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ARYLOXAZOLYL-SUBSTITUTED RHODAMINE C DERIVATIVES

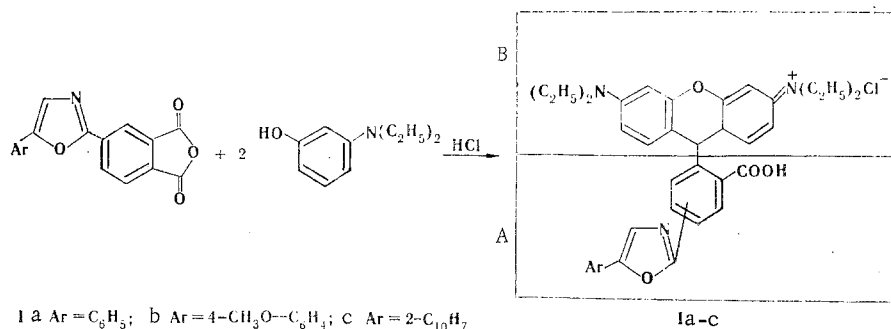
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Aryloxazolyl-substituted rhodamine C derivatives were synthesized by condensation of 4-(5-aryloxazol-2-yl)phthalic anhydrides with *m*-diethylaminophenol, and their spectral-luminescence properties were investigated. The individual compounds and their mixtures with 4-aminonaphthalic acid phenylimide were used to obtain daytime fluorescent pigments and paints. Effective intermolecular transfer of the electronic excitation energy is observed in mix compositions, and its mechanism is discussed.

Rhodamine dyes and their derivatives are widely used as luminophores in daytime fluorescent pigments and paints [1], in tunable lasers [2], as active dyes in biological investigations [3], and for other purposes.

We have synthesized aryloxazolyl derivatives of rhodamine C (I) — compounds that contain two fluorophores with a common aromatic ring — by using our previously described 4-(5-aryloxazol-2-yl)phthalic anhydrides [4].



The synthesis of Ia-c was realized by fusing 4-(5-aryloxazol-2-yl)phthalic anhydrides with *m*-diethylaminophenol at 180-190°C in a molar ratio of 1:2. The probability of the formation of two isomers that differ with respect to the mutual orientation of the aryloxazole residue and the pyrone ring in the carboxy-containing aromatic ring is not excluded in the reaction of aryloxazolylphthalic anhydrides with *m*-diethylaminophenol. Considering the fact that the visible color and fluorescence of rhodamines is due to the structure of the xanthene part of their molecules, which is in a mutually perpendicular plane with the carboxyphenyl group [5], the isomers should not differ substantially with respect to their spectral-luminescence properties. We therefore investigated the compounds obtained after chromatographic purification without isolation of the individual isomers (Table 1).

The absorption spectrum of Ia (Fig. 1) consists of two disconnected bands with a distance of 235 nm between the maxima. The short-wave band is due to transitions that are localized in the diphenyloxazole fragment and is identical to the absorption spectrum of 2-(*p*-carboxyphenyl)-5-phenyloxazole [λ_{\max} 315 nm ($\epsilon = 37,000$)]. Lengthening of the conjugation

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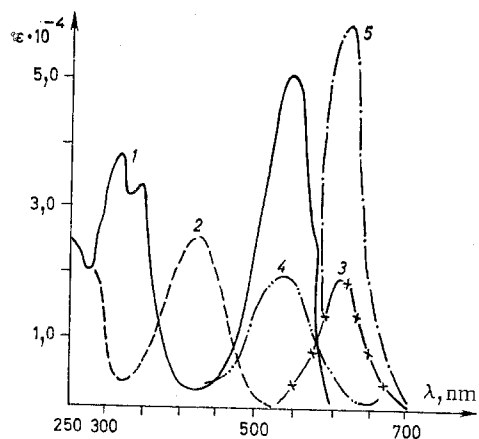


Fig. 1. Absorption spectra of Ia (1) and 4-aminonaphthalic acid phenylimide (2) in ethanol and luminescence spectra of Ia (3), 4-aminonaphthalic acid phenylimide (4), and their 1:1 binary mixture (5) in the MTSF polymer.

TABLE 1. Spectral-Luminescence Properties of Aryloxazolyl-Substituted Rhodamine C (Ia-c) in Ethanol

Compound	Absorption		Fluorescence	
	λ_{\max} , nm	$\epsilon \cdot 10^{-4}$	λ_{\max} , nm	B_{rel}^*
Rhodamine C	540	10,2	595	1,00
Ia	315	3,9	590	0,50
Ib	355	4,4	585	0,56
	545	5,2		
Ic	350	3,3	590	0,48
	545	5,4		

*Symbol B is the intensity of the luminescence with respect to rhodamine C.

tion chain in this fragment by replacement of the phenyl group by a 2-naphthyl group (Ic) leads to a long-wave ($\Delta\lambda = 25$ nm) shift of the maximum without a substantial change in the intensity of the band. The introduction of a methoxy group in the para position of the 5-phenyl group gives rise to an even greater bathochromic effect due to a shift of the electron density toward the aryloxazole grouping.

The position of the long-wave absorption band responsible for fluorescence is determined by intramolecular charge transfer in the xanthene fragment (fragment B) and is virtually independent of the structure of fragment A; its intensity is considerably lower than in the spectrum of unsubstituted rhodamine C (see Table 1). The decrease in the intensity of the luminescence of I as compared with the luminescence of rhodamine C is evidently a consequence of this.

The possibility of an increase in the intensity of the luminescence of rhodamine C in polycondensed resins by dissolving in them of binary mixtures of luminophores in which transfer of the electronic excitation energy from the luminophore donor to rhodamine is realized was demonstrated in [6, 7]. We investigated the luminescence properties of solid solutions of aryloxazolyl-substituted rhodamine C derivatives and their mixtures with 4-aminonaphthalic acid phenylimide (a luminophore with yellow-green luminescence) in a melamine-toluenesulfonamide-formaldehyde (MTSF) polymer, which has a polarity that is close to that of ethanol and is widely used as the base of daytime fluorescent pigments (DFP) [8]. For the investigation of the luminescent and colorimetric characteristics the obtained polymeric compositions were converted to daytime fluorescent enamel paints (DFP).

TABLE 2. Fluorescence of DFP That Contain Aryloxazoly-Substituted Rhodamine C Derivatives (with the MTSF polymer as the base)

	Individual compounds			Binary mixtures with 4-aminonaphthalic acid phenylimide		
	Ia	Ib	Ic	Ia	Ib	Ic
Fluorescence λ_{\max} , nm	610	610	610	605	610	610
B_{rel}^*	1,00	1,33	2,20	2,90	2,70	3,08

*Symbol B is the intensity of the luminescence with respect to Ia.

The absorption spectrum of Ia shows that intramolecular transfer of the electronic excitation energy between unconjugated fluorophores A and B cannot be realized. However, a substantial bathochromic shift of the short-wave band is observed when the phenyl group is replaced by a 2-naphthyl or 4-anisyl group, and, as a result, intramolecular transfer of the electronic excitation energy from fluorophore A to fluorophore B becomes possible. As a consequence of this, the intensity of the fluorescence of DFP that contain Ib, c increases as compared with the fluorescence of Ia (Table 2).

In the case of Ia the same effect can be achieved by using it in a mix composition with 4-aminonaphthalic acid phenylimide. It is known [9] that the use of this sort of mixture with unsubstituted rhodamine C in the MTSF polymer makes it possible to increase the intensity of the luminescence of rhodamine C due to intermolecular nonradiating transfer of the electronic excitation energy by a factor of ~ 1.5 .

The long-wave absorption band of the phenylimide is situated between the absorption bands of fragments A and B of I (Fig. 1). This made it possible to assume that the excited state of Ia can be deactivated by transfer of the electronic excitation energy to the 4-aminonaphthalic acid phenylimide molecule before the nonradiating transition in fluorophore A occurs. This may lead to cascade transfer of energy from fluorophore A to the phenylimide and then from the phenylimide to fluorophore B.

The intensity of the luminescence of Ia in the mix composition with the phenylimide in the MTSF polymer in the case of excitation with monochromatic light with a wavelength of 313 nm (in the region of the maximum absorption of fragment A) increases by a factor of approximately three as compared with the luminescence of the individual compound. The substantial increase in the intensity of the fluorescence of I in mix compositions with 4-aminonaphthalic acid phenylimide and the simultaneous quenching of the fluorescence of the phenylimide (Fig. 1) indicate that effective intermolecular transfer of the electronic excitation energy is realized in these systems; fluorophore A acts as the primary donor, and the phenylimide is simultaneously the acceptor of this energy and a secondary donor with respect to fluorophore B. This serves as an additional confirmation of the fact that the molecules of the synthesized compounds consist of two "quasi-autonomous" fragments — the diaryloxazole and xanthene fragments. It should be noted that when Ib, c are introduced into mix compositions with 4-aminonaphthalic acid phenylimide, the increase in the intensity of the fluorescence is considerably smaller than in the case of the mixture of the phenylimide with Ia, in the molecules of which intramolecular transfer of the electronic excitation energy between fluorophores A and B is absent.

The introduction of Ia-c into the MTSF polymer leads to the production of bright purple DFP and enamel paints from them (brightness B = 49, 53, 52; color purity P = 41, 38, 42; color tone $\lambda' = 496', 494', 494'$, respectively).

EXPERIMENTAL

The absorption spectra of alcohol solutions were recorded with an SF-4 spectrophotometer. The luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, an FEU-49 optical emission detector, and an M-95 microammeter. Photoluminescence was excited with an SVDSH-500 lamp, from the spectrum of which the light with a wavelength of 365 nm was isolated by means of a DMR-4 quartz monochromator.

TABLE 3. Aryloxazolyl-Substituted Rhodamine C Derivatives (Ia-c)

Compound	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
		Cl	N		Cl	N	
Ia	192—194	5,8	6,4	C ₃₇ H ₃₆ ClN ₃ O ₄	5,6	6,8	47
Ib	195—197	5,4	6,6	C ₃₈ H ₃₈ ClN ₃ O ₅	5,4	6,4	52
Ic	208—210	5,0	6,3	C ₄₁ H ₃₈ ClN ₃ O ₄	5,3	6,3	58

Aryloxazolyl-Substituted Rhodamine C Derivatives (Ia-c). A thoroughly ground (in a porcelain mortar) mixture of 0.01 mole of 4-(5-aryloxazol-2-yl)phthalic anhydride and m-diethylaminophenol (0.02 mole) was placed in a porcelain crucible, and the latter was heated gradually in a Wood's alloy bath to 180°C. The mixture was maintained at this temperature for 45-60 min, after which it was cooled. The resulting dark-claret-colored melt was triturated in a mortar and dissolved in 2% sodium carbonate solution (at 40-60°C), and the solution was acidified with hydrochloric acid. The precipitate was removed by filtration, washed with water, and dissolved in acetone. The acetone solution was chromatographed with a continuous-action column filled with aluminum oxide. The solvent was evaporated, and the residue was treated with a 5% solution of hydrochloric acid. The precipitate was removed by filtration, washed with distilled water until the wash filtrate was neutral with respect to litmus, and dried.

The characteristics of the substances obtained are presented in Table 3.

Daytime Fluorescent Pigments. These pigments were obtained by the method in [10]. A mixture consisting of p-toluenesulfonamide, melamine, a luminophore, disubstituted sodium phosphate, and formalin (40%) was heated on an oil bath while slowly raising the temperature at 125-130°, after which it was maintained at this temperature for 1-1.5 h and then under vacuum (~133.322 hPa) for 1 h. The mixture was then cooled to 20°C without switching off the vacuum, and the pigment in the form of a porous mass was ground to a fine powder and sifted through a screen with a particle size of 50-60 μ. The softening temperature of the pigments ranged from 115 to 130°C.

For all of the pigments 0.26 mole of melamine, 4 moles of formalin, 0.002 mole of disubstituted sodium phosphate, and the optimal experimentally selected amounts of the luminophores — 3·10⁻³ mole of the aryloxazolyl-substituted rhodamine C derivatives and 3·10⁻³ mole of 4-aminonaphthalic acid phenylimide — were used per mole of p-toluenesulfonamide.

Daytime Fluorescent Enamels. These enamels were obtained in the form of fine suspensions of the corresponding pigments in SVM-31 lac [11]. The pigment:lac weight ratio was 1:5. For the colorimetric measurements the enamel paints were applied in three layers to Whatman drawing paper that had been previously coated with two layers of AS-599 white enamel. The colorimetric characteristics of the paints obtained were determined by analogy with ordinary paints [12].

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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 2,5-DIARYLOXAZOLES
THAT CONTAIN A DIFLUOROMETHYLSULFONYL GROUP

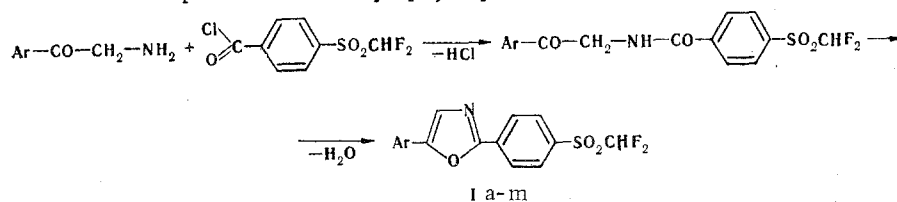
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A number of 2-(4-difluoromethylsulfonylphenyl)-5-aryloxazoles were synthesized by condensation of 4-difluoromethylsulfonylbenzoyl chloride with ω -aminomethyl aryl ketones and subsequent cyclodehydration of the resulting amides in sulfuric acid. The spectral-luminescence properties of these products were investigated. The introduction of a difluoromethylsulfonyl group in the 2-phenyl ring of 2,5-diphenyloxazole leads to significant bathochromic and bathofluoric effects and an increase in the quantum yields and photostabilities of the compounds obtained. Complication of the structure of the 5-phenyl ring is accompanied by a further long-wave shift of the absorption and fluorescence spectra without substantial changes in the fluorescence quantum yields. A positive solvatochromism effect is displayed distinctly in the fluorescence spectra of the compounds obtained on passing to polar solvents; this effect increases markedly as the polarity of the solvent increases.

Continuing our study of the effect of electron-acceptor substituents on the spectral-luminescence properties of 2,5-diaryloxazoles [1, 2], we synthesized and investigated compounds that contain a difluoromethylsulfonyl group in one of the aromatic rings (I).

The strong electron-acceptor effect of the SO_2CHF_2 group was established by one of us in an investigation of the chromaticity of organic compounds of various classes [3, 4]; in a number of cases the introduction of this grouping in organic dye molecules led to a substantial increase in their photostability [3, 5].



1a Ar=C₆H₅; b C₆H₅-C₆H₄; c 1-C₁₀H₇; d 2-C₁₀H₇; e 4-CH₃-C₆H₄; f 2,4,5-(CH₃)₃-C₆H₂;
g 4-CH₃O-C₆H₄; h 4-NH₂-C₆H₄; i 4-(CH₃)₂N-C₆H₄; j 4-CH₃COHN-C₆H₄; k 4-Cl-C₆H₄;
l 4-Br-C₆H₄; m 4-NO₂-C₆H₄

The introduction of a difluoromethylsulfonyl group in the 2-phenyl ring of 2,5-diphenyloxazole (II) leads to substantial bathochromic and bathofluoric effects with a simultaneous increase in the fluorescence quantum yield (for example, compare II and Ia in Table 1).

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