Influence of a substituent in the phenylic cycle on the lasing properties of pyridylphenyloxazole derivatives

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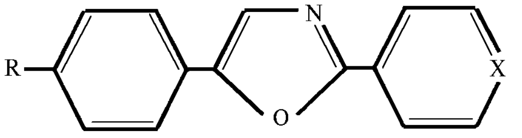
Spectral-luminescent and lasing properties of 4PyPO derivatives at XeCl*-laser pumping are studied depending on a solvent (hexane, ethanol, acetonitrile) and concentration. The causes of anomalous long-wave shift of the luminescence spectrum of 4PyPON$(CH_3)_2$ in a polar solvent are discussed using quantum-chemical calculations. The connection between quantum yields of the photoproducts and lifetime of laser medium operation is established. An explanation of the mechanism of photoproducts' formation is proposed.

Introduction

Many practical and research problems that use spectrally selective interaction between optical radiation and substance require powerful sources of tunable coherent radiation. Lasers based on solutions of organic luminophores excited by excimer lasers can serve as such sources. Although the number of organic compounds lasing under conditions of such pumping is rather large, the choice of luminophores that are photostable in some parts of spectrum is too limited.

To create a photostable laser medium capable of generating stimulated radiation in the blue-green spectral region, we have studied 2-(4 pyridyl)-5-phenyloxazole (4PyPO) and its substituted analogs (Fig. 1).



X : N **R** : H, OCH_3, $N(CH_3)_2$

Fig. 1. The structure of the compounds studied.

Preliminary experimental study of the spectral-luminescent properties of these compounds demonstrates that one can obtain various forms and conformations of the initial molecules by varying proton-donor properties of a solvent and its polarity.[1,2] As it was emphasized in Ref. 1, formation of ion forms of these pyridylphenyloxazoles occurs due to addition of a proton from the solvent to one or two proton-acceptor centers of the molecule. The position of the centers depends on the dye's structure, its state, and on the solvent.[1,2]

Experimental study of dimethylamine-substituted 4PyPO, i.e., 4PyPON$(CH_3)_2$, revealed individual behavior of this compound in polar media.[2] In alcohol solvents ($\varepsilon = 17.7$–25.2), high-polar acetonitrile ($\varepsilon = 37$), this compound demonstrated anomalous Stokes shifts (of the order of 9000 cm^{-1} in magnitude) and deterioration of radiative properties; at the same time, in viscous polar glycerin ($\varepsilon = 42$) and frozen ethanol solutions, the Stokes shift is two times lower, and intensity increases by 2–3 times.[2] On the base of this study, the authors supposed the presence of a conformation reconstruction of a 4PyPO molecule with a dimethylamine substitute in a polar medium under excitation, i.e., TICT-conformation.[2] This paper is devoted to further study of the properties of 4PyPOOCH_3 and 4PyPON$(CH_3)_2$ molecules by methods of quantum chemistry and laser spectroscopy.

Investigation technique

Quantum-chemical calculations of spectral characteristics of polyatomic heterocyclic molecules were performed by use of the semi-empirical method of a partial neglect of the differential overlapping (PNDO).[3] In a real situation, dye molecules are surrounded by solvent molecules, so one must take into account the interaction among those. Specific interactions are taken into account by the method of molecular electrostatic potential (MESP).[4]

The absorption spectra of solutions have been obtained in a quartz cell ($l = 1$ cm) in a SPECORD M–40 spectrophotometer, and fluorescence in a HITACHI 850 spectrofluorometer.

Characteristics of lasing and photostability of pyridylphenyloxazoles were obtained at excitation of solutions in a rectangular quartz cell in its lateral variant with an excimer XeCl*-laser having the following parameters: $\lambda_{las} = 308$ nm, E_{las} up to 50 mJ, $\tau_{las} = 10$ ns. The resonator was formed by a 100% reflection dielectric mirror and a wall of the cell. Energy of pumping and lasing were measured with IMO–2N calorimeter. Photostability characteristics were determined following the technique described in Ref. 9.

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Discussion of the results

Based on the experimental data,[2] we have supposed that a 4PyPO molecule, in a polar solvent, with a dimethylamine substitute in the excited state can exist in the non-plane (TICT) conformation. As shown in Ref. 5, this conformation is favored by the high degree of the charge separation in the molecule at excitation and interaction with the polar solvent. Based on this fact, the spectra of a 4PyPON$(CH_3)_2$ molecule were calculated in plane and non-plane geometry when the substitute is removed from the molecule frame plane at 90° angle. Interaction with the solvent was taken into account by simulating the hydrogen bond between alcohol molecules and proton-acceptor centers of the molecule, namely, nitrogen atoms of the pyridyl and oxazole cycles.

Table 1. The results of quantum-chemical calculations of a 4PyPON$(CH_3)_2$ molecule, for an absorbing conformer, fluorescing in the plane conformation, with the allowance for specific interaction between the solvent and non-plane TICT-conformation

	E, cm^{-1} $S_\iota \to S_\kappa$ transition type	μ^*, D	μ_0, D	F
Absorption, without a solvent ($\beta = 15°$, $\alpha = 0°$)	30929 $S_0 \to S_1$ $\pi\pi^*$	13.7	7.23	1.2
	32358 $S_0 \to S_2$ $\pi\pi^*$	7.5	–	0.57
	35568 $S_0 \to S_3$ $n\pi^*$	3.7	–	0.005
Fluorescence, without a solvent ($\beta = 0°$, $\alpha = 0°$)	25055 $S_1 \to S_0$ $\pi\pi^*$	17.56	9.98	1.47
	30669 $S_2 \to S_0$ $\pi\sigma^*$	12.33	–	0.003
	31663 $S_3 \to S_0$ $\pi\pi^*$	8.42	–	0.04
Fluorescence, with a solvent ($\beta = 0°$, $\alpha = 0°$)	25030 $S_1 \to S_0$ $\pi\pi^*$	22.4	14.4	1.5
	31362 $S_2 \to S_0$ $\pi\sigma^*$	16.14	–	0.003
	32264 $S_3 \to S_0$ $\pi\pi^*$	13.24	–	0.03
Fluorescence, without a solvent ($\beta = 0°$, $\alpha = 90°$)	26842 $S_1 \to S_0$ $\pi\pi^*$	13.35	7	1.4
	30339 $S_2 \to S_0$ $\pi\pi^*$	18.9	–	$4 \cdot 10^{-6}$
	32981 $S_3 \to S_0$ $\pi\sigma^*$	8.47	–	$2 \cdot 10^{-3}$

Note. μ_0 and μ^* are dipole moments of the molecule in the ground and excited states, respectively; F is the oscillator strength of the transition; α is the angle between the substitute and phenyl cycle; β is the angle between the planes of the cycles.

As seen from the calculated data given in Table 1 for 4PyPON$(CH_3)_2$ in the Franck-Condon and fluorescent conformations, the calculated results for a molecule with plane geometry of the substitute, both including and ignoring specific interactions with the solvent, do not coincide with the experimental results for this molecule observed in a polar solvent (in ethanol, $\nu_{fl}^{max} = 17800$ cm^{-1}, $\phi = 0.3$). Variation of the angle between the phenyl fragment and substitute has a weak effect upon the position of the lower excited levels but their nature is subjected to a change. There appears a state S_2, new in its properties, with a strong dipole moment ($\mu_{S_2} = 18.9$). It well interacts with the first excited state ($k_{ic}^{2\to1} \cong 10^9$). These results can be interpreted in the following way: with an increase in the rotation angle, mixing of the allowed S_1 and prohibited S_2 states grows due to the increase in their interaction. Such a "mixed" high-polar state takes lower energy under the influence of a polar solvent what results in deterioration of the emission properties of dimethylamine substituted 4PyPO and in an increase of the Stokes shift in non-viscous polar solvents.

This reasoning can be based on the Lippert formula which permits one to estimate energy of the state with the allowance for universal interactions with the solvent:

$$\Delta\nu_{stokes} = \nu_{fl} = \nu_{abs} = C(\mu^* - \mu_0)^2,$$

where ν_{abs} and ν_{fl} are frequencies of maximum absorption and emission bands, cm^{-1}, respectively; μ^* and μ_0 are the values of the dipole moments of the transitions from the excited and ground states, respectively; $C = 2\Delta f/hca^3$ is the constant for a given compound, h is the Planck constant, c is the speed of light, a is the radius of the solvate shell containing the molecule, Δf is the function describing universal interactions.

As seen from the formula, a sharper decrease in the energy of the S_2 level with larger dipole momentum is possible compared with the decrease in the S_1 state having smaller dipole moment. This is possible due to the difference between the dipole moments of the first and second excited states (see Table 1). As a result, they can converge and even intersect. As to the cause of the substitute's rotation, it seems to be connected with the specific interaction of the dimethylamine substitute with proton-donor or the electron-acceptor solvent. We believe that a more detailed study of this cause could require rather tedious additional investigations of the solvate shell by both experimental and quantum chemistry methods.

Table 2. Charges on the fragments of a 4PyPON$(CH_3)_2$ molecule

Molecule's conformer	State	Oxazole	Phenyl	Pyridyl	Amino group
Fluorescence ($\beta = 0°$, $\alpha = 0°$)	S_0	0.011	–0.068	–0.031	0.088
	S_1	0.005	0.212	–0.426	0.219
	S_2	0.105	0.01	−0.357	0.242
Fluorescence ($\beta = 0°$, $\alpha = 90°$)	S_0	0.032	0.018	–0.017	–0.033
	S_1	0.11	0.17	–0.257	–0.022
	S_2	0.024	0.	–0.099	–0.025

Analysis of electron distribution density for a 4PyPON$(CH_3)_2$ molecule in two geometries in different electron states (Table 2) demonstrates that this compound has irregular distribution of the electron density over molecular fragments that are both in the ground and excited state. The distribution strongly depends on the geometry of a molecule. As seen from Table 2, almost all negative charges in the plane geometry of a molecule in the excited S_1 and S_2 states are accumulated on the pyridine fragment. However, in the plane variant, the molecule is a dipole with a negative pyridine part and positive part consisting of the rest fragments of the molecule; in contrast to this, in the non-plane variant one can observe localization of the negative charge on the dimethylamine group together with the pyridine fragment, i.e., the characteristic charge separation is observed. This redistribution of electron density can lead to, first, high increase of proton-acceptor capacity of a molecule in the domain of a substitute in the excited state; second, it must have an effect on the interaction of a molecule with a polar solvent on its main properties and photostability. This is confirmed experimentally.

Data on the lasing properties of pyridinephenyloxazoles are given in Table 3 as functions of concentration and solvent type. One can see that, depending on a solvent, substituted 4PyPO generate stimulated emission in different spectral ranges, in every case in the domain of their fluorescence band. The difference is 70 nm for OCH_3-substituted and 180 nm for dimethylamine substituted 4PyPO.

Introducing the donor substitute OCH_3 deteriorates the lasing properties of 4PyPO: lasing efficiency considerably decreases in ethanol (from 15 to 2.4%); the operating lifetime of the laser-active medium decreases by an order of magnitude (see Table 3). This might be connected, first, with the existence of an efficient channel of phototransformations what is evidenced by a two-fold increase in the value φ, i.e., quantum output of the phototransformation as compared with that in 4PyPO; second, with presence of states with high rate of radiationless deactivation in the range of pumping energy. Non-optimum pumping conditions can be the other cause of low lasing ability of a $4PyPOOCH_3$ molecule because excitation occurs far from the maximum of the absorption band. These suppositions require additional experimental and quantum chemistry study which is planned to be performed later on.

It should be noted that there are little papers on the laser activity of compounds that form TICT-conformations, e.g., for naphthalimide derivatives[6] and dimethylamine derivatives of pyrromethene molecules.[7]

Efficiency of $4PyPON(CH_3)_2$ lasing in a polar solvent (ethanol, acetonitrile), where this compound forms a TICT-conformation, is two times higher as compared with that in a non-polar solvent; it is comparable with the efficiency of 4PyPO in ethanol (see Table 3). It is the presence of non-plane conformation in the excited state (which is different from the molecule's conformation in the ground state) that seems to promote formation of inverse population at the levels and appearance of efficient lasing of stimulated emission from dimethylamine substituted 4PyPO in a polar solvent.

The lifetime of a laser active medium (LAM) based on dimethylamine substituted 4PyPO in ethanol increases with the increase in the dye content, like in the case with 4PyPO (see Table 3). It was noted in Ref. 8 that the lifetime of 4PyPO is inversely proportional to the output of a photoproduct absorbing in the lasing range of the initial compound (P_l). A similar dependence is also characteristic of the dimethylamine substituted 4PyPO (see Table 3).

The proton-acceptor center of a 4PyPO molecule, i.e., the nitrogen atom of the pyridine cycle,[9] is one of the main reaction centers in formation of the photoproduct P_l of this molecule; and absorption and emission spectra of the photoproduct P_l coincide with those of the cation form of 4PyPO. The analogy with 4PyPO in formation of the photoproduct P_l is observed for $4PyPOOCH_3$: in fluorescence spectra of the solutions after irradiation, there appear bands in the range of the cation form of this molecule (Fig. 2). This means that the photoproduct with the absorption in the lasing range of $4PyPOOCH_3$ is formed with the participation of nitrogen atoms of the pyridine cycle of this molecule according to the same principle as in 4PyPO.[9]

The absorption and fluorescence spectra of the photoproduct P_l of $4PyPON(CH_3)_2$ coincide with the position of the dication's spectra of this molecule,[1] i.e., in this case, nitrogen atoms of the pyridine cycle and amino group are centers of the reaction in which the photoproduct P_l is formed (see Fig. 2). The increase in the output of the photoproduct P_l during a decrease of the dye concentration agrees with its ion nature: with the increase of the molecules' concentration, ion-neutral equilibrium is shifted to the neutral form, i.e., P_l output decreases with the growth of concentration. This explains the increase in the lasing resource with the increasing dye concentration (see Table 3).

Table 3. Parameters of lasing and photostability of a 4PyPO molecule with OCH_3 and $N(CH_3)_2$ substitutes depending on the solvent polarity

Compound	Medium	Concentration, mmole/l	Efficiency, %	λ_{las}, nm	$\varphi \cdot 10^{-3}$	P_p	P_l	P_{80}, J/cm^3
4PyPO	ethanol	0.5	16	398	1.8	0.18	0.08	16
4PyPO	ethanol	2	15	398	1.6	0.14	0.06	156
4PyPO	pentane	0.5	3	–	0.7	0.22	5.2	6
$4PyPOOCH_3$	ethanol	0.5	1	447	2.1	0.2	0.14	3.4
$4PyPOOCH_3$	ethanol	1	2.4	447	2.9	–	0.07	12
$4PyPOOCH_3$	hexane	1	6.2	378	2.5	–	1.8	2.3
$4PyPON(CH_3)_2$	ethanol	0.5	9	599	2	0.6	0.07	6.8
$4PyPON(CH_3)_2$	ethanol	1	14.4	599	1.1	–	0.03	22.2
$4PyPON(CH_3)_2$	hexane	1	6.5	418	1.2	–	0.42	5.2
$4PyPON(CH_3)_2$	acetonitrile	1	19.5	589	2	–	0.7	3.9

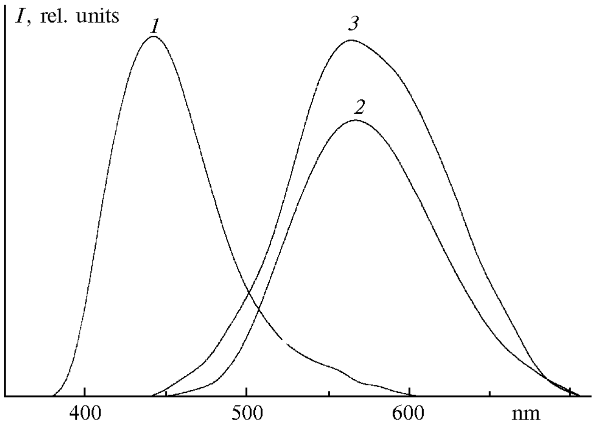

Fig. 2. The emission spectra of 4PyPOOCH$_3$ in ethanol solutions before (*1*) and after irradiation by a XeCl* laser (16 J/cm^3) (*2*), and that of a molecule cation in ethanol (*3*).

As a result of laser irradiation of the substituted pyridylphenyloxazoles studied, a photoproduct P_p with the absorption in the pumping range is formed together with the photoproduct that absorbs in the lasing range of the initial compound. Such a transformation in the short-wave range of the absorption spectra of a 4PyPO molecule is explained by the fact that irradiated ethanol solutions contain the photoproduct that is formed from a 4PyPO molecule by breaking of the oxazole ring.[9] Since introduction of a substitute does not effect the character of spectral changes in the short-wave range (connected with formation of the photoproduct P_p), we assume that for both 4PyPOOCH$_3$ and 4PyPON(CH$_3$)$_2$, just as for 4PyPO (Fig. 3), the photoproduct P_p is a result of oxazole cycle scission with a solvent. As seen from Table 3, introduction of substitutes into 4PyPO leads to an increase in the efficiency of photoproduct P_p formation by short-wave radiation.

Thus, introduction of an electron-donor substitute into the phenyl cycle of pyridylphenyloxazole does not improve lasing properties of 4PyPO. Deformation of the absorption spectra after irradiation with a laser radiation is caused by appearance of irreversible photoproducts one of which, namely, P_p, is formed due to scission of the oxazole cycle of the initial molecule. The photoproduct absorbing in the lasing range of the initial compound is formed with the participation of the proton-acceptor centers of dye molecules. Besides, it was established that, at excitation of dimethylamine substituted 4PyPO in polar solvents, a weakly emitting TICT-state with Stokes shift is formed. This state can provide for the generation of laser radiation, and the lasing efficiency exceeds that of the compound's lasing in a nonpolar solvent.

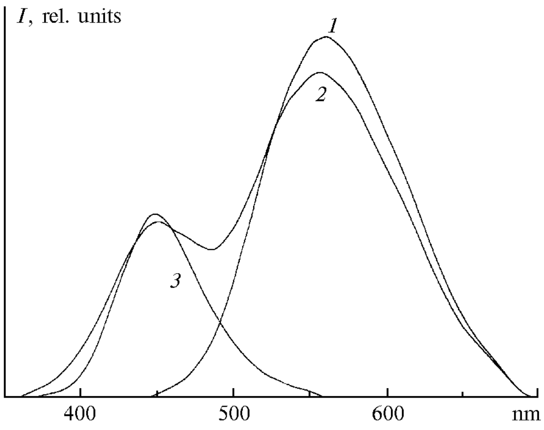

Fig. 3. Emission spectra of ethanol solutions of 4PyPON(CH$_3$)$_2$ before (*1*) and after irradiation with a XeCl* laser (15 J/cm^3) (*2*), the same for molecule's dication in ethanol (*3*).

Acknowledgments

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