SYNTHESIS AND LUMINESCENCE PROPERTIES OF ANHYDRIDES AND N-PHENYLIMIDES OF SUBSTITUTED 4-(5-PHENYL-2-OXAZOLYL)-NAPHTHALIC ACIDS

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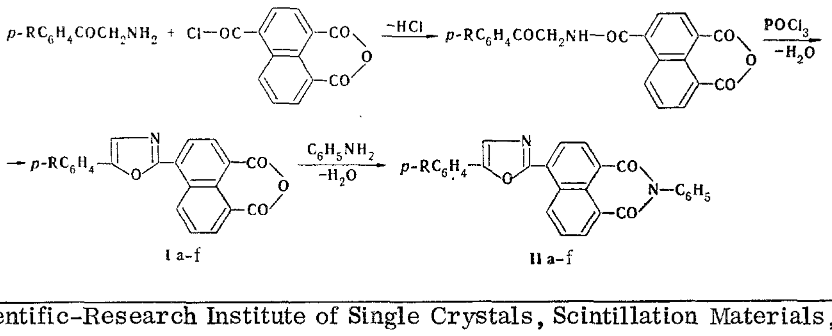
UDC 547.787.2'828'83.07:535.37:543.422.6

Anhydrides and N-phenylimides of 4-(5-phenyl-2-oxazolyl)naphthalic acids with various substituents in the para position of the phenyl ring were synthesized. Electron-donor substituents, particularly the dimethylamino group, induce an appreciable long-wave shift of the absorption maxima and the luminescence due to their interaction with the carbonyl group of the peri-anhydride grouping. A large Stokesian shift and a high photoluminescence quantum yield are characteristic for the dimethylamino-substituted anhydrides.

The union of mutually conjugated 2,5-diaryloxazole and naphthalic anhydride groupings has led [1-3] to the preparation of Ia (R = H), which absorbs and emits light over a considerably longer-wave region than each of the indicated fragments of its molecule.

It is known [4, 5] that the aryl groups in 2,5-diaryloxazoles and 2,5-diaryl-1,3,4-oxadiazoles interact with one another because of the pronounced electron-acceptor properties of the heterorings. The large difference in the spectral characteristics of 2-(α-naphthyl)-5-phenyloxazole and phenyloxazolylnaphthalic anhydride indicates that the electron-acceptor properties of the heteroring in the molecules of the latter under the influence of the markedly acceptor anhydride grouping play a considerably smaller role in the distribution of the electron density than in molecules of unsubstituted 2,5-diaryloxazoles. Nevertheless, the electron-acceptor character of the heteroring does retain a certain value, inasmuch as an analogous compound that contains a stronger electron acceptor – the oxidiazole ring – absorbs light and luminesces over a shorter-wave region of the spectrum [2].

We have synthesized Ib-f with various substituents in the para position of the phenyl ring in order to follow the effect of the electronic nature of the substituents on the optical characteristics of the compounds obtained (Table 1). The synthesis was accomplished by condensation of 4-chlorocarbonylnaphthalic anhydride [6] with substituted ω-aminoacetophenones and subsequent dehydration of the intermediates.



I a-f   II a-f

All-Union Scientific-Research Institute of Single Crystals, Scintillation Materials, and Ultrapure Chemical Substances, Khar'kov. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1049-1052, August, 1974. Original article submitted October 15, 1973.

TABLE 1. Anhydrides and N-Phenylimides of Aryloxazolylnaphthalic Acids

Compound	R	mp, °C	Empirical formula	N, %		Halogen, %		Absorption		Luminescence		Yield, %
				found	calc.	found	calc.	λ_{max} nm	lg ε	λ_{max}, nm	η	
Ia[3]	H	—	—	—	—	—	—	295, 398	4,03, 4,34	480	0,23	—
Ib	Cl	292	$C_{21}H_{10}ClNO_4$	3,4	3,7	9,1	9,4	300, 395	4,10, 4,40	480	0,39	85
Ic	Br	282	$C_{21}H_{10}BrNO_4$	3,5	3,3	18,6	19,0	300, 395	4,10, 4,40	480	0,35	67
Id	NO_2	323	$C_{21}H_{10}N_2O_6$	7,2	7,3	—	—	395	Slightly soluble	Does not luminesce		47
Ie	CH_3O	285	$C_{22}H_{13}NO_5$	3,9	3,8	—	—	305, 420	4,12, 4,35	515	0,44	78
If	$N(CH_3)_2$	310	$C_{23}H_{16}N_2O_4$	7,4	7,3	—	—	332, 472	Slightly soluble	628, 655*	0,75	32
IIa[3]	H	—	—	—	—	—	—	295, 398	4,12, 4,43	475	0,32	—
IIb	Cl	281	$C_{27}H_{15}ClN_2O_3$	—	—	8,0	7,9	295, 395	4,10, 4,40	478	0,35	65
IIc	Br	264	$C_{27}H_{15}BrN_2O_3$	—	—	16,3	16,2	298, 395	4,05, 4,33	478	0,27	69
IId	NO_2	305	$C_{27}H_{15}N_3O_5$	9,3	9,1	—	—	394	4,55	Does not luminesce		61
IIe	CH_3O	259	$C_{28}H_{18}N_2O_4$	6,2	6,3	—	—	300, 360*, 415	4,15, 4,35	510	0,46	73
IIf	$N(CH_3)_2$	227	$C_{29}H_{21}N_3O_3$	9,3	9,1	—	—	330, 460	Slightly soluble	580	0,35	63

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*Inflection on the curve.

The halogen atoms, like the nitro group, cause a barely noticeable hypsochromic shift of the K band. A different pattern is observed when electron-donor substituents are introduced. Even under the influence of a methoxy group, the maximum of the long-wave band in the absorption spectrum of toluene solution is shifted bathochromically by more than 20 nm. This effect is sharply intensified when a p-dimethylamine group is introduced ($\Delta\lambda = 74$ nm). The long-wave band in the spectrum of If is a charge-transfer band caused by electronic interaction of the dimethylamino and carbonyl groups, which are situated at opposite ends of the conjugation chain. Charge transfer is confirmed by a comparison of the molecular diagrams of Ia and If. The overall charge on the naphthalic anhydride residue in Ia in the ground state is -0.112 e, while in the first excited state it is -0.197 e; the corresponding overall charges in If are, respectively, -0.025 and -0.574 e [7]. Consequently, when strong electron-donor substituents are present the mutual effect of oppositely charged ends of the terminal groups proves to be more significant than the electron-acceptor effect of the oxazole ring. A similar principle was noted for the corresponding 1,3,4-oxadiazole derivatives [8].

One's attention is drawn to the large long-wave shift of the luminescence maxima under the influence of electron-donor substituents, which reaches ~150 nm for dimethylamino-substituted derivatives. A large Stokesian shift, which attests to the considerable structural changes that it undergoes on passing to the excited state, is characteristic for If. In particular, "compression," which is promoted by an appreciable increase in the order of the bond connecting the heteroring with the naphthalic anhydride residue, is possible. The excited molecule emits light, after which it exists in a more planar conformation. The absolute photoluminescence quantum yield (η) of If in toluene is much higher than in the case of the other substituted phenyloxazolylnaphthalic anhydrides.

Condensation of anhydrides Ib-f with aniline gave N-phenylimides IIb-f. Compound IIa was previously described in [2, 3].

The absorption and luminescence spectra of toluene solutions of the phenylimides differ only slightly from the spectra of the corresponding anhydrides, although the luminescence maxima of II are shifted to the short-wave region; this is displayed more distinctly in the case of the dimethylamino-substituted compounds.

The quantum yield and the Stokesian shift of the dimethylamino-substituted phenylimide IIf in toluene are considerably less than in the case of the corresponding anhydride (Ib). This is apparently due to weakening of the electron-acceptor properties of the imide group as compared with the anhydride group and, consequently, to weakening of its interaction with the dimethylamino group.

The luminescence maxima of toluene solutions of I-II lie over a broad range and encompass the region from the green to the red. These compounds absorb and emit light over a longer-wave region than the corresponding 1,3,4-oxadiazole derivatives [8].

Because of the quenching effect of the nitro group, Id and IId do not luminesce.

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds were measured with an SF-4A spectrophotometer. The luminescence spectra were recorded with an apparatus consisting of a ZMR-3 mirror monochromator, an FÉU-18 radiation detector, and an M-95 microammeter. Photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with wavelength 365 nm was isolated by means of a DMR-4 quartz monochromator. The absolute luminescence quantum yields were determined by the method of equal absorption [9]. Toluene (ultrapure) was used as the solvent for the spectral measurements.

4-(-Aryl-2-oxazolyl)naphthalic Anhydride (Ib-f). A 10% solution of sodium carbonate was added with vigorous stirring to a mixture of solutions of equimolecular amounts of 0.01 mole of 4-chlorocarbonyl naphthalic anhydride [6] in a 15-fold amount of benzene and ω-aminomethyl aryl ketone hydrochloride in a 20-fold quantity of water until the mixture was alkaline (pH ~ 9). Stirring was then continued at room temperature for 30 min, after which the mixture was weakly acidified with HCl. The resulting precipitate was removed by filtration, dried, and refluxed for 3 h with 15-fold amount of phosphorus oxychloride. The solution was poured over ice, and the resulting precipitate was removed by filtration, washed with water (80-90°), dried, and recrystallized from acetic anhydride (except for If, which was recrystallized from xylene) (Table 1).

4-(5-Aryl-2-oxazolyl)naphthalic Acid N-Phenylimides (IIb-f). A 1.5-fold excess of freshly distilled aniline was added to a solution of 1 mmole of anhydride Ib-f in a 10-fold amount of glacial acetic acid, and the mixture was refluxed for 4 h. The precipitate that formed when the mixture was cooled was removed by filtration, washed successively with 5% HCl, water, 5% sodium carbonate solution, and water until the wash waters were neutral. The product was then dried and recrystallized from xylene (Table 1).

LITERATURE CITED

1. S. E. Kovalev, B. M. Krasovitskii, and É. A. Shevchenko, USSR Author's Certificate No. 327,226; Byul. Izobr., No. 5, 76 (1972).
2. B. M. Krasovitskii and S. E. Kovalev, in: Scintillators and Organic Luminophores [in Russian], VNII Monokristallov, Kharkov (1972), p. 63.
3. S. E. Kovalev, B. M. Krasovitskii, and V. M. Shershukov, Khim. Geterotsikl. Soedin., 1331 (1973).
4. A. E. Lutskii, A. V. Shepel', O. P. Shvaika, N. P. Demchenko, and G. P. Klimisha, Khim. Geterotsikl. Soedin., 364 (1968).
5. A. E. Lutskii, A. V. Shepel', O. P. Shvaika, and G. P. Klimisha, Khim. Geterotsikl. Soedin., 461 (1969).
6. B. M. Krasovitskii, A. M. Kuznetsov, D. G. Pereyaslova, É. A. Shevchenko, V. V. Korshak, G. F. Slezko, V. V. Mikulenko, A. N. Izyneev, M. M. Seleznev, USSR Author's Certificate No. 292,953; Byul. Izobr., No. 5, 94 (1971).
7. S. E. Kovalev, Author's Abstract of Master's Dissertation, Kharkov (1973).
8. S. E. Kovalev, B. M. Krasovitskii, and N. A. Popova, Khim. Geterotsikl. Soedin., 461 (1974).
9. A. S. Cherkasov, Zh. Fiz. Khim., 29, 2209 (1955).