SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 4(5)-(1,5-DIARYL-Δ^2-PYRAZOLIN-3-YL)-1,8-NAPHTHOYLENE-1',2'-BENZIMIDAZOLE WITH FLUORINE-CONTAINING SUBSTITUENTS

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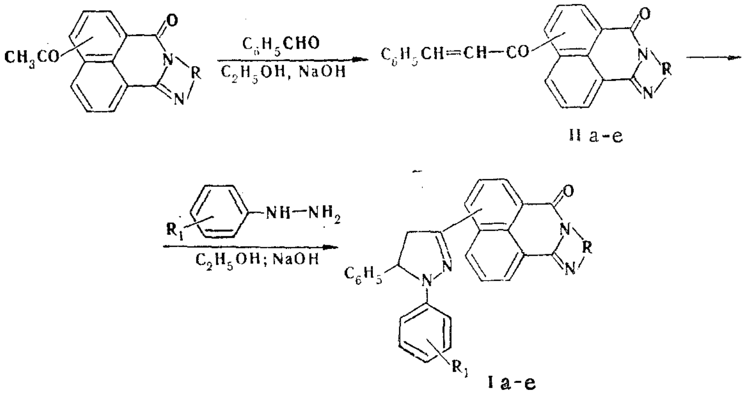
A number of 4(5)-(1,5-diaryl-Δ^2-pyrazolin-3-yl)-1,8-naphthoylene-1',2'-benzimidazoles with fluorine-containing substituents in the benzene ring of the naphthoylenebenzimidazole fragment or the N-aromatic grouping of the pyrazoline ring were synthesized by the reaction of 4(5)-acetyl-1,8-naphthoylene-1',2'-benzimidazole or its substituted derivatives with benzaldehyde and subsequent condensation of the resulting cinnamoylnaphthoylenebenzimidazoles with phenylhydrazine or substituted phenylhydrazines. The compounds obtained fluoresce intensively in liquid organic solvents and in polymeric matrices and have increased photostability.

We have previously shown [1] that fluorine-containing substituents, inasmuch as they are electron acceptors, not only have a substantial effect on the spectral-luminescence properties of 1,3,5-triaryl-Δ^2-pyrazolines but also increase their stability with respect to UV radiation significantly.

Continuing our study of the effect of fluorine-containing substituents on the properties of organic luminophores [1-4] we have synthesized and investigated compounds with fluorine-containing substituents that include the fluorophore groupings of 1,3,5-triaryl-Δ^2-pyrazolines and 1,8-naphthoylene-1',2'-benzimidazole (NBI) (Ia-e). They can be regarded as triarylpyrazolines in which the NBI fragment acts as an electron-acceptor substituent that interacts with the π—p—π system of the pyrazoline ring and the N-aromatic grouping bonded to it.

The synthesis of I was realized by the reaction of 4(5)-acetyl-NBI or its substituted derivatives with benzaldehyde and subsequent condensation of the resulting cinnamoyl-NBI (IIa-e) with phenylhydrazine or substituted phenylhydrazines.



I a $R=C_6H_4$, $R_1=H$; b $R=C_6H_3CF_3$, $R_1=H$; c $R=C_6F_4$, $R_1=H$; d $R=C_6H_4$, $R_1=m\text{-}CF_3$; e $R=C_6H_4$, $R_1=p\text{-}SO_2CHF_2$; II a,d,e $R=C_6H_4$; b $R=C_6H_3CF_3$; c $R=C_6F_4$

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TABLE 1. Spectral-Luminescence Characteristics of I

Compound	Absorption in toluene		Fluorescence									
			in toluene			in poly(methyl methacrylate)			in polystyrene		
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	B_{rel}		λ_{max}, nm	B_{rel}		λ_{max}, nm	B_{rel}	
				before irradiation	after irradiation		before irradiation	after irradiation		before irradiation	after irradiation
Ia	505	2,50	595	100	26	635	100	83	626	100	50
Ib	515	2,80	605	110	81	—	—	—	—	—	—
Ic	520	2,40	615	110	82	—	—	—	—	—	—
Id	485	3,10	565, 580	125	99	585	130	120	582	140	108
Ie	470	3,36	545, 575	150	94	575	190	178	575	160	120

TABLE 2. Characteristics of I and II

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		F	N		F	N	
Ib	315—317	10,2	10,1	$C_{34}H_{21}F_3N_4O$	10,2	10,0	57
Ic	300—301	13,5	9,7	$C_{33}H_{18}F_4N_4O$	13,5	9,9	50
Id	261—263	10,2	10,0	$C_{34}H_{21}F_3N_4O$	10,2	10,0	50
Ie	374—375	6,4	9,2	$C_{34}H_{22}F_2N_4O_3S$	6,3	9,3	48
IIb	108—110	12,3	6,0	$C_{18}H_{13}F_3N_2O_2$	12,2	6,0	49
IIc	241—242	16,3	5,8	$C_{27}H_{12}F_4N_2O_2$	16,1	5,9	45

The formation of a mixture of isomers that differ with respect to the position of the substituent in the benzene ring of the NBI fragment and the 1,5-diarylpyrazolinyl residue in the naphthalene fragment is possible in this case. On the basis of the data in [5] regarding the closeness of the fluorescence characteristics of the 4- and 5-substituted isomers of 1,5-diphenyl-3-pyrazolinyl-NBI and considering the constancy of the fluorescence properties of the compounds that we obtained in the case of repeated syntheses and purifications, we did not isolate the individual isomers but investigated their mixtures.

The intensification of the electron-acceptor character of the NBI fragment when fluorine-containing groups are introduced into the benzene ring of the latter leads to a long-wave shift of the absorption and fluorescence spectra as compared with the spectra of unsubstituted compound Ia (Table 1).

Trifluoromethyl and difluoromethylsulfonyl groups in the N-phenyl grouping of luminophore Ia give rise to hypsochromic and hypsofluoric effects, which become greater when the electron-acceptor properties of the fluorine-containing substituent are intensified; splitting of the fluorescence bands in the spectra of Id,e occurs in this case. It may be assumed that "disengagement" of the unified chromophore system occurs as a result of effective interaction of the unshared electron pair of N_1 with the π system of the phenyl grouping, which includes a trifluoromethyl and, particularly, a difluoromethylsulfonyl group, and the fluorescence spectra of Id,e are the superimposition of two bands. The chromophore system of the molecule as a whole is responsible for the long-wave bands, which are similar to the fluorescence band of unsubstituted pyrazolinyl-NBI (Ia). The short-wave bands are due to the fragment that includes an N-aromatic grouping with a fluorine-containing substituent and the N_1 atom of the pyrazoline ring.

The investigation of the dependence of the relative photoluminescence light output (B_{rel}) of toluene solutions of the synthesized compounds during their irradiation with the light of a xenon lamp, which is close in spectral composition to daylight, makes it possible to conclude that there is an increase in the photostability of compounds with fluorine-containing substituents, particularly when they are introduced into the N-aromatic grouping (Table 1). We associate this with the significant decrease in the electron density on the pyrazoline ring, which undergoes photooxidation most readily.

Compounds Id,e are most photostable in toluene solutions, and for comparison with them unsubstituted luminophore Ia was investigated also in polymeric matrices, viz., polystyrene and poly(methyl methacrylate), at a luminophore concentration of $1.7 \cdot 10^{-3}$ mole/liter (Table 1).

The introduction of Id,e into polymers leads to the production of brightly colored fluorescing plastics. Their fluorescence spectra, in contrast to the spectra of the toluene solutions, have one maximum that lies at the same wavelength as the long-wave fluorescence maximum of toluene solutions or close to it. The reason for the absence of a short-wave band in the spectrum can be found in intensification of the conjugation of the NBI residue with the π–p–π system of the pyrazoline ring due to the more planar rigidly fixed structure of the molecules in solid solutions and, in this connection, due to weakening of the "autonomy" of the arylimine fragment, which includes the fluorine-containing substituent. The photostabilities of solid solutions in polymers exceed those of toluene solutions of the same luminophores (Table 1). The highest photostability is characteristic for solutions of the luminophores in poly(methyl methacrylate).

EXPERIMENTAL

The 4(5)-(1,5-diaryl-Δ^2-pyrazolin-3-yl)-1,8-naphthoylene-1',2'-benzimidazoles (I) and their synthesis products — 4(5)-cinnamoyl-1,8-naphthoylene-1',2'-benzimidazoles (II) — were synthesized by a method similar to the synthesis of 1,5-diphenyl-Δ^2-pyrazolinyl-1,8-naphthoylene-1',2'-benzimidazone [5]. Compounds I were purified by chromatography of their benzene solutions on aluminum oxide, while II were purified by recrystallization from acetic acid.

The results of analysis, the melting points, and the yields of the synthesized substances are presented in Table 2.

The absorption spectra were measured with an SF-4 spectrophotometer while the fluorescence spectra were obtained with an apparatus consisting of a ZMR-3 mirror monochromator, an FEU-18 or FEU-49B optical emission detector, and an M-95 microammeter. The photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was separated with a DMR-4 quartz monochromator. The fluorescence spectra in the polymers were measured in disks with a diameter of 16 mm and a thickness of 3 mm.

The photostabilities were estimated from the change in the intensity of the luminescence of the luminophores at the fluorescence maximum with respect to nonirradiated samples of the luminophores. The measurements were made with a Ksenotest-450 apparatus at a relative humidity in the chamber of 80-85% and a temperature on the surface of the samples of 26-28°C. The time of irradiation of the toluene solutions of the luminophores was 20 h, as compared with 60 h for the solid solutions in the polymers.

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