2-(4-CYANOPHENYL)-5-ARYLOXAZOLES

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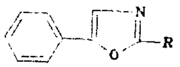
2-(4-Cyanophenyl)-5-aryloxazoles have been obtained by dyhydration of 4-(5-aryloxazolyl-2)benzamides with thionyl chloride in DMFA, then the spectral and luminescent properties of the former have been investigated. Introduction of the cyano group into the 2-phenyl radical of 2,5-diphenyloxazole leads to significant bathochromic and bathofluoric effects.

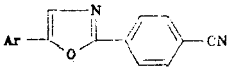
The bathochromic and bathofluoric effects, in several cases an enhancement of the quantum yield of luminescence, and the resistance of 2,5-diaryloxazoles toward UV irradiation during introduction of electron-withdrawing substituents in their aromatic rings [1, 2] are the factors which set the basis for synthesis of 2-(4-cyanophenyl)-5-aryloxazoles (I) (Table 1) and studies on application thereof as organic luminophores.

The previously synthesized amides of the corresponding 4-(5-aryloxazolyl-2)benzoic acids [3] served as the intermediates in preparation of I by reaction with thionyl chloride in DMFA.

Introduction of the cyano group in the para-position of the 2-phenyl radical in 2,5-diphenyloxazole (IIa) leads to significant bathochromic and bathofluoric effects. All the synthesized compounds intensively radiate light in toluene solutions in the blue-green region of the spectrum with the quantum yield (η) of 0.45-0.60 (Table 2).



IIa-g



Ia-f

I a $Ar=C_6H_5$, b $Ar=4\text{-}CH_3—C_6H_4$, c $Ar=4\text{-}Cl—C_6H_4$, d $Ar=4\text{-}CH_3O—C_6H_4$, e $Ar=4\text{-}C_6H_5—C_6H_4$, f $Ar=1\text{-}C_{10}H_7$; II a $R=C_6H_5$, b $R=4\text{-}HOOC—C_6H_4$, c $R=4\text{-}H_3COOC—C_6H_4$, d $R=4\text{-}ClOC—C_6H_4$, e $R=4\text{-}H_2NOC—C_6H_4$, f $R=4\text{-}F_2HCO_2S—C_6H_4$, g $R=C_6H_3—(CO)_2O$

Compounds Ib, c, containing a methyl group or chlorine in the 5-phenyl radical, practically do not differ in their spectral and luminescent properties from the unsubstituted 2-(4-cyanophenyl)-5-phenyloxazole (Ia). On introduction into the 5-phenyl radical of an electron-releasing substituent, the methoxy group (Id), interacting with the cyano group along the conjugated chain, we observed a significant long-wave shift of the absorption and luminescence maxima. The same effect takes place when the structure of the 5-aryl fragment becomes more complex; the phenyl radical is replaced by the 4-biphenylyl (Ie). The absorption maximum of the compound with a 1-naphthyl radical (If), having in the ground state less planar structure than in the excited state, is, as a rule, shifted toward shorter wavelengths, as compared with the compound containing a 4-biphenylyl radical. According to the location of their luminescence maxima, these compounds are similar.

Comparison of the spectral and luminescent properties of compound Ia with those of the previously studied 2,5-diaryloxazoles, containing other electron-withdrawing substituents (IIb-f) in the para-position of the 2-phenyl ring, shows that the cyano group, according to the induced by itself bathochromic and bathofluoric effects, is close to the carboxyl,

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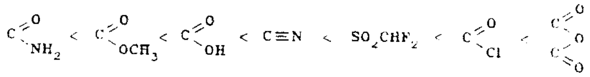
TABLE 1. 2-(4-Cyanophenyl)-5-aryloxazoles Ia-f

Compound	MP, ℃	Found N, %	Empirical formula	Calc. N, %	Yield, %
Ia	179—180	11,2	$C_{16}H_{10}N_2O$	11,4	88
Ib	185—186	10,6	$C_{17}H_{12}N_2O$	10,8	96
Ic	249—250	10,1	$C_{16}H_9ClN_2O$	10,0	91
Id	164—165	10,0	$C_{17}H_{12}N_2O_2$	10,1	90
Ie	229—230	8,9	$C_{22}H_{14}N_2O$	8,7	88
If	145—146	9,4	$C_{20}H_{12}N_2O$	9,5	83

TABLE 2. Spectral and Luminescent Properties of Compounds I and II in Toluene

Compound	Absorption		Luminescence		Compound	Absorption		Luminescence	
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	η		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm	η
Ia	337	3,50	395	0,62	IIa	307	2,58	365	0,51
Ib	339	2,17	405	0,51	IIb	335	4,75	400	0,58
Ic	337	2,49	395	0,51	IIc	335	3,15	395	0,56
Id	350	2,43	425	0,48	IId	354	2,25	430	0,54
Ie	346	2,71	420	0,42	IIe	327	3,33	395	0,55
If	340	1,90	425	0,43	IIf	340	2,74	405	0,78
					IIg	364	1,87	455	0,61

carbomethoxy, and difluoromethylsulfonyl groups. Taking into consideration the effect of electron-withdrawing substituents on the spectral and luminescent properties of 2,5-diaryloxazoles they can be arranged in the following order:



$$C(=O)NH_2 < C(=O)OCH_3 < C(=O)OH < C{\equiv}N < SO_2CHF_2 < C(=O)Cl < C(=O)OC(=O)$$

EXPERIMENTAL

The absorption spectra of the toluene solutions were measured on a Hitachi-330 spectrophotometer (c $1 \cdot 10^{-4}$); the luminescence spectra were taken on a system consisting on a ZMR-3 monochromator, an FEU-18 receiver of optical radiation, and an M-95 microammeter. The photoluminescence was induced by an SVDSh-500 lamp, from the spectrum of which light with the wavelength of 365 nm was isolated using a DMR-4 monochromator. The absolute quantum yields of luminescence were determined by the equal absorption method [4].

2-(4-Cyanophenyl)-5-aryloxazoles (Ia-f). To a solution of 0.1 mmole of 2-(4-carbamidophenyl)-5-aryloxazole [3] in 100 ml of DMFA at 0°C was added dropwise, with vigorous stirring, 5 ml of thionyl chloride, maintaining temperature below 3°C. The reaction mixture was stirred at this temperature for 1 h and then for 3 h at 60°C. The obtained solution was poured on ice and the precipitate was filtered, washed with water, and dried (Table 2).

The compounds were purified by chromatography of their hexane (for Ia, b, f) or heptane (Ic-e) solutions on Silochrom S-120 in a continuous action column.

LITERATURE CITED

1. B. M. Krasovitskii and V. M. Shershukov, Khim. Geterotsikl. Soedin., No. 1, 35 (1979).
2. B. M. Krasovitskii, V. M. Shershukov, and L. M. Yagupol'skii, Khim. Geterotsikl. Soed., No. 8, 1042 (1982).
3. B. M. Krasovitskii, V. M. Shershukov, and V. L. Volkov, Khim. Geterotsikl. Soed., No. 9, 1261 (1986).
4. A. S. Cherkasov, Zh. Fiz. Khim., 29, 2209 (1955).