ANHYDRIDES AND PHENYLIMIDES OF 4-(5-ARYL-2-OXAZOLYL)NAPHTHALIC ACIDS

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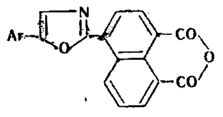
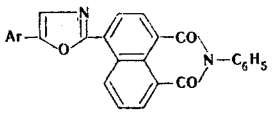
A number of 4-(5-aryl-2-oxazolyl)naphthalic anhydrides were obtained by condensation of 4-chloroformylnaphthalic anhydride with ω-aminomethyl aryl ketones and subsequent cyclization of the resulting amides; N-phenylimides were obtained from the anhydrides by reaction with aniline. The relationship between the structures of the substances obtained and their UV and luminescence spectra was investigated.

In recent years a number of new organic luminophores, viz., arylimides of various substituted naphthalic acids, have been proposed. Among these are compounds with blue luminescence, which are used as optical bleaches [1, 2], and luminophores with longer-wave luminescence, which are used for coloring plastics [3, 4].

We have synthesized anhydrides (I) and phenylimides (II) of 4-(5-aryl-2-oxazolyl)naphthalic acids.



I



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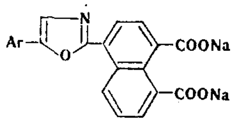
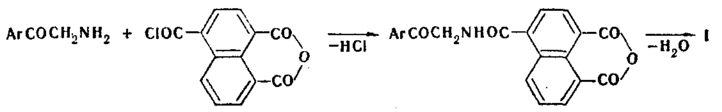


III

These compounds, in addition to a naphthalic anhydride or N-phenylnaphthalimide residue, contain the 2,5-diaryloxazole groupings characteristic for effective luminophores (chiefly of violet and blue luminescence, that are used as activators of liquid and plastic scintillators [5, 6].

The starting substance for the synthesis was naphthalene-1,4,5-tricarboxylic acid, which is accessible by oxidation of 4-acetylacenaphthene with potassium dichromate in acetic acid in the presence of iron salts, a method that was recently described by one of us [7]. When naphthalenetricarboxylic acid or its anhydride is heated with thionyl chloride, 4-chloroformylnaphthalic anhydride is readily formed [8]. By condensing the latter with ω-aminomethyl aryl ketones, we obtained substituted amides and then, by cyclization of them, aryloxazolyl-substituted naphthalic anhydrides (I). Anhydrides I were heated with aniline to obtain phenylimides (II).



Unsubstituted naphthalic anhydride has violet fluorescence in hydrocarbon solvents and blue fluorescence in the solid state. The introduction of aryloxazolyl residues into the 4 position of the naphthalene ring gives substances that have intense green or yellow-green luminescence in hydrocarbon solvents and intense yellow or orange luminescence in the solid state.

Replacement of a phenyl group by two-ring groupings – 4-diphenylyl and 1- or 2-naphthyl – does not affect the character of the absorption spectra of toluene solutions (Table 1) but shifts the K band by 10-12 nm to the long-wave region.

All-Union Scientific-Research Institute of Single Crystals, Kharkov. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1331-1333, October, 1973. Original article submitted July 12, 1972.

TABLE 1. Spectral Characteristics of 4-(5-Aryl-2-oxazolyl)-naphthalic Acid Derivatives

Comp.	Ar.	Absorption in toluene		Luminescence		
		λ_{max}, nm	$\varepsilon \cdot 10^{-4}$	λ_{max}, nm		η in toluene
				in toluene	in 5% NaOH	
Ia	C_6H_5	295, 398	1,06; 2,20	480	440	0,23
Ib	4-$C_6H_5C_6H_4$	310, 410	2,02; 2,47	495	460	0,48
Ic	1-$C_{10}H_7$	308, 410	1,67; 2,44	495	460	0,47
Id	2-$C_{10}H_7$	305, 408	1,56; 2,40	495	462	0,43
IIa	C_6H_5	295, 398	1,31; 2,69	475	—	0,32
IIb	4-$C_6H_5C_6H_4$	310, 405	2,56; 3,39	490	—	0,50
IIc	1-$C_{10}H_7$	305, 405	1,99; 3,13	490	—	0,51
IId	2-$C_{10}H_7$	305, 405	1,73; 2,72	485	—	0,50

TABLE 2. 4-(5-Aryl-2-oxazolyl)naphthalic Acid Derivatives

Comp.	Ar	mp, °C	Empirical formula	N, %		Yield, %
				found	calc.	
Ia	C_6H_5	250	$C_{21}H_{11}NO_4$	4,3	4,1	76
Ib	4-$C_6H_5C_6H_4$	256	$C_{27}H_{15}NO_4$	3,3	3,4	84
Ic	1-$C_{10}H_7$	263	$C_{25}H_{13}NO_4$	3,4	3,6	80
Id	2-$C_{10}H_7$	271	$C_{25}H_{13}NO_4$	3,8	3,6	89
IIa	C_6H_5	264	$C_{27}H_{16}N_2O_3$	6,6	6,7	85
IIb	4-$C_6H_5C_6H_4$	275	$C_{33}H_{20}N_2O_3$	5,6	5,7	93
IIc	1-$C_{10}H_7$	289	$C_{31}H_{18}N_2O_3$	6,1	6,0	84
IId	2-$C_{10}H_7$	290	$C_{31}H_{18}N_2O_3$	6,0	6,0	84

A similar regularity is observed in the luminescence spectra of toluene solutions, which are observed as one structureless band in all of the investigated substances. The most interesting result of lengthening the conjugation chain in the aryloxazolyl radical is an increase in the absolute photoluminescence quantum yield in toluene by a factor of two (Table 1).

Compounds I, which are naphthalic anhydride derivatives, are soluble in aqueous alkali solutions to give salts (III).

Solutions of the salts have blue luminescence, and the differences in the structures of the two-ring groupings have virtually no effect on the position of the luminescence maxima; the luminescence curves of solutions of compounds with two rings and naphthyl groups practically coincide. The intense luminescence of solutions of the alkali metal salts makes it possible to use them as water-soluble luminophores.

The N-phenylimides (II) differ very little with respect to absorption spectra and luminescence characteristics from the anhydrides from which they are obtained (Table 1). In contrast to the anhydrides, the phenylimides are insensitive to the action of alkalis at normal temperatures.

EXPERIMENTAL

The absorption spectra of toluene solutions were measured with an SF-4A spectrophotometer; the luminescence spectra of solutions and of the solid substances were measured with an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical emission adapter, and an M-95 microammeter. The photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with wavelength 365 nm was isolated with a DMR-4 quartz monochromator. The absolute quantum luminescence yields were determined by the method of equal absorption [10]. "Especially pure" toluene was used as the solvent for the spectral measurements.

4-(5-Aryl-2-oxazolyl)naphthalic Anhydrides (Ia-d, Table 2). A 10% solution of NaOH was added at room temperature with vigorous stirring to a mixture of equimolecular amounts of 4-chloroformylnaphthalic anhydride in a 15-fold amount of benzene and ω-aminomethyl aryl ketone hydrochloride in a 20-fold amount of water (ω-aminomethyl 4-diphenylyl ketone in 10% aqueous acetone) until the mixture was alkaline to litmus. The resulting precipitate was removed by filtration, washed with water, dried, and refluxed with a 15-fold amount of phosphorus oxychloride for 3 h. The solution was poured over ice, and the resulting precipitate was removed by filtration, washed with hot water, dried, and recrystallized successively from acetic anhydride, xylene, and acetic anhydride.

N-Phenylimides of 4-(5-Aryl-2-oxazolyl)naphthalic Acids (IIa-d, Table 2). Compounds Ia-d were dissolved in a 100-fold amount of glacial acetic acid, and a 1.5-fold excess of freshly distilled aniline was added. The mixture was refluxed for 4 h and then cooled to room temperature. The precipitate was removed by filtration and washed successively with 5% hydrochloric acid, water, and 5% sodium carbonate and then again with water until it was neutral.

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