aqueous mixture was neutralized with Na_2CO_3. The precipitate was removed by filtration and crystallized from ethanol to give IIIa-e.

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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF HETARYLETHYLENE DERIVATIVES OF 2,5-DIPHENYLOXAZOLE AND 2,5-DIPHENYL-1,3,4-OXADIAZOLE

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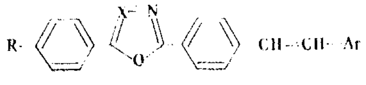
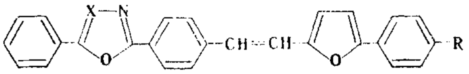
A number of new organic luminophores was synthesized by PO olefination from 2-(4'-bromomethylphenyl)-5-phenyloxazole and -1,3,4-oxadiazole and various heterocyclic aldehydes that contain a furan ring. The absorption and fluorescence spectra of the products in toluene, as well as their scintillation characteristics, were measured. The effect of the electronic nature of the substituents on the spectral-luminescence properties of the luminophores is discussed.

The synthesis of organic luminophores with various structures among arylethylene derivatives of 2,5-diphenyloxazole and 2,5-diphenyl-1,3,4-oxadiazole (I) has demonstrated the possibility of the preparation of intensely luminescing substances that have found the most diverse application [1-5].



I

The present communication is devoted to the synthesis and investigation of the fluorescence and scintillation properties of hetarylethylene derivatives of 2,5-diphenyloxazole and 2,5-diphenyloxadiazole (II, III) that have more complex structures and contain a furan ring.



II, III

II X=CH; III X=N

The synthesis of II and III was accomplished by PO olefination, which usually leads to the trans isomers [6]. The starting compounds were 2-(4'-bromomethylphenyl)-5-phenyloxazole or -1,3,4-oxadiazole and the corresponding substituted 5-arylfurfural.

The structures of the compounds obtained were confirmed by data from the IR spectra, in which out-of-plane deformation vibrations of the hydrogen atoms of the trans-vinylene group at 955-970 cm^{-1} and the characteristic frequencies of the furan ring appear.

The results of an investigation of the spectral-luminescence properties of the products in toluene are presented in Tables 1 and 2.

All-Union Scientific-Research Institute of Single Crystals, Scintillation Materials, and Ultrapure Chemical Substances, Kharkov 310141. A. M. Gor'kii Kharkov State University, Karkov 310077. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 617-621, May, 1982. Original article submitted September 23, 1981.

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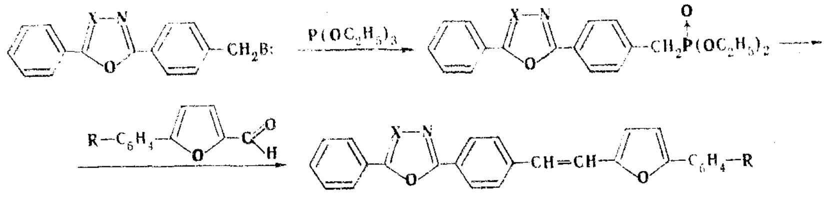
TABLE 1. Spectral Characteristics of Aryl- and Hetarylethylene Derivatives of 2,5-Diphenyloxazole and 2,5-Diphenyl-1,3,4-oxadiazole

Compound	Absorption	
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$
Ia	355	6,34
Ib	368	7,11
Ic	340	4,98
Id	355	7,53
IIa	395	6,40
IIIa	395	5,92

TABLE 2. Spectral-Luminescence Characteristics of IIa-*l* and IIIa-*l*

Compound	Absorption λ_{max} nm ($\varepsilon \cdot 10^{-4}$)	Fluorescence λ_{max}, nm (η)	Compound	Absorption λ_{max} nm ($\varepsilon \cdot 10^{-4}$)	Fluorescence λ_{max}, nm (η)
IIa	395 (6,40)	460 (0,54)	IIIa	395 (5,92)	455 (0,31)
IIb	395 (7,38)	463 (0,63)	IIIb	390 (6,84)	460 (0,51)
IIc	395 (6,00)	460 (0,57)	IIIc	395 (6,30)	450 (0,32)
IId	393 (5,50)	460 (0,77)	IIId	395 (6,75)	460 (0,52)
IIe	420 (5,64)	468 (0,66)	IIIe	390 (4,97)	460 (0,41)
IIf	418 (7,00)	455 (0,48)	IIIf	385 (5,12)	455 (0,27)
IIg	425 (4,30)	465 (0,60)	IIIg	415 (4,02)	455 (0,41)
IIh	400 (2,80), 460 (4,70)	530 (0,50)	IIIh	417 (4,02)	520 (0,39)
IIi	425 (5,10)	—[a]	IIIi	385 (5,62)	—[b]
IIj	398 (3,12)	—[a]	IIIj	373 (3,72)	—[b]
IIk	398 (5,40)	465 (0,63)	IIIk	393 (4,15)	465 (0,38)
II*l*	430 (6,10)	475 (0,66)	III*l*	425 (5,41)	450 (0,44)

[a] Does not luminesce. [b] Weak yellow luminescence.



II, III

IIa–*l* X=CH; IIIa–*l* X=N; II, III a R=H; b R=4-Cl; c R=2-Cl; d R=2,4-di-Cl; e R=4-Br; f R=2-Br; g R=4-I; h R=4-NO_2; i R=3-NO_2; j R=2-NO_2; k R=4-CH_3; *l* R=C_6H_5

Two bands with markedly different intensities, viz., a short-wave low-intensity band with a maximum at 300-320 nm (ε = 15000-20000 liters·mole^{-1}·cm^{-1}) and an intense long-wave K band, which is responsible for fluorescence and is most sensitive to various changes in the phenylfuryl grouping, are generally observed in the absorption spectra. The interpretation of the short-wave band in the absorption spectra of II and III is difficult because of the possibility of superimposition of several electron transitions localized in the arylazole and furylethylene fragments. We will subsequently therefore consider only the long-wave K band.

Lengthening of the conjugation chain by introduction of a furan ring in the conjugation chain of the simplest I significantly changes the character of the absorption spectra and is accompanied by a substantial bathochromic shift of the long-wave band (Table 1). The indicated effects are undoubtedly associated with enlargement of the π system of IIa and IIIa as compared with Ia. At the same time, a comparison of the spectral characteristics of IIa and its π-isoelectronic analog Ib shows that replacement of the benzene ring by a furan ring also gives rise to a significant bathochromic effect ($\Delta\lambda$ = 27 nm). This long-wave shift is not only a consequence of enlargement of the π system but is also associated with the electron-acceptor character of the furan ring, which was previously noted during a study of the spectral-luminescence properties of 1-phenyl-Δ^2-pyrazolines that contain furyl groups in the 3 and 5 positions of the pyrazoline ring [7].

TABLE 3. Characteristics of the Synthesized Compounds

Compound	mp, °C	Empirical formula	N, %		Yield,[a] %
			found	calc.	
IIc	159—160	$C_{27}H_{18}ClNO_2$	8,4[b]	8,4[b]	24
IId	162—163	$C_{27}H_{18}ClNO_2$	15,8[b]	15,5[b]	40
IIf	159—161	$C_{27}H_{18}BrNO_2$	17,3[c]	17,1[c]	26
IIi	180—181	$C_{27}H_{18}N_2O_4$	6,8	6,5	61
IIj	214—215	$C_{27}H_{18}N_2O_4$	6,4	6,4	47
IIIa	198—199	$C_{26}H_{18}N_2O_2$	3,8	3,6	45
IIIb	204—205	$C_{26}H_{17}ClN_2O_2$	8,5[b]	8,4[b]	51
IIId	166—167	$C_{26}H_{16}Cl_2N_2O_2$	15,2[b]	15,5[b]	54
IIIe	220—221	$C_{26}H_{17}BrN_2O_2$	17,4[c]	17,1[c]	47
IIIf	161—162	$C_{26}H_{17}BrN_2O_2$	16,9[c]	17,1[c]	39
IIIh	250—251	$C_{26}H_{17}N_3O_4$	9,5	9,6	41
IIIi	220—221	$C_{26}H_{17}N_3O_4$	9,3	9,6	55
IIIj	176—177	$C_{26}H_{17}N_3O_4$	9,9	9,7	22
IIIk	187—189	$C_{27}H_{20}N_2O_2$	7,0	6,9	36

[a] The yields of the chromatographically pure products are presented.
[b] Analysis for the Cl content. [c] Analysis for the Br content.

The introduction of a chlorine atom in the phenyl ring bonded to the furan ring (Table 2, IIb and IIIb) has virtually no effect on the position of the absorption bands. Transition from chloro- to bromo- and then to iodo-substituted compounds is accompanied by a significant bathochromic shift. The absorption spectra of the isomeric o- and p-halo-substituted compounds (IIb,c,e,f and IIIb,c,e,f) are almost identical.

It has been shown [8] that the long-wave absorption band in the spectrum of Ia corresponds primarily to localization of the electronic excitation during the $S_0 \rightarrow S^*_1$ transition in the arylazolylethylene fragment and is the result of superimposition of electron shifts that proceed in two directions, viz., from the phenylazole grouping and from the phenylfuryl grouping that contains the substituent to the ethylene bridge.

As in the I series, the introduction of a nitro group in the phenylfuryl fragment leads to a significant change in the nature of the long-wave absorption band [8], which becomes a band involving charge transfer from the phenylazole grouping to the nitrophenylfuryl grouping.

The absorption spectra of IIh and IIIh, which contain a nitrophenylfuryl grouping, differ markedly from the spectra of the other compounds with respect to a significant shift of the long-wave band to the red region and a substantial decrease in the intensity. A low-intensity band with an absorption maximum at 400 nm appears in the spectrum of IIh in addition to this band. Whereas the long-wave band of IIh is shifted significantly bathochromically as compared with the corresponding band of IIa ($\Delta\nu = 3550\ \mathrm{cm}^{-1}$), this effect is substantially smaller for IIIh ($\Delta\nu$ as compared with IIIa is only $1350\ \mathrm{cm}^{-1}$).

As compared with the para isomers, the m-nitro derivatives (IIi and IIIi) are characterized by a significant short-wave shift of the absorption band. The o-nitro-substituted isomers also differ from the para isomers (IIh,j and IIIh,j) with respect to the position of the absorption maxima. As in the case of the m-nitro derivatives, the inductive effect of the nitro group is evidently primarily manifested here, since its mesomeric effect may be weakened significantly by steric factors, which remove the nitro group from the plane of the molecule.

Lengthening of the conjugation chain of II*l* and III*l* when the phenyl group is replaced by a biphenyl group gives rise to a long-wave shift (35 and 30 nm, respectively) without changing the character of the absorption band.

Compounds II and III in the crystalline state and in toluene solutions fluoresce intensively when they are irradiated with UV light. The fluorescence spectra are characterized by one band with a distinctly expressed maximum. In contrast to most of the previously investigated arylethylene derivatives of diarylazoles, among which compounds with an oxadiazole ring fluoresce in a shorter-wave region than their oxazole analogs [8], this difference in the fluorescence spectra is almost absent in the case of II and III, except for III, which contains a biphenylyl group. However, the oxadiazole derivatives have considerable lower luminescence quantum yields than their oxazole analogs.

A study of the fluorescence of the isomeric compounds shows that the position of the chlorine atom in the phenyl ring has virtually no effect on either the character of the fluorescence bands or the quantum yield. A hypsofloric effect, which is accompanied by a decrease in the fluorescence intensity, is observed for the ortho isomer when one compares the isomeric o- and p-bromo-substituted compounds. Only weak yellow luminescence is observed for o- and m-nitro-substituted IIi,j and IIIi,j in the case of irradiation with UV light, while the quantum yields of the para isomer are close to the quantum yields of the unsubstituted compounds.

Arylethylene derivatives of 2,5-diaryloxazoles and 2,5-diaryloxadiazoles are used in scintillation technique as activating additives and spectra shifters in liquid scintillators (LS) [2,3].

We investigated II as spectra shifters (0.1 g/liter) in LS; the advantage of II is the longer-wave fluorescence, which lies in the region of greater sensitivity of the photomultipliers used than in the case of the well-known spectra shifter 1,4-bis(5-phenyl-2-oxazolyl)-benzene (POPOP). As the activator (2 g/liter) we used 1-(5-phenyl-2-oxazolyl)-4[5-(4-chlorophenyl)-2-oxazolyl]benzene (IV), the fluorescence spectrum of which (λ_{max} 435 nm) overlaps considerably with the absorption spectrum of II. The scintillation effectiveness of the LS was measured from the change in the photocurrent of an FÉU-13 detector with ^{137}Cs as the source of γ-excitation. A solution of a mixture of p-terphenyl (4 g/liter) with POPOP (0.1 g/liter) in toluene, which is usually employed for this purpose, was used as the standard scintillator.

In order to select the most suitable solvent (base) we investigated the scintillation efficiency of a mixture of IIa and IV in the indicated ratios in various hydrocarbons that are usually employed as LS bases, viz., toluene, p-xylene, α-methylnaphthalene, dicumylmethane, pseudocumene, and isopropylbiphenyl. The highest scintillation efficiency (114%) was obtained when α-methylnaphthalene was used. Mixtures of IV and IIa,b,d,k,*l* have the same scintillation effectiveness.

The compounds that we obtained can be used as spectra shifters in the preparation of LS with longer-wave fluorescence than in the case of POPOP.

EXPERIMENTAL

The absorption spectra of toluene solutions (c $5 \cdot 10^{-5}$ M) of the compounds were measured with a Specord spectrophotometer. The fluorescence spectra were measured with an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical emission detector, and an M-95 microammeter. Photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with a wavelength of 365 nm was isolated with a DMR-4 quartz monochromator. The IR spectra were measured with a UR-20M spectrophotometer.

Hetarylethylene derivatives of 2,5-diphenyloxazole and -1,3,4-oxadiazole were obtained by the method in [9] and were purified by chromatography on aluminum oxide in benzene with subsequent recrystallization from benzene. The results of analysis, the melting points, and the yields of the synthesized substances are presented in Table 3.

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ACYLATION OF 2H,6H-2,6-DIMETHYL-4-AMINO-1,3,5-DITHIAZINE AND TAUTOMERISM OF THE REACTION PRODUCTS

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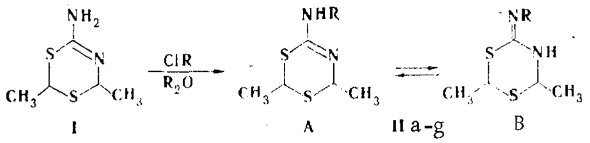
The acylation of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine with the chlorides and anhydrides of saturated carboxylic and sulfonic acids leads to N-monoacyl derivatives of dithiazine in 85-96% yields. It was established by IR and UV spectroscopy that 2H,6H-2,6-dimethyl-4-acylamino-1,3,5-dithiazines with donor substituents exist primarily in the amino form and that the equilibrium is shifted to favor the imino form for compounds with acceptor substituents to a greater degree in solutions than in the crystalline state.

The present communication, which is devoted to the synthesis and study of the tautomerism of N-acyl derivatives of 2H,6H-2,6-dimethyl-4-amino-1,3,5-dithiazine (I) by IR and UV spectroscopy, is a continuation of research on the physicochemical properties of this compound, which was obtained from divinyl sulfide and thiourea [1], and is directed to the search for new potentially biologically active compounds [2].

The action of chlorides and anhydrides of saturated carboxylic acids on dithiazine I gives N-monoacyl derivatives IIa-g in 85-96% yields, which can exist in tautomeric forms A or B:



IIa $R=COCH_3$; b $R=COCH_2Cl$; c $R=COC_3H_7$-*n*; d $R=COC_4H_9$-*n*; e $R=COC_4H_9$-*t*;
f $R=COC_6H_5$; g $R=SO_2C_6H_4CH_3$-4

The reaction of dithiazine I with acid chlorides is realized in chloroform or benzene, and the HCl is tied up by excess dithiazine I or Na_2CO_3. Acylation with excess amounts of carboxylic acid anhydrides proceeds readily and quantitatively. The formation of diacylation products is not observed either under severe conditions or in the presence of catalytic amounts of H_2SO_4. The use of pyridine as the solvent [3] lowers the yield of acylated product IIg, which can be explained by the instability of dithiazine I to the action of amines [4].

The reaction of acrylyl chloride with dithiazine I gives, instead of the expected monoacyl derivative, polymeric products, which are isolated in the form of powders that are soluble in acetone and dimethyl sulfoxide (DMSO) and have molecular masses of 900 to 2100.

The PMR spectrum of these powders in d_6-DMSO contains a number of broad peaks that are characteristic for polymeric products. Signals of the protons of the methyl groups are ob-

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