

PECULIARITIES OF LASING EMISSION OF THE ORGANIC COMPOUNDS WITH THE CHAIN STRUCTURE CONTAINING DIMETHYLAMINE GROUP

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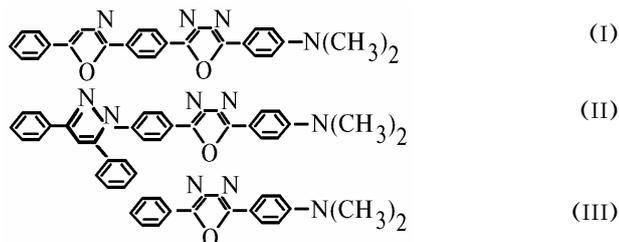
An anomalously large shift ($\Delta\lambda \sim 100\text{--}150\text{ nm}$) of the fluorescence and generation spectra of the compounds containing dimethylamine group dissolved in toluene compared to that observed in alcohol solution was discovered. It was revealed that, in alcohols there takes place generation of complexes possessing the charge transfer between the excited molecules of the compounds containing $\text{N}(\text{CH}_3)_2$ group and the polar molecules of a solvent. It is shown that the bathochromic shift of the generation band relative to the fluorescence one is caused by an intense $S_1 - S_n$ absorption in the region of the fluorescence band maximum. The effect revealed in this study makes it possible to develop a dye laser with an active media of a single compound emitting in a wide spectral range (violet and yellow regions).

It is well known that organic compounds whose lowest excited states are the triplet and singlet levels of the π, π^* type possess rather good fluorescence^{1,2} and lasing³ properties. In the fluorescence and lasing spectra of these compounds one can observe a bathochromic shift when changing a nonpolar solvent for a polar one, whose value varies for different compounds from units to tens of nanometers.⁴ The value of shifts significantly increases for the compounds which have strong donor and acceptor groups.

Investigation of spectral position of the lasing emission band of *n*-dimethylamine-2,5-diphenyloxadiazole-1,-3,-4 (PPD- $\text{N}(\text{CH}_3)_2$) in different solvents showed that the value of the band shift is anomalously large when changing the cyclic hydrocarbons for the alcohols. Therefore, the wavelength of the maximum of the lasing emission spectrum in cyclohexane is equal to 375 nm, while that in ethanol is 540 nm (Ref. 5). Analysis of the data available from the literature did not allow us to find other lasing compounds with so large value of the lasing emission band shift.

This paper presents some results of investigations of the spectral-luminescent and lasing properties of the organic compounds containing, as a fragment, *n*-dimethylamine-2,5-diphenyloxadiazole-1,-3,-4. The mechanism of an anomalously large shift of the PPD- $\text{N}(\text{CH}_3)_2$ lasing emission band from the violet to green spectral region is discussed in this paper as well.

The structure formulas of the compounds under study are the following:



For measuring the absorption spectra we used a Specord M40 spectrophotometer. Spectral and polarization characteristics of the fluorescence of the compounds under study were measured with an SDL-2 spectrometer. Fluorescence duration was determined with the help of a pulsed fluorometer PRA-300.

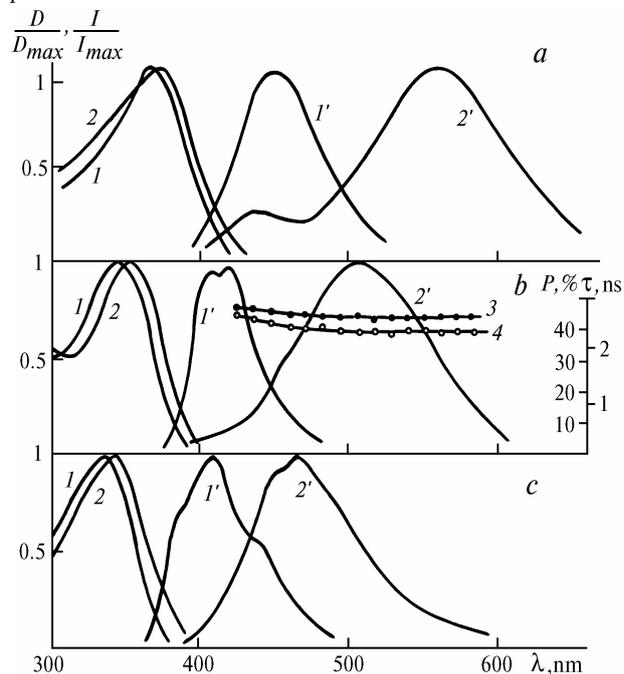


FIG. 1. Absorption spectra (1, 2), fluorescence spectra (1', 2'), polarization spectra of fluorescence (3), and spectral dependence of the fluorescence duration (4) of the compounds I(a), II(b) and III(c) in toluene (1, 1') and ethanol (2, 2'). D is the optical density and I is the fluorescence intensity in rel. units.

Investigation of the lasing properties was carried out using a transverse arrangement with a pulsed nitrogen laser AL-202 as a source of pumping. The wavelength of the nitrogen laser emission ($\lambda = 337$ nm) is close to the maxima of the wavelengths of long-wave absorption bands of the compounds under study. The laser emission spectra were recorded using an ISP-30 spectrograph. Power of the laser emission was measured with an IMO-2N power and energy meter.

The absorption and fluorescence spectra of the compounds I–III dissolved in toluene and ethanol are shown in Fig. 1. As can be seen from Fig. 1, the absorption spectra of these compounds are subjected to some bathochromic shift when comparing the toluene and ethanol solutions. As follows from a comparison of the spectral positions of the absorption bands of the compounds I and III PPD-N(CH₃)₂ just the enlargement of the generalized π -system of a molecule results in the bathochromic shift of the absorption band in the given solvents. However, for the compounds II and III having different lengths of molecules the values of the wavelengths corresponding to the maxima of the absorption bands are close (see Fig. 1 and Table I). In Ref. 6 this fact is interpreted as the effect of dominant localization of the electron transition which is responsible for the long-wave absorption band of the compound II on the *n*-dimethyl-amine-2,-5-diphenyloxadiazole fragment of a molecule.

TABLE I. Spectral–luminescent characteristics and lasing parameters of the investigated compounds.

Compound	Solvent	λ_{max}^{abs} , nm	λ_{max}^{fl} , nm	γ	λ_{max}^{gen} , nm	$\Delta\lambda^{gen}$, nm
I	toluene	368	448	0.58	452	12
	ethanol	368	565	10^{-3}	—	—
II	toluene	346	417	0.61	422	8
	ethanol	351	505	0.41	568	9
III	toluene	338	405	0.82	579	13
	ethanol	341	462	0.40	540	9

In contrast to the absorption spectra the spectra of fluorescence of the investigated compounds are subjected to a more considerable bathochromic shift when coming from a solution in toluene to that in ethanol. As follows from the table, the minimum value of the fluorescence spectrum shift is $\Delta\lambda = 57$ nm for the compounds III, and the maximum value is $\Delta\lambda = 117$ nm for the compound I.

One can see from Fig. 1 that there appear two bands in the fluorescence spectrum of the compound I. It was shown in Ref. 6 that a short-wave band results from a fluorescence of a monomeric form of molecules of the compound I, while the long-wave band is due to the fluorescence of the complexes with the charge transfer that form, when in the excited states, molecules of the compounds under study with the solvents.

Investigation of a great number of organic compounds carried out using methods of picosecond spectroscopy showed⁷ that the presence of electron–donor or electron–acceptor groups within the molecular structure results in formation of the complexes of the activating agent molecules with one or several alcohol molecules at room temperature. Most efficiently the complexes are formed at temperatures 0–30°C that well agrees with the conditions of our experiment.

Large values of the fluorescence quantum yield and the only emission band in its spectrum are characteristic features of the compounds II and III. However, an anomalously great shift of the emission bands of compounds II and III when

coming from toluene solution to the ethanol one at practically invariable position of the absorption spectrum is indicative of a common nature of the fluorescence bands of three investigated compounds containing the diethylamine group.

To identify the sources of fluorescence of the compound II we have studied the dependences of the polarization degree and fluorescence duration on the wavelength. Invariability of the polarization degree of the fluorescence over its spectrum for the compound II in the ethanol solution at $T = 173$ K (Fig. 1 *b*, curve 3) shows that this band belongs to one center of fluorescence. This is also confirmed by the fact that lifetimes of the excited state measured in different spectral regions (Fig. 1 *b*, curve 4) of the emission band are the same.

Figure 2 illustrates the fluorescence spectra of the compound II dissolved in ethanol at room temperature as a function of sulfuric acid concentration added into the solution. As can be seen from Fig. 2, an addition of some quantity of H₂SO₄ into the solution results in quenching of the fluorescence of the compound II because of blocking the process of the charge transfer by the acid ions in the system of foreign molecule and the solvent molecule. For the acid concentration $C = 0.05$ mole/liter the fluorescence of complexes is practically negligible and in the emission spectrum of the compound II there appears a maximum at $\lambda = 435$ nm typical of the fluorescence of the monomeric form of the molecules of this compound (Fig. 2, curve 4).

Compound I, in its monomeric form, dissolved in toluene or dioxane shows lasing effect, while no laser emission was observed on the complexes formed in ethanol solution of this compound. This fact is most probably caused by radiationless depletion of the S_1 level.

Compounds II and III give an intense lasing emission when dissolved in toluene, dioxane, and ethanol and pumped by radiation of a pulsed nitrogen laser. Maxima of the fluorescence and laser emission spectra of the compound III dissolved in toluene are at the same wavelength $\lambda = 405$ nm, while the maximum of laser emission of this compound dissolved in ethanol is bathochromically shifted by $\Delta\lambda = 80$ nm with respect to its fluorescence spectrum. Similar situation is observed with the fluorescence and laser emission spectra of the compound II. As follows from the table, maximum of laser emission of the compound II dissolved in ethanol is at 75 nm longer wavelength compared to the position of the fluorescence spectrum maximum, although these maxima are close values for the solution of this compound in toluene.

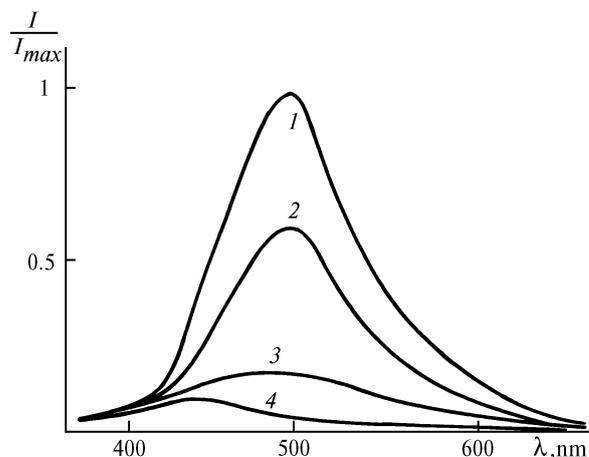


FIG. 2. Fluorescence spectra of the compound II in ethanol as a function of concentration of the sulfuric acid admixture: $C = 0$ (1), 0.01 (2), 0.03 (3), and 0.05 mole/liter (4).

In order to elucidate the origin of the long-wave shift of the laser emission spectrum with respect to the fluorescence spectrum we have studied spectra of the induced $S_1 - S_n$ absorption and estimated the effect of triplet-triplet absorption on the lasing process for the compound II dissolved in toluene and ethanol. The rates κ_{st} of intercombination transition calculated using formulas from Ref. 8 for this compound are $\kappa_{st} = 10 \cdot 10^7 \text{ s}^{-1}$ in the toluene solution and $\kappa_{st} = 21 \cdot 10^7 \text{ s}^{-1}$ in the ethanol solution. Since the duration of the exciting radiation pulse from a nitrogen laser is about $2.5 \cdot 10^{-9} \text{ s}$ one can state that the triplet-triplet absorption does not dominate in formation of the laser emission spectrum of the compound II dissolved in the above solvents.

Figure 3 illustrates $S_1 - S_n$ absorption spectra of the compound II measured in toluene and ethanol for different time lags ($\Delta\tau$) of probing radiation.

As can be seen from Fig. 3 the spectra of singlet-singlet induced absorption from the first excited state are practically of the same view in a wide range of time lags between the excitation pulse and the pulse of probing radiation (10–400 ps) what is indicative of stability of centers responsible for laser emission in the toluene solution of this compound. Minimum of the $S_1 - S_n$ absorption of the compound II dissolved in toluene is at 425 nm that corresponds to the wavelength of the laser emission maximum for such a toluene solution of this compound.

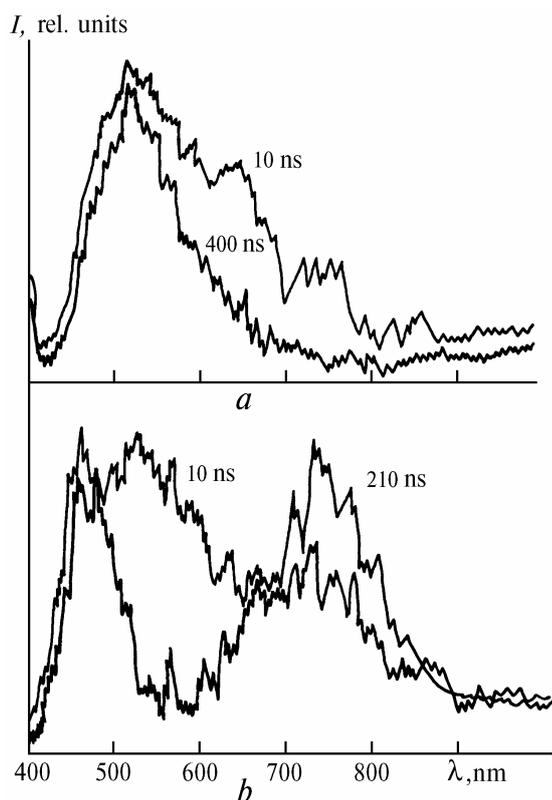


FIG. 3. The $S_1 - S_n$ absorption spectra of the compound II in toluene (a) and ethanol (b).

The measurements of spectra of the induced absorption from the first excited state of the compound II dissolved in ethanol show that the view of such spectra strongly depends on the above-mentioned time lags. For example, in Fig. 3 b

at $\Delta\tau = 10 \text{ ps}$ one can see an intensive $S_1 - S_n$ absorption everywhere in the spectral region corresponding to the laser emission. However, for $\Delta\tau = 210 \text{ ps}$ in the spectrum of singlet-singlet absorption there appears a gap with the minimum at 575–580 nm. Further increase of the time lag does not result in changing the shape of the induced absorption spectrum. A correspondence between the wavelength of the minimum of $S_1 - S_n$ absorption spectrum of the compound II in ethanol solution and that of the maximum of the laser emission band shows that the bathochromic shift of the laser emission band in comparison with the position of the emission band can be explained by significant $S_1 - S_n$ absorption within the region of maximum of the fluorescence spectrum.

Since lasing of the alcohol solutions of the compounds under study is produced by the molecular complexes, it was of great interest to estimate the time required for the formation of a complex of the impurity and solvent molecules possessing the ability of a charge transfer. Information about this process can be obtained from investigation of the kinetics of the solution optical density due to $S_1 - S_n$ absorption using sounding radiation with the wavelength from the laser emission band. Figure 4 shows the optical density of solution due to the induced singlet-singlet absorption as a function of the lag time between the sounding radiation at the wavelength $\lambda = 574 \text{ nm}$. Mathematical processing of the obtained results shows that the characteristic time required for forming the complexes of the compound II in ethanol is 30 ps.

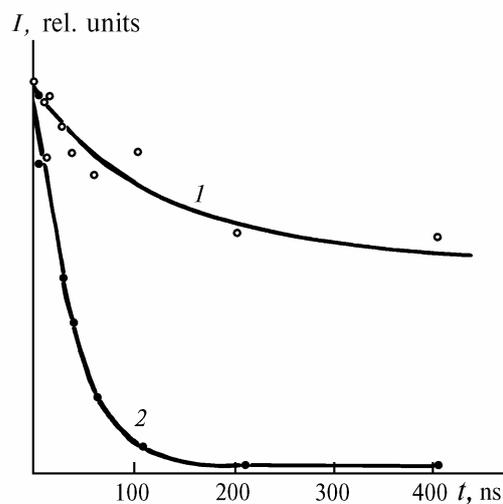


FIG. 4. Kinetics of intensity variation of the $S_1 - S_n$ absorption intensity for different wavelengths of the probing radiation $\lambda = 740 \text{ nm}$ (1) and $\lambda = 547 \text{ nm}$ (2).

Thus, the use of different techniques in the study made it possible to elucidate the nature of the fluorescence of compounds containing as a fragment *n*-dimethyl-amine-2,5-diphenyloxadiazole-1,-3,-4 in ethanol solution and to explain the shift of the laser emission spectrum with respect to the fluorescence spectrum. An intense lasing of the compounds II and III in toluene and ethanol can result in developing lasers based on a single compound but capable of emitting in different spectral regions (violet and yellow).

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REFERENCES

1. R.N. Nurmukhametov, V.G. Plotnikov, and D.N. Shigorin, *Zh. Fiz. Khim.* **40**, 1154–1157 (1966).
2. V.V. Gruzinskii, V.I. Danilova, T.N. Kopylova, V.G. Maier, and V.K. Shalaev, *Kvant. Elektron.* **8**, No. 8, 1702–1707 (1981).
3. N.A. Borisevich and V.V. Gruzinskii, *Kvant. Elektron. Lazer Spektrosk (Minsk)*, 81–119 (1971).
4. R.N. Nurmukhametov, *Absorption and Luminescence of Aromatic Compounds* (Khimiya, Moscow, 1971), 215 p.
5. V.V. Gruzinskii, *Tables of Active Media of Polyatomic Molecules for Lasers*, Preprint No 133, Institute of Physics of the Academy of Sciences of the BSSR, Minsk (1977).
6. V.V. Gruzinskii, M.A. Senyuk, Neira Bueno Oskar Leon, and L.Sh. Afanasiadi, *Zh. Prikl. Spektrosk.* **54**, No. 4, 600–604 (1991).
7. B.A. Bushuk, Author's Abstract of the Doct. Phys.–Math. Sci. Dissert., Minsk (1992).
8. V.V. Gruzinskii and T.G. Staneva, *Zh. Prikl. Spektrosk.* **29**, No. 4, 614–620 (1978).