinated action of the electron-donor methoxy group and pyridine fragment, having an electron-acceptor character, on the distribution of the electron density in the molecule.

The absorption spectra of ethanolic solutions of compound II in the $23,810-40,000-cm^{-1}$ region are characterized by the presence of two bands, whose absorption and molar extinction coefficient ε values depend on the electronic nature of the substituents (Table 1). The most intense absorption bands lie in the 26,670-40,000-cm⁻¹ region. All the compounds have a high fluorescence quantum yield η and a large Stokes shift (up to 7,000 cm⁻¹ in methoxy and phenyl-substituted compounds).

It should be noted that the type of the anion does not have any noticeable influence on the spectral-luminescent properties of compounds II.

Compounds II are readily soluble in water, while compounds I dissolve in water only when an acid is added (for example acetic acid), due to the protonation of the N-heterocyclic nitrogen atom. Table 2 shows the spectral-luminescent characteristics of aqueous solutions of pyridylaryloxazoles. The absorption spectra in the 24,390-41,670-cm⁻¹ region are in the form of two bands, whose position depends on the type of substituents (Table 1 shows the characteristics of the longest-wave absorption band). The increase in the acetic acid content in water practically has no influence on the positions of the absorption and fluorescence spectra, but leads to increase in the extinction and fluorescence quantum yield.

The study of the lasing properties of pyridylaryloxazoles was carried out in a laser containing a 1-cm-thick quartz cuvette with the solution of the compound studied, placed in a resonator formed by flat dielectric mirrors with reflection coefficients of 30 and 100% in the 14,290-23,260-cm⁻¹ region of the spectrum. The pumping of the solutions was carried out by an emission of a second harmonic of a ruby laser.

The ethanolic solutions were studied in a lateral variant of pumping with a maximal energy density of 0.1 J/cm^2 . The aqueous solutions were studied at a quasilongitudinal (under an angle of 10°) pumping with a maximal energy density of the order of magnitude of 1 J/cm^2 . The pumping and lasing energies were measured by an IMO-2 apparatus. The lasing spectrum was determined by means of a STE-1 spectrograph.

Table 3 shows the lasing characteristics of compounds I and II. The maximal transformation coefficient of the pumping energy into the lasing energy (KTr_{max}) and the lasing spectrum (v_1) are shown. The per-volume content of acetic acid in the solvent (water) is given in parentheses.

Acidified aqueous solutions of the compounds studied effectively lase emission in the spectral range of 16,130-20,410 cm⁻¹. The ethanolic solutions of compounds I are considerably less effective than the acidified aqueous solutions and lase emission in a shorter-wave region of the spectrum (23,260-25,640 cm⁻¹). The aqueous and ethanolic solutions of compounds II are similar to each other in both the energy and spectral characteristics.

Acidification of the aqueous solutions by acetic acid increases the lasing energy, practically without changing the position of the emission spectrum. The position of the emission spectrum is also independent of the concentration of the compound studied in the concentrations range from 10^{-4} to 10^{-3} mole/liter.

The longest-wave lasing is observed in the aqueous solutions of methoxy- (compounds Id, IIg, IIh, IIi) and phenyl-substituted compounds (Ic, IIe, IIf) at the same time, while for the methoxy-substituted compounds, the wave length of the lased emission is close to a fluor-escence maximum, the lasing spectrum of phenyl-substituted compounds is shifted with respect to the fluorescence maximum to the long wave side by nearly 1,200 cm⁻¹.

A somewhat smaller long-wave shift $(^1,000 \text{ cm}^{-1})$ also takes place for the chlorine-substituted compounds Ib, IIc, and IId. The observed long-wave shirt of the lasing spectrum for compounds with an inappreciable overlapping of spectra of fluorescence and absorption from the ground state is probably due to the presence of absorption from the excited state in the region of maximum fluorescence.

The compounds studied are thus prospective for lasing emission in the 16,130-20,410 cm^{-1} region.

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