HETARYLETHYLENE DERIVATIVES OF 2,5-DIPHENYLOXAZOLE

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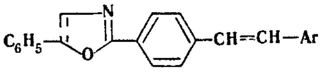
A number of new effective luminophores were synthesized by PO olefination from 2-(4-bromomethylphenyl)-5-phenyloxazole and various heterocyclic aldehydes containing a furan ring. All of the compounds obtained have intense fluorescence in toluene and, depending on the nature of the substituents, the color of the luminescence changes from blue to green. It is shown that chloro, bromo, and methyl substituents have little effect on the spectral-luminescence properties of the compounds obtained, whereas a nitro group causes a decrease in the fluorescence quantum yield.

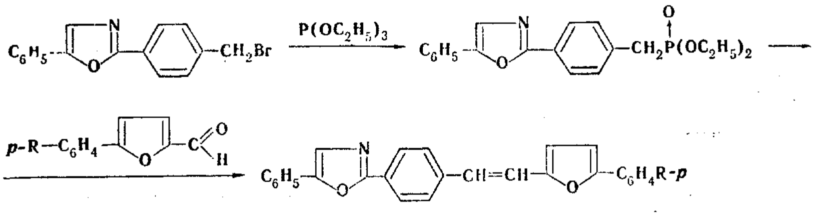
Arylethylene derivatives of 2,5-diphenyloxazole (I) are included among the effective organic luminophores used as activators [1] and shifters of the spectra [2] of liquid scintillators, active media for lasers [3], and in "cascade" compositions in daylight fluorescent pigments and dyes [4].



I

The subject of the present communication is the synthesis of hetarylethylene derivatives of 2,5-diphenyloxazole that contain a furan ring (II) and investigation of their spectral luminescence properties.

The trans isomers were synthesized by PO olefination; the starting compounds were 2-(4-bromomethylphenyl)-5-phenyloxazole and the corresponding substituted 5-arylfurfural.



II

R = H, CH_3, C_6H_5, Cl, Br, NO_2

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

An intense K band, which is responsible for the fluorescence and is most sensitive to the effect of the substituents in the phenylfuryl grouping, is clearly seen in the UV absorption spectra of toluene solutions of II.

Lengthening the conjugation chain by introduction of a furan ring in the simplest of the compounds I (Ar = C_6H_5) changes the character of the K band significantly (as evidenced by the appearance of a vibrational structure) and shifts it 40 nm to the red region (Table 1).

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 considerable

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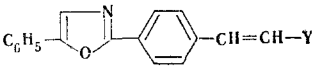
TABLE 1. Spectral Characteristics of Arylethylene and Hetarylethylene Derivatives of 2,5-Diphenyloxazole



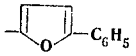
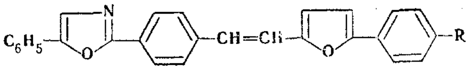
Compound	Y	Absorption	
		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$
Ia	C_6H_5	355	6,40
IIa		395	6,34
Ib	p-C_6H_4—C_6H_5	368	7,11
III	$CH{=}CH$—$CH{=}CH$—C_6H_5	380	6,20

TABLE 2. Spectral Characteristics of Hetarylethylene Derivatives of 2,5-Diphenyloxazole



Compound	R	Absorption		Luminescence	
		λ_{max}, nm	$\varepsilon \cdot 10^{4}$	λ_{max}, nm	B_{rel}
IIa	H	395	6,40	460	1,00
IIb	CH_3	398	5,40	465	1,22
IIc	Cl	395	7,38	463	1,10
IId	Br	420	5,64	468	1,00
IIe	I	425	4,30	Does not fluoresce	
IIf	NO_2	400	2,80		
		460	4,70	525	0,68
IIg	C_6H_5	430	6,10	475	1,20

bathochromic shift ($\Delta\lambda$ = 27 nm), which is associated not only with lengthening of the conjugation chain (compare Ib and III) but also with the aromatic properties of the furyl group and its electron-acceptor character. Similar properties of the furan ring have also been noted previously during an investigation of 1-phenyl-Δ^2-pyrazolines containing furyl groups in the 3 and 5 positions [5].

Methyl and chloro substituents have little effect on the position of the maximum and the character of the absorption curves; replacement of chlorine by bromine and iodine leads to a rather significant red shift of the K band and to a decrease in the intensity of the absorption (Table 2). This can evidently be ascribed to the increased electron-acceptor effect in the order 4-chlorophenyl < 4-bromophenyl < 4-iodophenyl and to an increase in this order of the polarizabilities of the groups. A similar effect is also observed in the case of the nitro derivative, and splitting of the K band takes place. In all likelihood, the long-wave absorption band in the case of the nitro derivative and in the case of the nitrophenylethylene derivative of 2,5-diphenyloxazole [6] is a charge-transfer band (CTC) with charge transfer from the phenyloxazole fragment of the molecule to the nitro group.

Further lengthening of the conjugation chain by replacement of the phenyl group by a diphenylyl group (compare IIa and IIg) does not change the character of the absorption band but gives rise to a long-wave shift of 35 nm, which is considerably larger than the value observed on passing from Ia to Ib (see Table 1).

One should note the high intensity of the absorption of all of the compounds obtained.

Toluene solutions of the hetarylethylene derivatives of 2,5-diphenyloxazole fluoresce intensely when they are irradiated with UV light (365 nm), and the fluorescence spectra are characterized by one band with a distinctly expressed maximum. Depending on the structures of II, the position of the maxima of the emission of their toluene solutions ranges from 460 to 525 nm, and the Stokesian shifts have relatively small values (1900-3700 cm^{-1}).

The methyl group and chlorine and bromine atoms do not change the fluorescence maxima, but the relative quantum yields of IIb and IIc are increased somewhat as compared with the yield of IIa (Table 2).

TABLE 3. Characteristics of the Synthesized Compounds

Compound	mp, °C	Empirical formula	N, %		Yield, %
			found	calc.	
IIa	184—185	$C_{27}H_{19}NO_2$	3,7	3,6	10
IIb	202—203	$C_{28}H_{21}NO_2$	3,4	3,5	25
IIc	201—202	$C_{27}H_{18}NO_2Cl$	8,3*	8,4*	17
IId	209—210	$C_{27}H_{18}NO_2Br$	19,2*	19,2*	21
IIe	219—220	$C_{27}H_{18}NO_2I$	2,8	2,7	12
IIf	214—215	$C_{27}H_{18}N_2O_4$	6,4	6,4	47
IIg	221—222	$C_{33}H_{23}NO_2$	2,8	3,0	27

*Analysis for the halogen content.

The nitro group, which in most cases has a quenching effect, gives rise to a decrease in the quantum fluorescence yield (compare IIa and IIf).

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds ($5 \cdot 10^{-5}$ M) were recorded with a Specord spectrophotometer. The fluorescence spectra were recorded 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 recorded with a UR-20M spectrometer.

Hetarylethylene Derivatives of 2,5-Diphenyloxazole. A mixture of 0.01 mole of 2-(4-bromomethylphenyl)-5-phenyloxazole and triethyl phosphite in 20 ml of xylene was refluxed on an oil bath for 4-5 h, after which the xylene was removed by distillation, and the phosphonate, which was formed in almost quantitative yield, was dissolved in 30 ml of dimethylformamide. An 0.01-mole sample of the corresponding aldehyde and a solution of sodium methoxide (0.23 g of sodium metal in 2-3 ml of methanol) were added, and the mixture was allowed to stand at room temperature for 3 h. The resulting precipitate was separated, dried, and purified by chromatography of a benzene solution on aluminum oxide with subsequent recrystallization from benzene. The results of analysis and the melting points of the synthesized compounds are presented in Table 3.

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