

SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF STILBENE
DERIVATIVES WITH TWO UNCONJUGATED FLUOROPHORES

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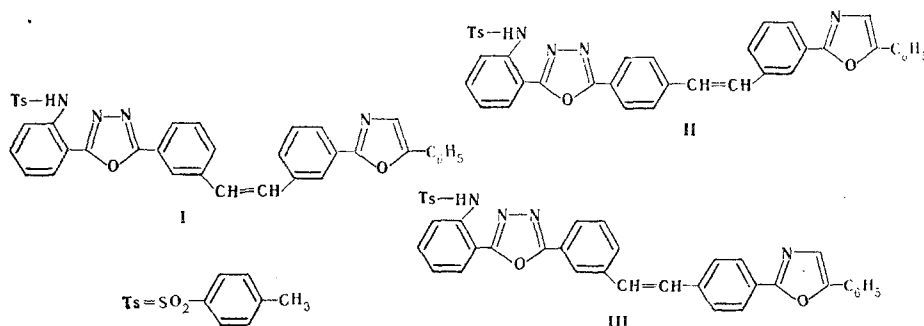
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Compounds that contain 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole fluorophore groupings that are not conjugated with one another were obtained by the phosphonate modification of the Wittig reaction from 2-[4(3)-bromomethylphenyl]-5-(2-tosylaminophenyl)-1,3,4-oxadiazoles and 2-phenyl-5-[4(3)-formylphenyl]-1,3-oxazoles. The absorption and fluorescence spectra of the compounds obtained and the individual fluorophores that constitute the molecules of these compounds were investigated. Intramolecular nonradiating transfer of the electronic excitation energy between the fluorophores that make up the compounds and in binary mixtures of the corresponding luminophores was observed in solutions and in polymeric matrices.

Arylethylene derivatives of 2,5-diphenyloxazoles and 2,5-diaryl-1,3,4-oxadiazoles have found application as effective activators of liquid and plastic scintillators [1, 2] and are used in laser technology [3] and in "cascade" compositions in daylight fluorescent pigments and paints [4].

We have obtained and investigated compounds that contain simultaneously 1,3-oxazole and 1,3,4-oxadiazole structural groupings linked by a vinylene group; the heterorings of the two fluorophore fragments are not conjugated with one another (I-III, Table 1).

These compounds were obtained in the form of trans isomers by means of PO olefination from the corresponding 2-[4(3)-bromomethylphenyl]-5-(2-tosylaminophenyl)-1,3,4-oxadiazoles and 2-phenyl-5-[4(3)-formylphenyl]-1,3-oxazoles.



A tosylamino group, which usually easily forms an intramolecular hydrogen bond (IHB) with the heteroatoms of the azole rings, was introduced into the ortho position of one of the aromatic rings of the diaryloxadiazole fragments.

The formation of this sort of bond could promote an increase in the intensity of the luminescence of the synthesized substances. In addition, in a number of cases the formation of an IHB in the case of compounds that contain an o-tosylamino group leads to an anomalously large Stokesian shift ($\Delta\nu = 10,000\text{--}12,000\text{ cm}^{-1}$), which is advantageous in the practical utilization of luminophores [5, 6].

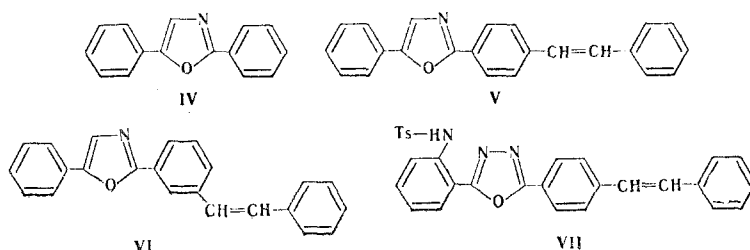
All-Union Scientific-Research Institute of Single Crystals, Kharkov 310141. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 9, pp. 1188-1191, September, 1982. Original article submitted October 22, 1981; revision submitted March 19, 1982.

TABLE 1. Spectral-Luminescence Characteristics of I-VII in Toluene

Compound	Absorption	Fluorescence		$\Delta\nu$
	λ_{\max} , nm ($\epsilon \cdot 10^{-4}$)	λ_{\max} , nm	φ	
I	320*	455	0,31	9270
II	345 (6,91)	385	0,21	4290
	370 (inflection)	405		
III	350 (7,31)	405, 425	0,59	5040
IV	310 (3,06)	365	0,50	4860
V	355 (6,34)	475	0,88	7070
VI	310 (5,50)	355	0,61	4090
VII	335*	380, 400	0,54	4850

*Only slightly soluble.

The spectral-luminescence characteristics of toluene solutions of the compounds obtained and, for comparison, the same characteristics of model compounds (IV-VII), which are their individual structural fragments, are presented in Table 1:



A large Stokesian shift ($\Delta\nu = 9272 \text{ cm}^{-1}$) is observed for I, the vinylene group of which is not conjugated with the heterorings. The absorption maximum of a toluene solution of this substance occupies an intermediate position between the maxima of the individual fluorophores. When the vinylene group is conjugated with the heteroring of one of the fluorophores (II, III), the Stokesian shift has its normal values.

It is interesting to compare the fluorescence quantum yields of solutions of the compounds obtained. Compound III has the highest luminescence intensity. The higher quantum yield of this compound is evidently due to the 2,5-diphenyloxazole fragment with the arylethylene grouping conjugated with it (compare III and V).

It has been previously shown that the fluorescence of compounds that consist of two fluorophore groupings with a common aromatic ring that are not included in a single conjugated system is due to the nonradiating transfer of energy via an inductive-resonance mechanism [7, 8]. Considering these data, we assumed that intramolecular transfer of the electronic excitation energy is realized in the case of I-III in toluene solutions.

In order to make a more detailed study of this problem we investigated the spectral-luminescence properties of II, which is more soluble in toluene than III.

To ascertain the existence of energy transfer between the fluorophores in this molecule we made a parallel study of the intermolecular transfer of energy between compounds with structures similar to the component fluorophores in solutions of mixtures of them in toluene and in polystyrene.

Primarily the 2,5-diphenyloxazole group absorbs when solutions of II ($c 1 \cdot 10^{-4}$ mole/liter) are irradiated with light with a wavelength of 313 nm, and the character of the fluorescence spectrum is similar to the spectrum of the arylethylene derivative of 2-(o-tosylaminophenyl)-5-phenyl-1,3,4-oxadiazole (VII). The intensity of the luminescence of II both in toluene and in polystyrene increases by a factor of two as compared with VII (Fig. 1), and this constitutes evidence for the nonradiating transfer of the electronic excitation energy from the fluorophore donor to the fluorophore acceptor of II. A similar pattern is also observed when the concentration of the solution is increased ($c 5 \cdot 10^{-4}$ mole/liter).

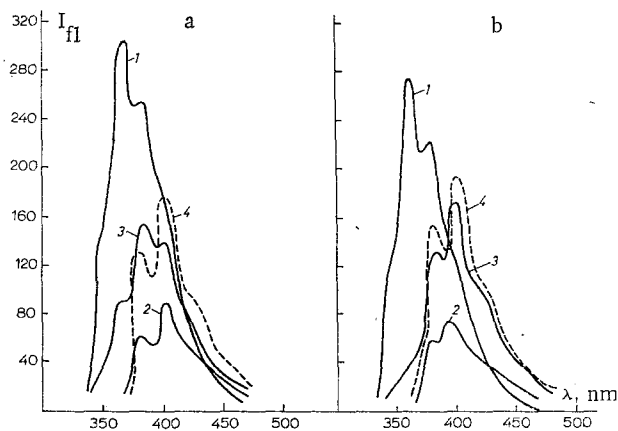


Fig. 1. Fluorescence spectra of 2,5-diphenyloxazole (1), 1-phenyl-2-[5-phenyl-2-(2-tosylaminophenyl)-1,3,4-oxadiazolyl]ethylene (2), an equilibrium mixture of the former (3), and II (4) in toluene (a) and in polystyrene (b).

Quenching of the fluorescence of the donor and an increase in the intensity of the luminescence of the acceptor were observed in an equimolar mixture of 2,5-diphenyloxazole (donor) and the aryethylene derivative of 2-(2-tosylaminophenyl)-5-phenyl-1,3,4-oxadiazole (acceptor) at concentrations of $1 \cdot 10^{-4}$ and $5 \cdot 10^{-4}$ mole/liter in toluene and polystyrene. It should be noted that, as a consequence of the lower effectiveness of the transfer of energy, the increase in the intensity of the luminescence of this mixture is smaller than in the case of II. As in the case of the compounds that we previously described [8], the mutual orientation of the molecules evidently plays an important role in this system.

EXPERIMENTAL

The absorption spectra of I-III in toluene (concentration $3 \cdot 10^{-5}$ mole/liter) were measured with an SF-4 spectrophotometer. An apparatus consisting of a ZMR-3 mirror monochromator, an FEU-18 optical emission detector, and an M-95 microammeter was used to investigate the fluorescence ($c 10^{-3}$ mole/liter). The photoluminescence was excited with an SVDSH-500 lamp, from the spectrum of which the exciting light with a wavelength of 313 nm was isolated by means of a DMR-4 quartz monochromator. The spectra obtained were corrected with allowance for the spectral sensitivity of the apparatus. The absolute fluorescence quantum yields were determined by the equal-absorption method [9].

The films were prepared by dissolving a weighed sample of the investigated substance (from calculation, 10^{-3} mole/liter) and 0.5 g of polystyrene by heating in 10 ml of toluene, after which 1 ml of the resulting solution was applied to glass (30 by 30 mm) with a pipette and allowed to stand for 10 h. The average fluorescence intensities obtained in the measurement of three films are presented.

2-(3-Phenylformyl)-5-phenyl-1,3-oxazole. A 21-g (0.15 mole) sample of urotropin was added to a solution of 15.7 g (0.05 mole) of 2-(3-bromomethylphenyl)-5-phenyloxazole in 250 ml of 50% acetic acid, and the mixture was refluxed for 1.5 h. Hydrochloric acid (15 ml) was added, and the mixture was refluxed for another 5 min. It was then cooled, and the resulting precipitate was removed by filtration and recrystallized from methanol to give 8.4 g (68%) of a light-yellow precipitate with mp 136-137°C. Found: C 77.4; H 4.5; N 5.5%; M 249. $C_{16}H_{11}NO_2$. Calculated: C 77.1; H 4.4; N 5.6%.

3(4)-[5-(2-Tosylaminophenyl)-1,3,4-oxadiazol-2-yl]-3'(4')(5-phenyl-2-oxazolyl)stilbenes (I-III). A 0.8-ml (0.01 mole) sample of triethyl phosphite was added to a solution of 7.5 g (0.01 mole) of 2-[4(3)-bromomethylphenyl]-5-(2-tosylaminophenyl)-1,3,4-oxadiazole in 20 ml of xylene, and the mixture was refluxed on an oil bath at 150°C for 4 h. The xylene was removed by distillation, and the residual phosphonate in the form of a yellow oil, which solidified upon cooling, was dissolved in 15 ml of dimethylformamide (DMF), and 0.23 g (0.01 mole) of sodium metal in 2 ml of methanol and 2.5 g (0.01 mole) of 2-[4(3)-phenyl-

formyl]-5-phenyl-1,3-oxazole in 10 ml of DMF were added. The reaction mixture was then allowed to stand at 20°C for 2 h. Compounds I-III were purified by chromatography on activity II aluminum oxide by elution with benzene.

Compound I, with mp 255-256°C, was obtained in 23% yield. Found: C 71.7; H 4.4; S 5.0%. $C_{38}H_{28}N_4O_4S$. Calculated: C 71.7; H 4.4; S 5.0%.

Compound II, with mp 214-215°C, was obtained in 25% yield. Found: C 71.9; H 4.4; S 5.1%. $C_{38}H_{28}N_4O_4S$. Calculated: C 71.7; H 4.4; S 5.0%.

Compound III, with mp 198-199°C, was obtained in 30% yield. Found: C 71.5; H 4.6; S 5.3%. $C_{38}H_{28}N_4O_4S$. Calculated: C 71.7; H 4.4; S 5.0%.

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