

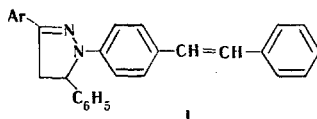
SYNTHESIS AND SPECTRAL LUMINESCENCE PROPERTIES OF STILBENE
DERIVATIVES CONTAINING 2-PYRAZOLINYL AND 1,3-OXAZOLYL GROUPINGS

B. M. Krasovitskii, L. A. Kutulya, A. E. Shevchenko,
L. Sh. Afanasiadi, N. P. Egorova, and A. L. Shvorina

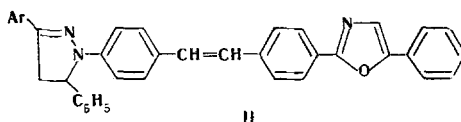
UDC 535.37:547.778.2'787

A number of trans-stilbene derivatives containing 2-pyrazolinyl and 1,3-oxazolyl groupings were synthesized by PO olefination from 1-(4-formylphenyl)-3-aryl-5-phenyl-2-pyrazolines and 2-(4-bromomethylphenyl)-5-phenyl-1,3-oxazole. The products fluoresce intensely in the green or yellow-green region (quantum yields 0.4-0.57). The intense long-wave absorption band of the investigated compounds is due to an electron transition that is localized primarily in the stilbene fragment of their molecules that includes, as a substituent, the amine nitrogen atom of the pyrazoline ring; the less intense shortwave band corresponds to localization of the electronic excitation in the hydrazone grouping.

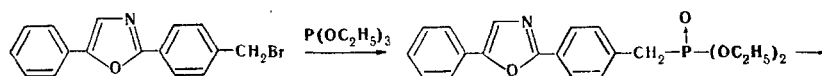
The development of a practicable method for the preparation of 1,3,5-triaryl-2-pyrazolines containing a p-formyl group in the 1-phenyl ring [1, 2] has opened up possibilities for the synthesis of fluorescing pyrazolinyl-substituted 1,2-diarylethylenes. The simplest of these - I, which we described in [3] - luminesce in the blue-green or green region of the spectrum when they are subjected to UV irradiation.



It was expedient to synthesize a number of 4-(3-aryl-5-phenyl-1-pyrazolinyl)-4'-(5-phenyl-1,3-oxazol-2-yl)stilbenes (II) (see Table 1) for which, on the basis of the data in [4], one might have assumed a shift in the fluorescence spectra to the longer-wavelength region as compared with pyrazolinyl-substituted stilbenes I.



We obtained II by PO olefination in the form of the trans isomers from the corresponding 1-(4-formyl)-3-aryl-5-phenyl-2-pyrazolines and 2-(4-bromomethylphenyl)-5-phenyl-1,3-oxazole:*



*A study of the generation properties of some compounds of this type, in particular, II with Ar = phenyl and styryl, was recently reported [5], but the method of preparation and the characteristics of the investigated compounds were not presented.

All-Union Scientific-Research Institute of Single Crystals, Scintillation Materials, and Ultrapure Chemical Substances, Kharkov, 310086. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 5, pp. 656-661, May, 1977. Original article submitted April 13, 1976; revision submitted July 8, 1976.

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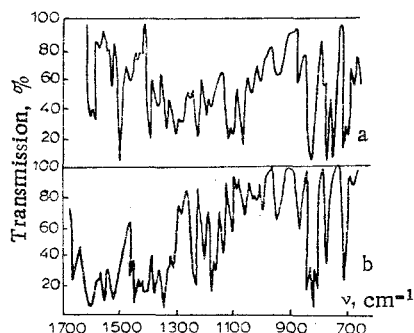
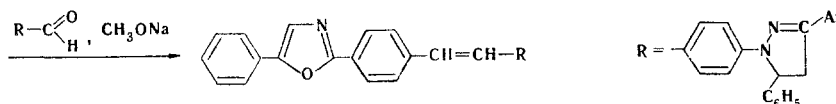
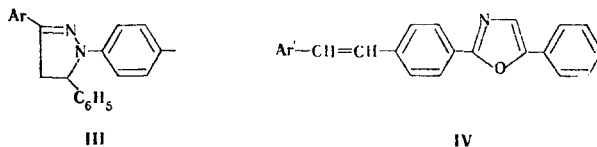


Fig. 1. IR spectra of KBr pellets of: a) 1,5-diphenyl-3-(4-dimethylaminophenyl)-2-pyrazoline; b) 1-(4-formylphenyl)-3-(4-dimethylaminophenyl)-5-phenyl-2-pyrazoline.



The structures of the synthesized compounds were confirmed by data from the IR spectra, in which an intense absorption band of the out-of-plane deformation vibrations of the CH bond of the trans-ethylene grouping at 970 cm^{-1} is observed and a number of absorption bands characteristic for 1,3,5-triaryl-2-pyrazolines [6] are retained.

1-(4-Formylphenyl)-3-(4-dimethylaminophenyl)-5-phenyl-2-pyrazoline was synthesized for the first time as one of the intermediates by Vilsmeier formylation of 1,5-diphenyl-3-(4-dimethylaminophenyl)-2-pyrazoline. The latter was obtained by reaction of 1-phenyl-3-(4-dimethylaminophenyl)-propen-3-one with phenylhydrazine in alcohol solution in the presence of alkali. The substance that we obtained differs considerably with respect to its appearance and melting point from the compound described in [7], which was synthesized via a similar scheme but in acetic acid. Intense absorption corresponding to the stretching vibrations of a C=N bond ($\nu_{\text{C=N}}$) at 1600 cm^{-1} , as well as a number of other bands characteristic for aryl-2-pyrazolines, in conformity with the data in [6], is observed in the IR spectrum of the compound that we obtained. This, together with the absence at $3200\text{--}3400\text{ cm}^{-1}$ of ν_{NH} absorption of the possible reaction product — the corresponding phenylhydrazone — confirms the 2-pyrazoline derivative structure of our product. In addition, intense $\nu_{\text{C=O}}$ absorption at 1680 cm^{-1} appears in the IR spectrum of its formylation product (Fig. 1b).



The spectral luminescence characteristics of solutions of the investigated II in toluene are presented in Table 1. The character of the absorption and fluorescence curves of some of them are shown in Fig. 2. The molecules of the investigated II contain III and IV groupings. They can also be considered to be diarylethylenes I substituted in the para position of the stilbene fragment by a 5-phenyl-1,3-oxazol-2-yl grouping. Data for some I, III, and IV, which are the structural fragments of the investigated stilbene derivatives (II), are therefore presented for comparison in Table 1.

Two bands, the intensities of which, as a rule, differ markedly, appear distinctly in the absorption spectra of II. The long-wave band (A) is shifted substantially bathochromically as compared with the corresponding bands in the spectra of I, III, and IV (for example, compare IIa with Ia, IIIa, and IVa). Its intensity exceeds the intensity of the long-wave band of III by a factor of 2.5-3 and is similar to the intensities observed for substituted stilbenes I and IV. The shorter-wave band (B) in the spectra of the investigated compounds is of considerably lower intensity than the A band (see Fig. 2). Its position and intensity are close to those of the corresponding band in the spectra of III, in which it is overlapped considerably by the long-wave A band [9]. An exception to this is IIe, for which one observes a considerable increase in intensity of the B band and its substantial bathochromic shift, as a consequence of which the A and B bands in the spectrum of this compounds are substantially overlapped (Fig. 2).

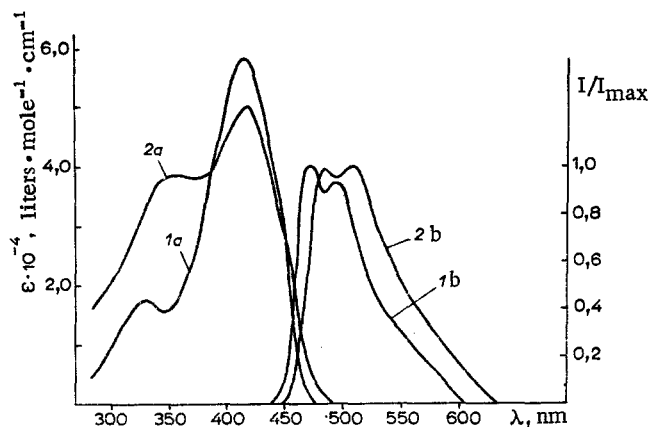
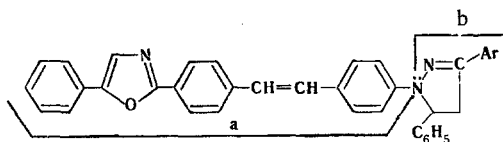


Fig. 2. Absorption (a) and fluorescence (b) spectra in toluene: 1) 4-(3,5-diphenyl-2-pyrazolin-1-yl)-4'-(5-phenyl-2-oxazolyl)stilbene (IIa); 2) 4-[3-(4-dimethylaminophenyl)-5-phenyl-2-pyrazolin-1-yl]-4'-(5-phenyl-1,3-oxazol-2-yl)stilbene (IIe).

To interpret the nature of the observed absorption bands we feel it is necessary to take into account the fact that the chromophore system of the investigated molecules includes two interacting cross-conjugated a and b fragments,



which have in common the electron-donor amine nitrogen atom of the pyrazoline ring. A certain localization of the electronic excitation on the individual fragments can be expected for systems of this type. In [10] it was assumed (and a number of proofs were presented) that in the case of 1,4-diphenyl-3-aryl-2-pyrazolines (III) the $2p_z$ electron pair of the amine nitrogen atom is delocalized in two directions during excitation: on the N-phenyl group and on the azomethine $-N=C-Ar$ grouping. In this case the relative contribution of the electronic shifts in the first fragment increases regularly when electron-acceptor substituents of various strengths are introduced in the phenyl ring. A similar change can also be expected when the length of the π -electron system introduced in the 1 position of the pyrazoline ring is increased, as in the case of II. A comparison of the characteristics of the A band in the spectra of IIa and IVb (Table 1) shows that they differ only slightly with respect to their transition energies ($\Delta\nu = 1600 \text{ cm}^{-1}$). It may therefore be assumed that the corresponding transition is primarily localized in fragment a, although the $N=C-Ar$ grouping does have a substantial perturbation effect on it, evidently due to certain delocalization in this direction of the $2p_z$ electron pair of the 1-N atom. The validity of this consideration is confirmed by the fact that the perturbation effect of the $N=C-C_6H_5$ grouping during the $S_0 \rightarrow S_1$ transition remains practically unchanged when substituents with relatively weakly expressed electronic effects (CH_3 , OCH_3 , and Cl) are introduced in the phenyl ring (compare the λ_{max} values of the A band of IIa-d). However, a small bathochromic shift of the A band as compared with the unsubstituted IIa is observed for IIe, which contains a strong electron donor — a dimethylamino group — in the 3-phenyl ring. This may be a consequence of the considerable conjugation of the unshared electron pair of the nitrogen atom of the $N(CH_3)_2$ group with the $C=N$ bond, which promotes delocalization of the electrons in principal fragment a thereby giving rise to a certain decrease in the transition energy.

An increase in the length of the conjugation chain of the aryl group in the 3 position of the pyrazoline ring (II f, g) also produces a certain bathochromic shift of the absorption spectrum due to intensification of the perturbation effect of the π -electron system of the arylazomethine grouping.

TABLE 1. Characteristics of the Synthesized and Model Compounds

Compound	Ar	mp, °C	N found, %	Empirical formula	N calc., %	Absorption λ_{\max} , nm ($\epsilon \cdot 10^{-4}$)	Fluorescence λ_{\max} , nm (η)	$\Delta\nu_{st}$, cm^{-1}	Yield, %
IIa	Phenyl	232—234	7,77; 7,35	$\text{C}_{38}\text{H}_{29}\text{N}_3\text{O}$	7,75	415 (5,80); 325 (1,72)	470 495 (0,57)	2800	40
IIb	4-Tolyl	256—257	7,42; 7,34	$\text{C}_{39}\text{H}_{31}\text{N}_3\text{O}$	7,54	415 (6,55); 325 (2,18)	475; 500 (0,49)	3000	58
IIc	4-Anisyl	240—242	7,69; 7,47	$\text{C}_{39}\text{H}_{31}\text{N}_3\text{O}_2$	7,33	415 (6,45); 325 (2,12)	475; 505 (0,47)	3000	54
IId	4-Chloro-phenyl	202—204	7,11; 7,24	$\text{C}_{38}\text{H}_{28}\text{N}_3\text{OCl}$	7,27	420 (6,23); 330 (1,82)	475; 500 (0,50)	2800	52
IIe	4-Dimethyl-amino	192—194	9,69	$\text{C}_{40}\text{H}_{34}\text{N}_4\text{O}$	9,58	422 (5,05); 365 (3,80)	485; 510 (0,40)	3000	37
IIf	4-Diphenyl	280—281	6,95; 6,68	$\text{C}_{44}\text{H}_{33}\text{N}_3\text{O}$	6,78	425 (6,30); 332 (1,68)	485; 510 (0,52)	2900	35
IIg	Styryl	259—260	7,18; 7,52	$\text{C}_{40}\text{H}_{31}\text{N}_3\text{O}$	7,36	432 (7,75); 330 (1,62)	495; 515 (0,47)	2900	35
Ia	Phenyl	—	—	—	—	390 (4,15); 325 b	470 (0,45)	4400	—
IIIa	Phenyl	—	—	—	—	360 (2,00); 315 b	440 (0,45)	4700	—
IVa	Phenyl	—	—	—	—	355 (6,34) ^c	415 (0,88) ^c	4100	—
IVb	4-Dimethyl-amino	—	—	—	—	390 (3,95) ^c	460 (0,14) ^c	3900	—

a) These are the yields of the chromatographically pure products.

b) Inflection. c) Data from [8].

The long-wave absorption band of the investigated stilbene derivatives is considerably more intense than in the case of model compound IVb. This increase in the probability of the electron transition is the only consequence of the perturbation effect of cross-conjugated fragment b and the increase in the overall length of the π -electron system of the molecule, owing to which the probability of its interaction with the light-wave field increases [11].

The bathochromic shift of the A band of II relative to I (compare Ia and IIa) is evidently due mainly to the increase in the π -electron system of fragment a when a phenyloxazolyl grouping is introduced.

The validity of the interpretation of the long-wave electron transition of II as localized primarily in fragment a could also be confirmed by the presence in the spectrum of bands corresponding to localization of the excitation in fragment b. In order to verify whether this is the B band of the investigated compounds, we compared its characteristics with the data for 1-methyl-3,5-diphenyl-2-pyrazoline (V). A band with λ_{\max} at 305 nm (ϵ 11,600 liter \cdot mole $^{-1}\cdot$ cm $^{-1}$) is observed in the absorption spectrum of this compound in hexane [9]. Thus with respect to its energy and the probability of electron transition, the B band of the investigated compounds (see Table 1) is similar to the same band in the spectrum of model compound V and can therefore be tentatively assigned to a $\pi \rightarrow \pi^*$ transition localized primarily in fragment b. The bathochromic shift of this band in the case of II, as compared with pyrazoline V ($\Delta\nu = 2000$ cm $^{-1}$), is due to the perturbation effect of the substituted stilbene grouping bonded to the 1-N atom of the pyrazoline ring. It is apparent that the mutual perturbation of the cross-conjugated a and b fragments ($\Delta\nu = 1600$ and 2000 cm $^{-1}$) is approximately identical for the investigated compounds.

The absorption band corresponding to fragment b is only slightly sensitive to the introduction of CH_3 and OCH_3 groups and the Cl atom in the phenyl ring, but, as one might have expected, it changes substantially when there is a dimethylamino group in this ring (IIe). The considerable hyperchromic and bathochromic effects as compared with IIa-d that are observed in this case for the B band are due to the possibility of charge transfer from the dimethylamino group to the C=N group. The introduction of a dimethylamino group in benzaldehyde azomethine [12, 13] and hydrazone [14] molecules has a similar effect. These facts constitute an additional confirmation of the validity of our approach to the interpretation of the nature of the absorption bands of the investigated compounds.

All of the stilbene derivatives obtained (II) fluoresce intensely when they are irradiated with UV light. Their quantum yields range from 0.4 to 0.5 and are substantially higher than in the case of model compound IVb; this is evidently a consequence of the more planar and more rigid structure of the pyrazoline ring as a substituent in the stilbene fragment of IV as compared with the dimethylamino group.

Like the previously investigated oxazolyl-substituted 1,2-diarylethylenes [4], the fluorescence spectra of the compounds obtained in this research have a clearly expressed vibrational structure. Like the A band in the absorption spectra, the fluorescence spectra of II are shifted bathochromically relative to I and IV. It is interesting that the Stokesian shift of the intense shortwave component to the fluorescence band relative to the maximum of the A absorption band is substantially less for the investigated II than for I and IV (see Table 1).

The substituents in the 3 position of the pyrazoline ring have relatively little effect on the position of the fluorescence bands, although a tendency toward an increasing bathochromic shift of these bands when electron-donor substituents are introduced in the phenyl ring [$\text{CH}_3 < \text{OCH}_3 < \text{N}(\text{CH}_3)_2$] can be noted. As in the absorption spectra, a substantial shift of the fluorescence band to the longer wavelength region is observed when the 3-phenyl group of the pyrazoline fragment of II molecules is replaced by a diphenyl and, particularly, a styryl grouping.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds at $700\text{--}4000\text{ cm}^{-1}$ were measured with a UR-20 spectrometer. The absorption and fluorescence spectra were measured as in [3]. The fluorescence quantum yields were determined by the method in [15] relative to 1.8-naphthoylene-1',2'-benzimidazole ($\eta = 0.55$).

1,5-Diphenyl-3-(4-dimethylaminophenyl)-2-pyrazoline (IIIb). A 9-g (0.035 mole) sample of 1-phenyl-3-(4-dimethylaminophenyl)propen-3-one was dissolved by heating in 300 ml of ethanol, and a solution of 4 ml (0.035 mole) of phenylhydrazine in 50 ml of ethanol and 20 ml of 10% NaOH solution (0.05 mole) were then added dropwise in succession. The mixture was then refluxed and stirred for 4 h, after which it was cooled, and the resulting precipitate was removed by filtration and washed to neutrality with water-alcohol (1:1) to give 7.5 g (62%) of product. Recrystallization (twice) from hexane-benzene (3:1) with aluminum oxide gave white crystals with blue fluorescence and mp $200\text{--}201^\circ$ (reddish needles with mp 187° according to the data in [7]). IR spectrum: $\nu_{\text{C}=\text{N}} 1598\text{ cm}^{-1}$. Found, %: N 11.99, 12.00. $\text{C}_{23}\text{H}_{23}\text{N}_3$. Calculated, %: N 12.34.

1-(4-Formylphenyl)-3-(4-dimethylaminophenyl)-5-phenyl-2-pyrazoline (VI). This compound was obtained by formylation of pyrazoline IIIb with DMF in the presence of phosphorus oxychloride. The Vilsmeier reagent [8 ml (0.09 mole) of POCl_3 in 10 ml (0.13 mole) of DMF] was added dropwise with stirring at 25° to a suspension of 5.8 g (0.017 mole) of pyrazoline IIIb in 13 ml of DMF, and the mixture was then heated to 60° and maintained at this temperature for 3 h. After 12 h, the cooled mixture was poured over ice, and the aqueous mixture was neutralized with a cold saturated solution of sodium carbonate. The precipitate was washed with water and dried to give 5.5 g (88%) of product. The product was purified by three recrystallizations from methanol and ethanol to give yellow needles with turquoise fluorescence and mp $191\text{--}192^\circ$. IR spectrum: $\nu_{\text{C}=\text{O}} 1680\text{ cm}^{-1}$ and $\nu_{\text{C}=\text{N}} 1594\text{ cm}^{-1}$. Found, %: N 10.90, 11.02. $\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}$. Calculated, %: N 11.38.

4-(3-Aryl-5-phenyl-2-pyrazolin-1-yl)-4'-(5-phenyl-1,3-oxazol-2-yl)stilbenes (IIa-g). An 0.02-mole sample of triethyl phosphite was added to a solution of 0.02 mole of 2-(4-bromomethylphenyl)-5-phenyloxazole in 20 ml of xylene, and the mixture was refluxed on an oil bath for 4 h. The xylene was removed by distillation, and the resulting yellow oily phosphonate, which solidified on cooling, was dissolved in 15 ml of DMF. A solution of 0.46 g (0.02 mole) of sodium metal in 4 ml of methanol and a solution of 0.01 mole of the appropriate aldehyde in 10 ml of DMF were added to the solution of the phosphonate, and the mixture was allowed to stand at room temperature for 2 h. The resulting yellow precipitates were purified by chromatography of benzene solutions on aluminum oxide and subsequent recrystallization (twice) from suitable solvents (heptane, benzene, xylene, or mixtures of them).

The yields, melting points, and results of analysis of the synthesized II are presented in Table 1.

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STUDY OF THE STRUCTURES OF INDAZOLES, PYRAZOLO[3,4-b]PYRIDINES,
AND PYRAZOLO[3,4-b]PYRAZINE BY IR SPECTROSCOPY

L. V. Sennitskaya, Yu. D. Timoshenkova, B. S. Kikot', UDC 547.772.821.861:543.422.4:
Yu. A. Pentin, F. F. Blanco, I. A. Korbukh, and 541.62
M. N. Preobrazhenskaya

It is shown on the basis of a study of the IR spectra of indazoles, pyrazolopyridines, and pyrazolopyrazine in the solid state and of their N-deutero-substituted derivatives and hydrochlorides at room temperature and at the temperature of liquid nitrogen that these heterocycles exist in a tautomeric form in which the labile hydrogen atom is localized on the nitrogen atom of the pyrazole ring. It was established that 6-aminopyrazolopyridine exists in the crystalline state in the amino form and that it is protonated at the ring nitrogen atom rather than at the amino group. The applicability of the temperature-shift method for the detection not only of γ_{NH} bands but also of γ_{ND} bands is demonstrated.

Scientific Oncological Center, Academy of Medical Sciences of the USSR, Moscow 115478.
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