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4-(5-ARYL-2-OXAZOLYL)PHTHALIC ANHYDRIDES

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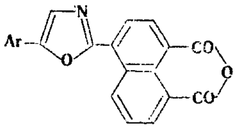
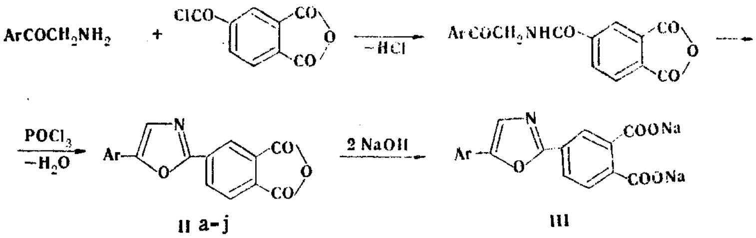
4-(5-Aryl-2-oxazolyl)-substituted phthalic anhydrides were synthesized from 4-chloroformylphthalic anhydride and various ω-aminomethyl aryl ketones. The spectral-luminescence properties of solutions of the products in toluene and 5% NaOH solution were investigated. It is shown that the introduction of substituents with different electronic natures in the 5-phenyl ring of 4-(5-phenyl-2-oxazolyl)phthalic anhydride has a significant effect on the spectral-luminescence characteristics of the synthesized compounds.

We have previously described [1-3] 4-(5-aryl-2-oxazolyl)-substituted naphthalic anhydrides (I), which are effective organic luminophores that are used in the preparation of daytime fluorescent pigments and dyes [4].



I

The present communication is devoted to the synthesis and study of the spectral-luminescence properties of analogous compounds that contain a phthalic anhydride grouping (II). The synthesis was accomplished via the following scheme, which includes the Robinson–Gabriel reaction:



In view of the high reactivities of both the anhydride and chloroformyl groups of 4-chloroformylphthalic anhydride it readily reacts with two molecules of amine. To prevent reaction at the anhydride grouping we carried out the condensation in a water–benzene medium

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TABLE 1. Spectral Characteristics of 4-(5-Aryl-2-oxazolyl)-phthalic Anhydrides (IIa-j) in Toluene

Compound	Ar	Absorption		Luminescence	
		λ_{max}, nm	$\varepsilon \cdot 10^{-3}$	λ_{max}, nm	η
Ia	C_6H_5	295, 398	10,6, 22,0	480	0,23
IIa	C_6H_5	364	15,7	455	0,61
IIb	p-$C_6H_5C_6H_4$	375	29,5	465	0,60
IIc	1-$C_{10}H_7$	365	15.3	480	0,45
IId	2-$C_{10}H_7$	380	25,5	465	0.50
IIe	4-ClC_6H_4	365	19,4	455	0,58
IIf	4-$NO_2C_6H_4$	365	—*	Does not luminesce	
IIg	4-$CH_3C_6H_4$	370	22,1	460	0.60
IIh	2,4,5-$(CH_3)_3C_6H_2$	372	14,4	473	0.61
IIi	4-$CH_3OC_6H_4$	380	15,8	485	0,49
IIj	4-$(CH_3)_2NC_6H_4$	330, 425	19,8, 8.2	560, 575	0,24

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*Not measured because of its very low solubility.

TABLE 2. Luminescence of 4-(5-Aryl-2-oxazolyl)phthalic Acid Salts

Compound	Ar	Luminescence in 5% NaOH	
		λ_{max}, nm	η
IIIa	C_6H_5	405	0,36
IIIb	4-$C_6H_5C_6H_4$	430	0,47
IIIe	4-ClC_6H_4	405	0,45
IIIg	4-$CH_3C_6H_4$	415	0,54

TABLE 3. 4-(5-Aryl-2-oxazolyl)phthalic Anhydrides

Compound	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	N		C	H	N	
IIa	203	70,1	3,0	5,0	$C_{17}H_9NO_4$	70.0	3.1	5.1	74
IIb	259	75,0	3.4	4.1	$C_{23}H_{13}NO_4$	75.2	3.5	3,8	76
IIc	232	73,4	3.6	4,0	$C_{21}H_{11}NO_4$	73,9	3,3	4.1	70
IId	241	73,9	3.4	4,2	$C_{21}H_{11}NO_4$	73,9	3,3	4,1	81
IIe	262	62.2	2,6	4,3	$C_{17}H_8ClNO_4$	62.3	2.5	4.3	71
IIf	255	—	—	8.7	$C_{17}H_8N_2O_6$	—	—	8,4	51
IIg	211	70.3	3,6	4.6	$C_{18}H_{11}NO_4$	70,8	3.6	4.6	63
IIh	193	—	—	4,2	$C_{20}H_{15}NO_4$	—	—	4,2	69
IIi	230,5	67,5	3,8	4,0	$C_{18}H_{11}NO_5$	67,3	3,4	4,4	74
IIj	276	—	—	9.6	$C_{19}H_{14}N_2O_4$	—	—	9,4	49

at 0-5°C. The spectral-luminescence characteristics of the synthesized substances and, for comparison, Ia are presented in Table 1.

Compound IIa absorbs and luminesces in a shorter-wave region of the spectrum and has a higher quantum yield than Ia. Lengthening of the conjugation chain in IIa by replacement of the phenyl ring by a 4-diphenylyl or 2-naphthyl grouping is accompanied by bathochromic and bathofluoric effects without an appreciable change in the quantum yield.

The compound with a 1-naphthyl grouping (IIc) is interesting. Because of the relatively small amount of steric hindrance caused by this grouping [5], the absorption maximum of IIc lies in a shorter-wave region than in the case of the isomer with a 2-naphthyl grouping. On passing to the excited state the IIc molecules evidently take on a more planar configuration, and this is reflected in the luminescence spectra. The maximum of the emission band is shifted bathofluorically not only with respect to IIa but also in comparison with IIb and IId.

It is interesting to trace the effect on the spectral-luminescence properties of substituents with different electronic natures in the para position of the phenyl ring of IIa. There is virtually no difference between the chloro derivative (IIe) and IIa. A nitro group in the 4 position of the phenyl ring of IIa does not have an appreciable effect on the position of the long-wave absorption band but quenches the luminescence (IIf).

More significant effects are observed when electron-donor substituents are introduced. Even the methyl group causes a small long-wave shift of the absorption and luminescence maxima. The bathofluoric effect is intensified when three methyl groups (IIh), two of which are included in the conjugation chain, are introduced. The steric hindrance in this compound, which is due to the 2-methyl group, is probably overcome (as in the case of IIc) during excitation of the molecules by UV rays. The bathochromic and bathofluoric effects are manifested to a considerably greater degree under the influence of methoxy and dimethylamino groups. The introduction of a methoxy group led to the production of an effective luminophore with green luminescence. The compound with a dimethylamino group (IIj) luminesces in the orange region of the spectrum. Owing to the donor—acceptor interaction of the dimethylamino group with the phthalanhydride grouping the long-wave band in the absorption spectrum of this compound is of relatively low intensity and is evidently a charge-transfer band (CTC). The large Stokesian shift in the case of IIj is in all likelihood associated with rearrangement of its molecules when they pass into the excited state.

However, it should be noted that this sort of analogy in the quantum yields of these compounds is not observed vis-à-vis the analogy in the effect of the structural changes in the I and II molecules on the position of the absorption and luminescence maxima. Whereas the quantum yield of IIj, which contains a dimethylamino group, is lower by a factor of almost three than in the case of the unsubstituted compound (0.24 and 0.61, respectively), the reverse of this dependence has been noted in a number of naphthalic anhydride derivatives (0.75 and 0.23). The methoxy-substituted derivatives in both series occupy intermediate positions and have close quantum yields.

Being derivatives of phthalic anhydride, II dissolve in aqueous alkali solutions to give salts (III), which luminesce with rather high quantum yields in a shorter-wave region than the anhydrides (Table 2) and can serve as water-soluble luminophores.

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds were recorded with an SF-4 spectrophotometer, and the luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical emission pickup, 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 isolated by means of a DMR-4 quartz monochromator. The absolute luminescence quantum yields of solutions of the compounds in toluene were determined by the equal absorption method.

4-(5-Aryl-2-oxazolyl)phthalic Anhydrides (IIa-j, Table 3). A 10% solution of sodium carbonate was added dropwise with vigorous stirring at 0-5°C to a mixture of solutions of 0.011 mole of 4-chloroformylphthalic anhydride [7] in 20 ml of benzene and 0.01 mole of the ω-aminomethyl aryl ketone in 50 ml of water until the mixture was alkaline with respect to litmus, after which stirring was continued for 1 h. The mixture was then acidified with hydrochloric acid, and the resulting precipitate was removed by filtration, washed with water, dried, and refluxed in 10 ml of phosphorus oxychloride for 2 h. The resulting solution was poured over ice, and the precipitate was removed by filtration, washed with water, dried, and recrystallized twice from acetic anhydride.

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1,2,4- AND 1,2,5-OXADIAZOLES.

1. POLAROGRAPHIC REDUCTION OF METHYL- AND PHENYLOXADIAZOLES IN ANHYDROUS DIMETHYLFORMAMIDE

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It is shown that the first step in the reduction of the investigated oxadiazoles on a dropping mercury cathode in dimethylformamide corresponds to two-electron cleavage of the N-O bond. The degree of reduction is determined by the nature and position of the substituents in the oxadiazole ring and by the rate of protonation of the intermediately formed particles.

There is no information in the literature regarding the polarographic behavior of oxadiazoles that have an N-O bond; only the polarography of condensed 1,2,5-oxadiazoles (furazans) has been described [1]. In the present research we investigated the reduction of 3,4-dimethyl-1,2,5- (I), 3,4-diphenyl-1,2,5- (II), 3,5-dimethyl-1,2,4- (III), 3,5-diphenyl-1,2,4- (IV), 3-phenyl-5-methyl-1,2,4- (V), and 3-methyl-5-phenyl-1,2,4-oxadiazole (VI) on a dropping mercury cathode in anhydrous dimethylformamide (DMF). From one to three waves are observed on the polarograms of the indicated compounds in a 0.05 M solution of tetrabutylammonium perchlorate (Table 1); in all cases the first wave corresponds to irreversible transfer of two electrons.

Since, from a formal point of view, the 1,2,4-oxadiazole ring includes fragments of oxazole and isoxazole rings, it is expedient to compare the polarographic reduction of the indicated heterocycles. We have previously established that phenylisoxazoles are capable of undergoing polarographic reduction in DMF and that the first step in the reduction is a two-electron process with cleavage of the N-O bond [2].

Oxazoles and 1,3,4-oxadiazoles can be reduced with the consumption of six electrons, i.e., with ring cleavage, or with the consumption of four electrons without ring cleavage [3]. However, the reduction of condensed 1,2,5-oxadiazoles proceeds with cleavage of both N-O bonds, but in DMF the first step is reversible and corresponds to the transfer of one electron with the formation of an anion radical [1].

TABLE 1. Half-Wave Potentials ($E_{1/2}$, V) and Current Diffusion Constants $\left(I = \frac{i_{\lim}}{c \cdot m^{2/3} t^{1/6}}\right)$ of Derivatives of 1,2,4- and 1,2,5-Oxadiazoles in DMF Containing 0.05 M Bu_4NClO_4 as the Base Electrolyte

		I	II	III	IV	V	VI	VII
$-E_{1/2}$, V	1	2,54	2.00	2.94	1.91	2.25	2,00	2,36
	2	2,97	2.53		2.75	2,93	2,92	2,53
	3		2.75					
I	1	4.37	3.46	3,64	3.34	3,95	3,13	1,28
	2	2,43	6.45		2,96	2.60	4.71	2,95
	3		3,34					
Sum of I		6,80	13,25	3,64	6.30	6.55	7,84	4,23

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