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SYNTHESIS AND LUMINESCENCE PROPERTIES OF 4-(2-METHYL-5-OXAZOLYL)NAPHTHALIC ANHYDRIDE AND THE PRODUCTS OF ITS CONDENSATION WITH AROMATIC AMINES

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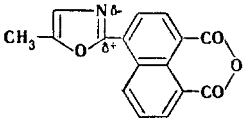
4-(2-Methyl-5-oxazolyl)naphthalic anhydride was synthesized by heating ω-aminomethyl 5-acenaphthyl ketone hydrochloride with acetic anhydride and subsequent oxidation of the resulting 2-methyl-5-(5-acenaphthyl)oxazole. 4-(2-Methyl-5-oxazolyl)-naphthalic acid phenylimide and 4(3)-(2-methyl-5-oxazolyl)-7-oxo-7H-benzimidazo-[1,2-b]benzo[de]isoquinoline were obtained by condensation of 4-(2-methyl-5-oxazolyl)naphthalic anhydride with aniline and o-phenylenediamine. The coincidence of the directions of polarization of the C=N bond of the oxazole ring and the electronic shifts in the π system of the anhydride and phenylimide molecules leads to an increase in the quantum luminescence yield.

We have explained the intense luminescence of 4-(5-methyl-2-oxazolyl)naphthalic anhydride (Ia), in contrast to 5-methyl-2-(1-naphthyl)oxazole, which is practically devoid of luminescence properties, by donor—acceptor interaction, although weak, of the methyl and carbonyl groups [1].



Ia

Polarization of the C=N bond of the oxazole ring, which has the opposite direction and is reinforced when the molecule passes into the excited state, can to a certain extent counteract this interaction. To evaluate its effect we synthesized and investigated isomeric Ib, in which the direction of polarization of the C=N bond coincides with the direction of the shift of π electrons from the methyl group to the carbonyl group.

The synthesis was accomplished by heating ω-aminomethyl 5-acenaphthyl ketone hydrochloride with acetic anhydride and subsequent oxidation of the resulting 2-methyl-5-(5-acenaphthyl)-oxazole. 4-(2-Methyl-5-oxazolyl)naphthalic acid phenylimide (IIb) was synthesized by condensation of anhydride Ib with aniline. (See scheme on following page.)

The PMR spectrum of Ib in trifluoroacetic acid contains a singlet of a methyl group of the oxazole ring [2] with a chemical shift of 3.26 ppm (relative to tetramethylsilane). This

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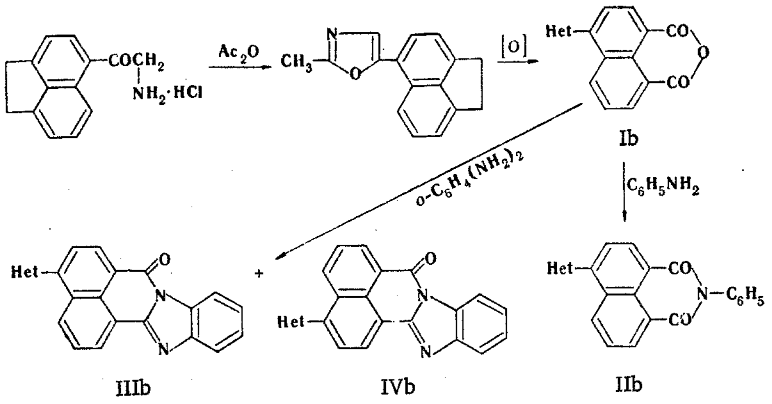

Het = 2-methyl-5-oxazolyl

signal, as a consequence of the inductive effect of the closely situated C=N bond, is shifted to the weak-field region as compared with isomeric Ia (δ_{CH_3} = 2.83 ppm).*

The absorption spectra of toluene solutions of the isomers (Table 1) are practically identical with respect to their character and the position of the maxima. A small long-wave shift accompanied by a substantial increase in the quantum yield (η) is observed in the luminescence spectra on passing from Ia to Ib.

With respect to its spectral-luminescence properties 4-(2-methyl-5-oxazolyl)naphthalic acid phenylimide (IIb) is similar to anhydride Ib, from which it was obtained. It does not differ with respect to the position of the absorption and luminescence maxima from its isomer — 4-(5-methyl-2-oxazolyl)naphthalic acid phenylimide (IIa) — but its quantum yield is twice that of IIb. Thus the same regularity that is observed during a comparison of the isomeric anhydrides — namely, when the polarization of the C=N bond in the oxazole ring coincides with the direction of the electron shifts in the π system of the molecules of these substances, the quantum yield increases — is also displayed in the spectral-luminescence properties of the phenylimides.

Mixtures of 3- and 4-substituted 7-oxo-7H-benzimidazo[1,2-b]benzo[de]isoquinolines with such close spectral-luminescence properties that there is no need to isolate each of the isomers for their practical utilization [3, 4] are usually formed in the reaction of 4-hetaryl-substituted naphthalic anhydride with o-phenylenediamine. One product of the reaction of anhydride Ib with o-phenylenediamine is also evidently a mixture of isomers (IIIb + IVb). It does not differ from the analogous product (IIIa + IVa) synthesized from 4-(5-methyl-2-oxazolyl)naphthalic anhydride (Ia) [1] not only with respect to the absorption and luminescence spectra, but also with respect to the quantum yield. In all likelihood the luminescence properties of these substances are determined primarily by the 7-oxo-7H-benzimidazo[1,2-b]benzo[de]isoquinoline grouping, which is an effective luminophore with yellow-green luminescence [5]. A change in the position of the nitrogen atom in the heteroring with respect to the CH_3 group has practically no effect on these properties.

EXPERIMENTAL

The absorption spectra were recorded with an SF-4 spectrophotometer. The luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, an FEU-18

TABLE 1. Spectral-Luminescence Properties of I-IV in Toluene

Compound	Absorption		Luminescence	
	λ_{max}, nm	$\varepsilon \times 10^{-4}$	λ_{max}, nm	η
Ia [1]	375	1,89	440	0,29
Ib	375	1,38	450	0,37
IIa	375	2,50	440	0,20
IIb	375	1,81	440	0,40
IIIa+IVa [1]	422	2,72	515	0,36
IIIb+IVb	420	1,78	520	0,36

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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 absolute quantum luminescence yields of solutions in toluene were determined by the equal-absorption method [6].

2-Methyl-5-(5-acenaphthyl)oxazole. A 10-g sample of ω-aminomethyl 5-acenaphthyl ketone hydrochloride [7] was refluxed in 60 ml of acetic anhydride for 6 h, after which the solvent was removed by distillation, and the residue was poured into water. The resulting precipitate was removed by filtration, dried, and chromatographed (benzene solution) with a continuous-action chromatographic column filled with aluminum oxide. The yield of product with mp 103°C was 7.5 g (88%). Found, %: N 6.5. $C_{14}H_{13}NO$. Calculated, %: N 6.7.

4-(2-Methyl-5-oxazolyl)naphthalic Anhydride (Ib). A 5-g (24 mmole) sample of 2-methyl-5-(5-acenaphthyl)oxazole was dissolved in 30 ml of glacial acetic acid, the solution was heated to 90°C, and 20 g (70 mmole) of sodium dichromate was added in small portions with vigorous stirring. The mixture was refluxed for 1.5 h, after which it was poured into 100 ml of 5% hydrochloric acid. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized from glacial acetic acid—acetic anhydride (1:1) to give 3 g (45%) of a product with mp 217°C. Found, %: C 68.5; H 3.5; N 4.8. $C_{16}H_9NO_4$. Calculated, %: C 68.8; H 3.2; N 5.0.

4-(2-Methyl-5-oxazolyl)naphthalic Acid Phenylimide (IIb). A 1.4-g (15 mmole) sample of freshly distilled aniline was added to a refluxing solution of 3 g (10.8 mmole) of Ib in 50 ml of glacial acetic acid, and the mixture was refluxed for 4 h. It was then poured into 100 ml of water, and the resulting precipitate was removed by filtration and washed successively with 5% HCl, water, 5% $NaHCO_3$, and water until the water washings were neutral. It was then dried to give 3.2 g (91%) of product. Crystallization from xylene and chromatographic purification of a benzene solution of the product with a continuous-action column filled with aluminum oxide gave a product with mp 283°C. Found, %: C 74.4; H 3.8; N 8.1. $C_{22}H_{14}N_2O_3$. Calculated, %: C 74.6; H 4.0; N 7.9.

Mixture of 3- and 4-(2-Methyl-5-oxazolyl)-7-oxo-7H-benzimidazo[1,2-b]benzo[de]isoquinolines (IIIb + IVb). A mixture of 2.8 g (10 mmole) of Ib and 1.6 g (15 mmole) of o-phenylenediamine was refluxed in 50 ml of glacial acetic acid for 4 h, after which it was cooled, and the resulting precipitate was removed by filtration, washed successively with 5% HCl, water, 5% $NaHCO_3$, and water, and dried. The yield of the IIIb + IVb mixture was 3.1 g (90%). Crystallization from xylene and chromatographic purification of a benzene solution of the mixture with a continuous-action column filled with aluminum oxide gave a product with mp 236°C. Found, %: C 75.0; H 3.5; N 12.0. $C_{22}H_{13}N_3O_4$. Calculated, %: C 75.2; H 3.7; N 12.0.

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