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4-(5-ARYLVINYL-2-OXAZOLYL)- AND 4-(5-ARYLBUTADIENYL-2-OXAZOLYL)-NAPHTHALIC ANHYDRIDES

B. M. Krasovitskii and V. M. Shershukov

4-(5-Arylvinyl-2-oxazolyl)- and 4-(5-arylbutadienyl-2-oxazolyl)naphthalic anhydrides were synthesized by a phosphonate modification of the Wittig reaction from 4-(5-bromomethyl-2-oxazolyl)naphthalic anhydride. The structures of the aryl radicals and the steric hindrance created by some of them have a substantial effect on the absorption and luminescence of these compounds in solution. The introduction of each of the vinylene groups between the aryl and heterocyclic radicals causes approximately identical shifts in the spectra, but the Stokesian shift increases. These effects are reinforced considerably under the influence of electron-donor substituents in the aryl radical. The luminescence maxima of the investigated substances range from 515 to 710 nm, and the absolute quantum yields range from 0.12 to 0.51.

Effective organic luminophores [1, 2] that have found application in the preparation of daylight fluorescent pigments [3] are found among 4-(5-aryl-2-oxazolyl)naphthalic anhydrides (I).



i n = 0; II n = 1; III n = 2

It was of interest to observe how lengthening of the conjugation chain by the introduction of vinylene groups between the aryl and heterocyclic groupings would affect the spectral luminescence properties of these compounds. For this purpose we obtained II. Their synthesis was accomplished by a phosphonate modification of the Wittig reaction via the scheme



Compounds with two vinylene groups (III) were synthesized via a similar scheme with the application of cinnamaldehyde and p-dimethylaminocinnamaldehyde.

A solution of IIa in toluene absorbs and luminesces over a longer-wavelength range and more intensely than the analogous Ia, which does not contain a vinylene group (Table 1). Lengthening of the chain of conjugated bonds by replacement of the phenyl group by diphenylyl and p-terphenylyl groups or groupings with condensed aromatic rings (IIb-f) leads to a further

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TABLE 1. Anhydrides I-III

Com- pound	· Ar	mp, °C	N found, %	Empirical formula	N calc.	Absorption λ_{\max} , nm	Lumi cence λ _{max}	nes- e n	Yield, %
Ia IIa IIb IIc IId IIf IIf IIf IIf IIf IIf IIf IIf III III III III IIIA	$\begin{array}{c} C_6H_5^{1}\\ C_6H_5^{1}\\ +C_6H_5C_6H_4\\ +C_6H_5C_6H_4C_6H_4\\ +C_10H_7\\ 2-C_{10}H_7\\ 9-C_{14}H_9\\ +C_1C_6H_4\\ +B_7C_6H_4\\ 4-B_7C_6H_4\\ 4-CH_3C_6H_4\\ +CH_3C_6H_4\\ +CH_3C_6H_4\\ +C(H_3)_2NC_6H_4\\ C_6H_5\\ 4-(CH_3)_2NC_6H_4\\ \end{array}$	202 254 300 272 282 227 258 252 350 219 231 206 230 224		$\begin{array}{c} C_{23}H_{13}NO_4\\ C_{29}H_{17}NO_4\\ C_{35}H_{21}NO_4\\ C_{27}H_{14}NO_4\\ C_{27}H_{14}NO_4\\ C_{31}H_{17}NO_4\\ C_{31}H_{12}NO_4\\ C_{23}H_{12}BrNO_4\\ C_{23}H_{12}D_7NO_4\\ C_{24}H_{15}NO_4\\ C_{24}H_{15}NO_5\\ C_{25}H_{15}NO_4\\ C_{27}H_{20}N_2O_4\\ \end{array}$	$\begin{array}{c} -\\ 3,8\\ 3,2\\ 2,7\\ 3,4\\ 3,4\\ 3,6\\ 3,5\\ 3,1\\ 6,8\\ 3,7\\ 3,5\\ 6,8\\ 3,6\\ 6,4\end{array}$	$\begin{array}{c} 298, \ 398\\ 330, \ 420\\ 340, \ 432\\ 348, \ 435\\ 345, \ 425\\ 335, \ 435\\ 355, \ 375, \ 390, \ 430\\ 330, \ 420\\ 330, \ 420\\ 350, \ 415\\ 330, \ 427\\ 338, \ 435\\ 362, \ 485\\ 340, \ 440\\ 385, \ 495\\ \end{array}$	480 515 530 525 535 525 580 515 505 530 555 675 560 710	$\begin{array}{c} 0.23\\ 0.38\\ 0.36\\ 0.45\\ 0.28\\ 0.37\\ 0.12\\ 0.38\\ 0.33\\ 0.34\\ 0.32\\ 0.31\\ 0.52\\ 0.26\\ 0.12 \end{array}$	

bathochromic shift of the absorption spectra. An even greater long-wave shift is observed in the luminescence spectra. The short-wave absorption band in the spectra of IIb-e depends to a certain extent on the structure of the aryl group: it is shifted to the long-wave side in the phenyl, 4-diphenylyl, and 4-(p-terphenylyl) series, as well as in the phenyl, 2-naphthyl, and l-naphthyl series. The position of the long-wave absorption band responsible for luminescence is determined by the π system of the entire molecule and by the conjugation of the structural fragments included in it.

The quantum yield (n) increases irregularly when a vinylene group is introduced in I and depends on the aryl groups present in them. The quantum yield is highest in the case of compounds in whose electronic spectra the lowest Stokesian shift, which is usually associated with radiationless energy losses, appears. The compound with a 1-naphthyl group, which in the ground state has a nonplanar structure [4] and in which a portion of the excitation energy is consumed in "compression" of the molecules on passing to the excited state, has the lowest quantum yield.

The absorption spectrum of the compound with a 9-anthryl group (IIf) differs markedly in character from the spectra of II with other aromatic groupings. Splitting of the absorption band due to the greater steric hindrance than in the compound with a 1-naphthyl group is observed in its spectrum, and the absorption of the 9-anthryl group, which is readily observable from the vibrational structure of the spectrum characteristic for anthracene, appears. The most sizeable Stokesian shift and the lowest quantum yield are observed for this compound.

The spectra of IIg-1 are sensitive to the electronic nature of the substituents introduced in the phenyl group of IIa. A methyl group, owing to its at least weak interaction with the strong electron-acceptor anhydride grouping, gives rise to a small bathochromic shift of the long-wave absorption maximum and shifts the luminescence maximum more appreciably. These effects are reinforced considerably when stronger electron-donor substituents — methoxy and dimethylamino groups — are introduced. Under the influence of the latter, the Stokesian shifts are increased to about 200 nm and constitute evidence for large structural changes in the molecules on conversion to the excited state. The long-wave band in the absorption spectrum of this substance is evidently a charge-transfer band. The dimethylamino-substituted compound luminesces in the red region and has the highest quantum yield.

The spectral luminescence properties of the chloro- and bromo-substituted compounds (IIg,h) are practically the same as those of unsubstituted 4-(5-styryl-2-oxazolyl)naphthalic anhydride (IIa). Under the influence of a nitro group the shortwave maximum undergoes a substantial bathochromic shift and the long-wave band sustains a small hypsochromic shift; the luminescence maximum is also shifted somewhat to the shortwave side. However, it is interesting that the luminescence intensity of IIi is practically the same as that of the compound containing a phenyl group, whereas the analogous substance without a vinylene group does not luminesce. This fact is in conformity with the previous observations that the nitro group does not have a quenching effect in those cases in which the compound that contains it has a luminescence maximum in the long-wave region above 500 nm [5].

When a second vinylene group is included in the chain (IIIa), the same effect in the absorption and luminescence as that observed in the case of the introduction of the first vinylene group is observed. However, it should be noted that the Stokesian shifts increase continuously in the series Ia-IIa-IIIa. While the long-wave absorption maximum is shifted bathochromically by about 20 nm with each vinylene group, in the luminescence spectra this shift is 35 nm. When one compares the quantum yields of these compounds, one may note that it is lower for IIIa than for the other two. It is possible that this is associated with radiationless expenditures of the excitation energy for intramolecular rotations and vibrations, which increase as the chain becomes longer.

The luminescence of IIIb lies farther in the red region (λ_{max} 710 nm) than that of the dimethylamino-substituted compounds in series I [2] and II and is also evidently due to charge transfer on conversion of the molecules to the excited state.

EXPERIMENTAL

The absorption spectra of toluene solutions of the compounds 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. 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 luminescence quantum yields of the toluene solutions were determined by the equal absorption method [6].

<u>4-(5-Arylvinyl-2-oxazolyl)-</u> and 4-(5-Arylbutadienyl-2-oxazolyl)naphthalic Anhydrides (IIa-1, IIIa,b, Table 1). A mixture of equimolar amounts (0.01 mole) of 4-(5-bromomethyl-2oxazolyl)naphthalic anhydride [7] and triethyl phosphite was refluxed in 70 ml of dry xylene for 6 h, after which the xylene was removed completely by distillation. The oily residual 4-[5-(diethylmethylenephosphonato)-2-oxazolyl]naphthalic anhydride was dissolved in 40 ml of dimethylformamide (DMF), and a small excess of the aldehyde (0.011 mole) and a methanol solution of sodium methoxide (0.45 g of sodium in 80 ml of methanol) were added to the solution. The reaction mixture was then allowed to stand at room temperature for 12 h, after which it was neutralized to pH 7 with 5% hydrochloric acid solution, and 50 ml of water was added. The resulting precipitate was removed by filtration, washed with water, and dried. To obtain the trans isomers, the product was refluxed in xylene for 6 h in the presence of crystalline iodine. The products were purified by successive crystallization from xylene, acetic anhydride, and xylene.

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