INFLUENCE OF A MEDIUM AND SUBSTITUTION ON LUMINESCENT PROPERTIES AND SPECTRAL CHARACTERISTICS OF THE COMPOUNDS WITH OXAZOLE AND PYRIDINE CYCLES

E.G. Breusova, R.T. Kuznetsova, and G.V. Mayer

V.P. Kuznetsov Siberian Physicotechnical Scientific–Research Institute at the State University, Tomsk

In this study we have investigated spectral properties of the luminescence as well as luminescent ability itself of three substitutes of the 2(4–pyridyl)–5–phenyloxazole depending on the parameters of ambience. In the course of this investigation we have revealed some very important peculiarities in the interaction of these compounds with the proton–donor and the proton–aceptor solvents at room temperature which are caused by the electron–donor ability of a substitute. The retardation of rotations in viscous media at room temperatures as well as in frozen polar solutions is indicative of conformation rearrangement of dye molecules. Investigations of the concentration dependence of the fluorescence showed that at low temperatures there occurs the formation of associates that do not appear at room temperatures.

Investigation of reversible of photochemical dissociation products, for example, different photoconformations and photocations appearing at excitation as a function of parameters of the environment, makes it possible to obtain important information about mechanisms of the intermolecular interactions. In its turn, the character of intermolecular interactions is essentially determined by the presence of electron–donor and electron–acceptor systems in the structure of a molecular compound and by the configuration of the electron cloud which changes considerably at excitation. In this connection, it is of great interest to investigate interconnections and interdependence of the medium and substitutes on the spectral characteristics and luminescent properties of the laser dyes in order to obtain an effective lasing compound with high operation qualities.

An object of the experimental study is the molecule of 2–(4–pyridyl)–5–phenyloxazole with the substitutes having different donor abilities (see Fig. 1). The choice was determined by the following qualities of compounds: the lasing ability within the blue–green spectral range for the unsubstituted base[1]; the presence of active end groups in these substances enables them to be active in specific interactions with different solvents; the presence of heteroatoms in the structure of molecules promotes the formation of photocations, whose emission spectra are displaced with respect to spectra of a neutral form that results in broadening of the lasing range.[2-5] The absorption spectra were recorded with a Specord UV–VIS spectrophotometer, and of the fluorescence–with a unit including the following parts: an excitation source, prism monochromator SF–4, photomultiplier FEU–79, amplifier U2–6, and potentiometer KSP–4. The technique for obtaining the spectra at the temperature 77 K is described in Ref. 6. The results of this study are given in Table I.

Comparative analysis of the data shows that strengthening of the electron–donor property of a substituent results in the increase of the probability of specific interactions with the solvent at 300 K. This leads to an anomalously large Stokes shift in the case of solution in alcohol and water at 300 K which takes its standard value when the solution is frozen (see the table).

Apparently, in the frozen solution "fixing" of a molecule by the solvent restricts its ability to conformation rearrangements at excitation (what results in a considerable shortwave displacement of the emission spectrum occurring at freezing (see Fig. 2)) and therefore one can suppose that the molecule emits from in the same conformation in which it absorbed a light quantum. The effect of "freezing" the rotational motion even at room temperature is observed in glycerine (see the table). High viscosity of the ambient medium prevents the conformation rearrangement of a molecule during the time it is in an excited state. For this reason no large Stokes shifts are observed in the case of media with large dielectric constants (see Table I).

$$R = CH_3, OCH_3, N(CH_3)_2$$
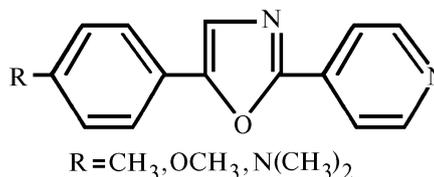
FIG. 1. Structure of the compounds under study.

As shown in Refs. 7–10 in the molecules containing rings connected by single and double bonds, the rotation of rings depending on the electron density distribution and the formation of the TICT–type conformations in a polar medium becomes possible. One can assume that such conformations occur in the compounds under study in alcohol and water media. Moreover, with increasing donor ability of a substituent in the series $CH_3 < OCH_3 < N(CH_3)_2$ realization of such conformations becomes easier, and therefore, the anomalous Stokes shift increases in value (see the table). As can be seen from the table the Stokes shift for all molecules in dioxane at room temperatures is a little bit larger than that observed in other aprotic solvents of close polarity. Taking into account the results from Ref. 11, one can assume that such an increase results from the "dioxane effect", or the ability of the dioxane molecule to the conformation rearrangement when interacting with a polar dye molecule. Moreover this effect becomes stronger with increasing donor properties of a substitute (see the table).

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TABLE I. *Spectral characteristics of the substituted 2 (4–pyridil)–5–phenyloxazole as functions of nature and phase condition of the solvent.*

Substituent	Solvent	T = 300 K; $c = 10^{-5}$ mole/liter				T = 77 K $c = 10^{-3}$ mole/liter
		ν_{max}^{abs}, cm^{-1} / λ_{max}^{abs}, nm	ν_{max}^{fl}, cm^{1} / λ_{max}^{fl}, nm	$\Delta\nu_{Stokes}$, cm^{-1}	Relative quantum yield, φ_{rel}	ν_{max}^{fl}, cm^{-1} / λ_{max}^{fl}, nm
1	2	3	4	5	6	7
CH$_3$	Pentane $\varepsilon = 1.84$	310000 / 323	27000 / 370	4000	0.85	22200 / 450 / 22200* / 450*
	Dioxane $\varepsilon = 2.21$	31000 / 323	25600 / 395	5400	1.35	20600 / 485
	CCl$_4$ $\varepsilon = 2.23$	30800 / 325	26300 / 380	4500	0.57	22300 / 448
	Ethanol $\varepsilon = 25.2$	30400 / 329	24270 / 412	6130	2.86	25300 / 395
	Ethylene–glycol $\varepsilon = 38.7$	29800 / 336	23800 / 420	6000	2.98	24700 / 405
	Glycerine $\varepsilon = 42.4$	30000 / 333	23800 / 420	6200	≪0.1	23300 / 430
	Water $\varepsilon = 78.7$	30600 / 327	23300 / 430 / 20400 / 490	7300 / 10200	—	25300 / 395
OCH$_3$	Pentane $\varepsilon = 1.84$	30400 / 328	26000 / 385	4400	0.74	21280 / 467
	Dioxane $\varepsilon = 2.21$	30000 / 333	24400 / 410	5600	—	18900 / 530 / 21300* / 470*
	CCl$_4$ $\varepsilon = 2.23$	30000 / 333	25300 / 395	4700	0.1	22500 / 445
	Ethanol $\varepsilon = 25.2$	29600 / 338	22700 / 440	6870	2.85	24400 / 410
	Ethylene–glycol $\varepsilon = 38.7$	29000 / 345	21740 / 460	7260	2.84	23300 / 430
	Glycerine $\varepsilon = 42.4$	29200 / 344	21740 / 460	7460	≪0.1	21300 / 470 / 23800 / 420
	Water $\varepsilon = 78.7$	29500 / 338	20830 / 480 / 18182 / 550	8900 / 11490	—	23500 / 425
	Pentane $\varepsilon = 1.84$	28000 / 357	23800 / 420	4200	1.6	18200 / 550
	Hexane $\varepsilon = 1.9$	28000 / 375	23500 / 425	4500	—	18900 / 530 / 23300* / 430*
	Dioxane $\varepsilon = 2.21$	27400 / 365	21300 / 470	6100	4.7	16950 / 590 / 16950* / 590*
	CCl$_4$ $\varepsilon = 2.23$	27300 / 366	18820 / 531	8480	≪0.1	22500 / 445
	Toluene $\varepsilon = 2.38$	27400 / 365	21740 / 460	5660	2.6	21740 / 460 / 22500* / 445*

TABLE I (continued)

1	2	3	4	5	6	7
	Butanol	26600	17900	8700	—	20000
	ε = 17.7	376	560			500
						20600*
						485*
N(CH$_3$)$_2$	Propanol	26600	18200	8400	—	20400
	ε = 19.7	376	550			490
						21300*
						470*
	Ethanol	26600	17540	9060	1	19600
	ε = 25.2	376	570			510
						20400*
						490*
	Ethylene−glycol	25800	16670	9130	0.11	19600
	ε = 38.7	388	600			510
						20000*
						500*
	Glycerine	25400	21050	4350	≪0.1	19600
	ε = 42.4	392	475			510
						19800*
						505*
	Water	28000	18182	9800	≪0.1	18182
	ε = 78.7	357	550			550
	Water+	28000	18182	9800		21300
	NaOH	357	550	6700		470
			21300			
			470			

*The results are obtained for the concentration 10^{-5} mole/liter of the substance.
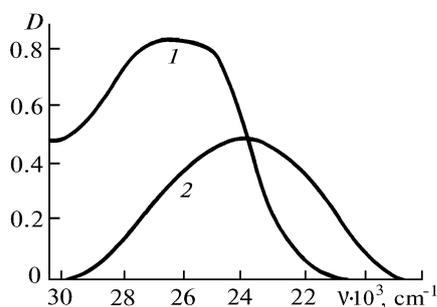
FIG. 2. *Absorption spectrum of ethanol solutions* 4PyPON(CH$_3$)$_2$ *in a capillary tube with* $l = 1$ mm, $C = 10^{-4}$ mole/liter *at 1)* 300 K *and 2)* 77 K.

It was noted in Refs. 12 and 13 that in the proton−donor media there occurs the formation of the 4PyPO cation via coupling the solvent proton to a nitrogen atom in a pyridine cycle, what is accompanied by the displacement of the absorption and emission spectra towards longer wavelengths. It is obvious that the appearance of two bands in the fluorescence spectrum of the CH$_3$− and OCH$_3$− substituted compounds in a water solution should be interpreted as a simultaneous emission from two forms, namely: neutral form emitting shortwave radiation, and the form of pyridine cation−emitting longwave radiation (see Table I and Fig. 3). In the molecule 4PyPON(CH$_3$)$_2$ the fluorescence is observed from the cation by pyridine nitrogen in water at room temperature (see the table). One can succeed in obtaining the radiation from the neutral form by adding 100 times larger quantity of NaOH into the solution compared to that in the case of CH$_3$ and OCH$_3$

substitutes but even in this case both forms emit at room temperature simultaneously (see the table). Thus, it can be seen that the efficiency of the cation formation increases with increasing donor properties of the substituent, moreover, for all compounds in the S_1 state the efficiency is higher than in the S_0 state, since during the excitation there occurs a charge localization on the pyridine nitrogen. If in a solvate shell there is a proton then a cation is formed in an excited state, what leads to the situation when the neutral form of these compounds is responsible for the light absorption, while the ion form for the emission.
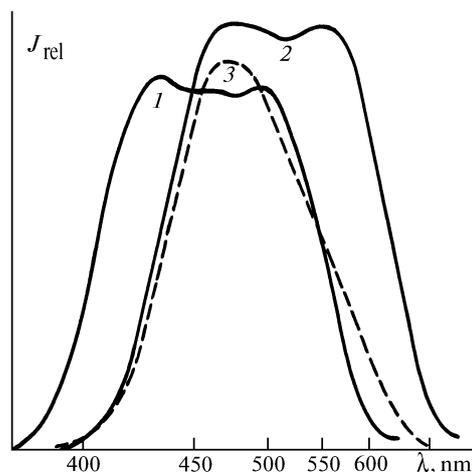
FIG. 3. *Fluorescence spectrum of water solutions* 4PyPOCH$_3$ *(1) and* 4PyPO(OCH$_3$) *(2), and* 4PyPOOCH$_3$ *with added* 10^{-2} mole/liter *quantity of* NaOH.

Behavior of dimethylamino–substituted 4PyPO in CCl_4 differs from the behavior of two other compounds under study and should be discussed especially. The emission spectrum of $4PyPON(CH_3)_2$ in CCl_4 at room temperature can be characterized by a sharp drop of the intensity and its considerable displacement towards longer waves in comparison with the CH_3– and OCH_3–substituted compounds (see the table). At the same time the absorption in the region of 22 000 cm^{-1} appears in the longwave end of the absorption band like in the case with the absorption by the pyridine cation by nitrogen $4PyPON(CH_3)_2$ in ethanol (see Fig. 4).
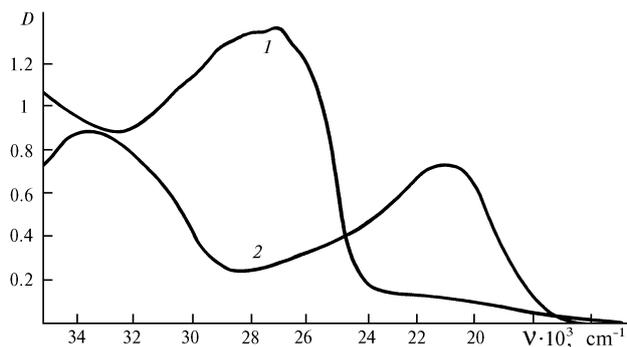
FIG. 4. Absorption spectrum $4PyPON(CH_3)_2$ in CCl_4, $C = 10^{-4}$ mole/liter (1) and in acidulated ethanol solution, $C = 5 \cdot 10^{-5}$ mole/liter (2).

It seems so that an electronegative solvent effects on an excess electron density of the pyridine nitrogen in the same way as the ion H^+, i.e., binds it due to the formation of a colored insoluble sediment in contrast to the soluble cation. Fluorescence yield of this formation is low, most likely because of a considerable interconversion caused by the presence of heavy chlorine atoms. It is obvious that this feature is the result of high donor ability of the dimethylamine group since in the case of other substituents such peculiarities are not observed.

In the frozen solutions all the above considered compounds show the dependence of the radiation wavelength on the concentration of substances, that does not occur in liquid media (see the table). The emission spectrum is subjected to a considerable displacement towards longer wavelength with increasing concentration of a compound especially, in nonpolar aprotonic media. At the same time as the solution becomes frozen it is getting more

saturated shift, i.e., the absorption region of the new formation is at longer wavelength than in a liquid solution. It is obvious that in solutions with high concentration at 77 K the molecular systems are formed between each other according to the principle "tail–head" what is promoted by the excess electron density of the nitrogen atom of the pyridine ring. For close packing and suppressed motion during the freezing, there probably occurs the formation of a system like to the system composed of molecules $4PyPOH(CH3)_2$ and CCl_4 (see the table).

Thus, the obtained data make it possible to conclude that the structure, photochemical and photophysical characteristics of the compounds under consideration essentially depend on the substituent and the medium in which they are available. Based on the observed changes in the spectrum we assumed that in the molecules of this type there occur the TICT–conformations and their stabilization becomes easier as the donor ability of the substituent increases. It is shown that the formation of photocations is similar to the formation of complexes with an electron–acceptor solvent in nonpolar aprotonic media.

REFERENCES

1. A.N. Fletcher, R.A. Henry, M.E. Pietrak, et al., Appl. Phys. **B43**, 155–160 (1987).
2. A.L. Lester and R.A. Robb, J. Quant. Electron. **43**, 155–162 (1987).
3. S.I. Druzhinin, S.A. Krashkov, and I.V. Troyanovskii, in: *Abstracts of Reports,* Tomsk (1986), Part 2, pp. 68.
4. B.M. Uzhinov, S.I. Druzhinin, and G.M. Radchenko, in: *Abstracts of Reports at the Fifth All–Union Conference on Photochemistry,* Moscow (1985), Part 1, pp. 102.
5. V.I. Alekseeva, L.Sh. Afanasiadi, et al., Zh. Prikl. Spektrosk. **44**, No. 3, 403–407 (1986).
6. V.Ya. Artyuchov, O.K. Bazyl', R.T. Kuznetsova, et al., Kvant. Elektron. (Kiev) **41**, 152–159 (1992).
7. K. Rotkiewich, Z.R. Grabowski, and K.H. Grellmann, Chem. Phys. Lett. **19**, No. 3, 315–321 (1973).
8. W. Retting, Chem. Phys. Lett. **147**, No. 5, 452–457 (1988).
9. W. Retting, Chem. Phys. Lett. **148**, No. 5, 761–765 (1988).
10. W. Retting and W. Majenz, Photochem. Photobiol. A.: Chem. **62**, 415–430 (1992).
11. V.A. Gorodyskii and N.A. Stepanova, *Reaction Ability of the Organic Compounds,* Tartu (1975), No. 72 413–423 pp.
12. R.T. Kuznetsova, A.I. Galeeva, R.M. Fofonova, et al., Zh. Priklad. Spectrosk. **47**, 865 (1987), VINITI, No. 6109–B87.
13. R.T. Kuznetsova, A.I. Galeeva, E.G. Sinenko, et al., Izv. Vyssh. Uchebn. Zaved., Fiz., No. 8, 48–52 (1987).