# SYNTHESIS AND STUDY OF THE LUMINESCENCE PROPERTIES OF ANHYDRIDES AND N-PHENYLIMIDES OF 4-(2-ARYL-1,3,4-OXADIAZOL-5-YL)NAPHTHALIC ACIDS

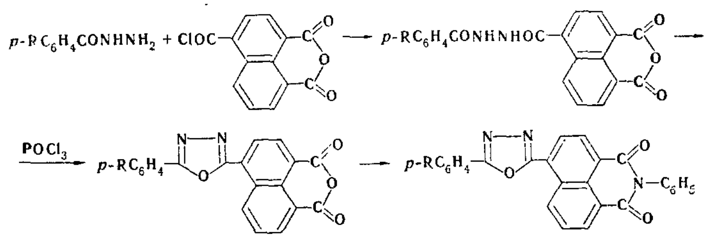
S. E. Kovalev, B. M. Krasovitskii,
and N. A. Popova

UDC 547.793.4'816.836.3.07: 542.953

4-(2-Aryl-1,3,4-oxadiazol-5-yl)naphthalic anhydrides were obtained by condensation of 4-chlorocarbonylnaphthalic anhydride with monohydrazides of substituted benzoic acids and subsequent cyclodehydration; the corresponding N-phenylimides were obtained from the 4-(2-aryl-1,3,4-oxadiazol-5-yl)naphthalic anhydrides. The UV and luminescence spectra are presented.

We recently [1] described 4-(2-phenyl-1,3,4-oxadiazol-5-yl)naphthalic anhydride (Ia), which luminesces in toluene in the violet region of the spectrum. The subject of the present communication is the synthesis and investigation of the optical properties of phenyl-substituted anhydrides (I) and the corresponding N-phenylimides (II).

Anhydrides I were synthesized by condensation of monohydrazides of substituted benzoic acids with 4-chlorocarbonylnaphthalic anhydride and subsequent cyclodehydration of the unsymmetrical N,N'-diaroylhydrazines by heating them with phosphorus oxychloride:



I II

I, II a R=H; b R=Cl; c R=NO$_2$; d R=CH$_3$; e R=OCH$_3$; f R=N(CH$_3$)$_2$

The corresponding N-phenylimides (IIa-f) were obtained by condensation of I with aniline.

The absorption spectra of naphthalic anhydride and Ia at 300-500 nm consist of broad bands with vibrational structures in the vicinity of the absorption maxima. The introduction of a phenyloxadiazolyl residue into the 4-position of the naphthalic anhydride causes a considerable shift in the absorption maximum (~35 nm) to the long-wave region of the spectrum and increases the absorption intensity.

It is known that the oxadiazole ring in diaryloxadiazole molecules in both the ground state and the excited states has an electron-acceptor effect, which is intensified in the excited state [2, 3]. This effect leads to a decrease in the electronic interaction of the phenyl and naphthalic anhydride portions of the molecule and is reflected in the shift of the absorption spectrum of phenyloxadiazolylnaphthalic anhydride to the short-wave region (~20 nm) as compared with its phenyloxazolyl analog [1], for which the electron-acceptor properties of the heterocyclic grouping in the excited state show up to a lesser extent [3].

---

All-Union Scientific-Research Institute of Single Crystals, Scintillation Materials, and Extremely Pure Chemical Substances, Kharkov. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 461-463, April, 1974. Original article submitted January 2, 1973.

TABLE 1. Anhydrides and Phenylimides of Aryloxadiazolylnaphthalic Acids

| Compound | R | mp, °C | Empirical formula | N, % | | Absorption | | Luminescence | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | found | calc. | $\lambda_{max}$, nm | lg ε | $\lambda_{max}$, nm | η | |
| Ia | H | | | | | 365, 385$^e$ | 4,30 | 425 | 0,14 | 57 |
| Ib | Cl | 200(dec.)$^a$ | $C_{20}H_9N_2O_4Cl$ | 7,8 | 7,4 | 365, 385$^e$ | — | 425 | Weak lum. | 22 |
| Ic | $NO_2$ | 350$^b$ | $C_{20}H_9N_3O_6$ | 10,7 | 10,8 | 365, 385$^e$ | — | — | — | 21 |
| Id | $CH_3$ | 259$^a$ | $C_{21}H_{12}N_2O_4$ | 7,9 | 7,9 | 365 | 4,31 | 430 | 0,34 | 58 |
| Ie | $OCH_3$ | 254$^a$ | $C_{21}H_{12}N_2O_5$ | 7,3 | 7,5 | 375 | 4,35 | 455 | 0,29 | 67 |
| If | $N(CH_3)_2$ | 100(dec. )$^c$ | $C_{22}H_{15}N_3O_4$ | 11,2 | 10,9 | 320, 425 | 4,44; 4,15 | 410 | 0,31 | 48 |
| IIa | H | 288$^a$ | $C_{26}H_{15}N_3O_3$ | 10,4 | 10,1 | 365, 385 | 4,43; 4,34 | 590 | Weak lum. | 70 |
| IIc | $NO_2$ | 265$^a$ | $C_{26}H_{14}N_4O_5$ | 12,0 | 12,1 | 365, 385 | 4,32; 4,24 | — | — | 50 |
| IId | $CH_3$ | 254$^a$ | $C_{27}H_{17}N_3O_3$ | 9,8 | 9,7 | 365 | 4,41 | 430 | Weak lum. | 67 |
| IIe | $OCH_3$ | 252$^d$ | $C_{27}H_{17}N_3O_4$ | 9,0 | 9,4 | 375 | 4,38 | 455 | 0,12 | 50 |
| IIf | $N(CH_3)_2$ | 100(dec. )$^c$ | $C_{28}H_{20}N_4O_3$ | 12,2 | 12,2 | 320, 415 | 4,38; 4,22 | 565 | 0,23 | 71 |

a)From acetic anhydride. b) From aqueous dimethylformamide. c) From ethanol. d) From xylene. e) Inflection.

One's attention is drawn to the inflection in the long-wave portion of the curve for I, which gradually vanishes as electron-donor substituents with increasing electron-donor properties are introduced but which, on the other hand, is displayed more distinctly when electron-acceptor substituents are introduced.* The spectra of methyl- (Id), chloro- (Ib), and nitro-substituted (Ic) compounds do not differ from the spectrum of Ia with respect to the position of the chief maximum; a small bathochromic effect (~10 nm) is observed when a methoxy group is introduced. The spectrum of If is considerably complicated. In addition to the band this is also present in the spectra of the other derivatives but shifted to the short-wave region ($\lambda_{max}$ 320 nm); there is a long-wave band ($\lambda_{max}$ 425 nm), which is apparently a charge-transfer band and is due to the electronic interaction of the dimethylamino and carbonyl groups at the ends of the conjugation chain.

The luminescence spectra of I which are represented by a structureless band differ little in character from one another. The electronic nature of the substituents introduced into the phenyl ring of the luminescing compounds affects the magnitude of the long-wave shift of the luminescence maximum, and the Stokesian shift increases considerably as the electron-donor properties of the substituents increase. The introduction of electron-donor substituents doubles the luminescence quantum yield. The nitro derivative (Ic) has practically no luminescence in either toluene or in the crystalline state; the chloro derivative (Ib) also has very weak luminescence.

The absorption spectra of toluene solutions of N-phenylimides of aryloxadiazolylnaphthalic acids are practically the same as the spectra of the anhydrides from which they were obtained. However, the phenylimides have less intense luminescence than the anhydrides.

## 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 FÉU-18 optical emission detector, and an M-95 microammeter; the photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light of wavelength 365 nm was isolated by means of a DMR-4 quartz monochromator. The absolute luminescence quantum yields of toluene solutions were determined by the equal absorption method [4].

4-[2-(4-Methoxyphenyl)-1,3,4-oxadiazol-5-yl]naphthalic Anhydride (Ie). A saturated sodium carbonate solution was added with vigorous stirring to a mixture of solutions of 1.66 g (0.01 mole) of 4-methoxybenzhydrazide in 100 ml of 10% hydrochloric acid and 2.6 g (0.01 mole) of 4-chlorocarbonyl-1,8-naphthalic anhydride in 50 ml of benzene until the mixture was alkaline. Stirring was then continued at room temperature for 2.5 h, after which the mixture was acidified with concentrated hydrochloric acid. The result-

---

*Because of the low solubilities of Ib and Ic, the absorption spectra of toluene solutions of these compounds were measured qualitatively.

ing precipitate was removed by filtration and washed successively with 10% sodium carbonate solution, water, and a small amount of ethanol. The product was refluxed in 40 ml of phosphorus oxychloride for 40 min, after which the mixture was poured over ice, and the precipitate was removed by filtration and washed with water until it gave a neutral reaction (Table 1).

A similar procedure was used to obtain 4-[2-(4-tolyl)-1,3,4-oxadiazol-5-yl]- and 4-[2-(4-dimethylaminophenyl)-1,3,4-oxadiazol-5-yl]naphthalic anhydrides (Id and If, Table 1).

4-[2-(4-Chlorophenyl)-1,3,4-oxadiazol-5-yl]naphthalic Anhydride (Ib). A mixture of solutions of equimolar amounts (0.01 mole) of 4-chlorobenzhydrazide and 4-chlorocarbonyl-1,8-naphthalic anhydride in pyridine was heated with stirring for 3 h up to the boiling point, after which it was refluxed for another hour. The reaction mixture was cooled to room temperature and poured into water. The precipitate was removed by filtration and washed with water and ethanol. The product was refluxed for 6 h in 50 ml of phosphorus oxychloride, after which the mixture was poured over ice, and the precipitate was removed by filtration and washed with water until it was neutral. It was then dried and chromatographed on activity II aluminum oxide with elution by acetone (Table 1).

A similar procedure was used to obtain 4-[2-(4-nitrophenyl)-1,3,4-oxadiazol-5-yl]naphthalic anhydride (Ic) (Table 1).

Aryloxadiazolylnaphthalic Acid Phenylimides (IIa-f). A mixture of solutions of 0.01 mole of aryloxadiazolylnaphthalic anhydride and 0.1 mole of aniline in 100 ml of acetic acid was refluxed for 6 h. The course of the reaction was monitored by thin-layered chromatography on aluminum oxide. The solvent was evaporated to one tenth of the starting volume, and the residue was cooled. The precipitate was removed by filtration, washed successively with 10% hydrochloric acid, water, and a small amount of ethanol, dried, chromatographed on activity II aluminum oxide (elution with acetone), and crystallized (Table 1).

## LITERATURE CITED

1. B. M. Krasovitskii, S. E. Kovalev, and É. A. Shevchenko, USSR Author's Certificate No. 327,226; Byul. Izobr., No. 5 (1972).
2. A. E. Lutskii, A. V. Shepel', O. P. Shvaika, and G. P. Klimisha, Khim. Geterotsikl. Soedin., 461 (1969).
3. L. M. Kutsyna, N. Ya. Makovetskii, and A. V. Shepel', in: Single Crystals, Scintillators, and Organic Luminophores [in Russian], No. 4, Kharkov (1968), p. 94.
4. A. S. Cherkasov, Zh. Fiz. Khim., 29, 2209 (1955).