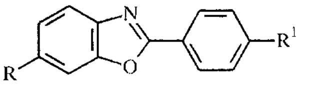
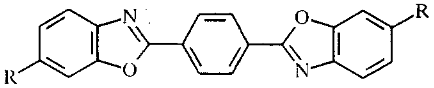
# SPECTRAL-LUMINESCENCE PROPERTIES OF SOME ARYL- AND STYRYLBENZOXAZOLES CONTAINING DIALKYLAMINO GROUPS

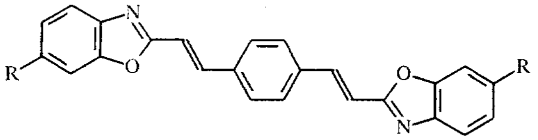
**E. M. Vernigor, E. A. Luk'yanets, L. P. Savvina,
and V. K. Shalaev**

*The spectral-luminescence properties of a series of 2-aryl- and 2-styrylbenzoxazoles containing dialkylamino groups were investigated. It was shown that the introduction of the diethylamino group at the position 6 of the benzoxazole fragment leads to an increase in the Stokes shift and quantum yield of the luminescence.*

In the continuation of our work on the study of the dependence of the spectral-luminescence properties of heteroaromatic compounds on their structure [1-5], we investigated the spectral-luminescence properties of 2-aryl- and 2-styrylbenzoxazoles substituted with dialkylamino groups (Ib-d), (IIb), and (IIIb), and the comparison with the analogous unsubstituted compounds (Ia), (IIa), and (IIIa).


Ia-d


IIa, b


IIIa, b

I-IIIa, c $R = H$, b, d $R = NEt_2$; Ia, b $R^1 = H$; c $R^1 = NMe_2$, d $R^1 = NO_2$

The 6-diethylamino-2-phenylbenzoxazole (Ib) and 1,4-bis(6-diethylaminobenzoxazol-2-yl)benzene (IIb) were synthesized by the condensation of the double tin salt of 5-diethylamino-2-aminophenol with benzoic acid or, correspondingly, terephthalic acid in polyphosphoric acid by analogy with the method of [6]. The 6-diethylamino-2-(4-nitrophenyl)benzoxazole (Id) was obtained by the reaction of 5-diethylamino-2-nitrosophenol with 4-nitrobenzaldehyde in mesitylene according to the method of [7]. The 1,4-bis[$\beta$-(6-diethylaminobenzoxazol-2-yl)vinyl]benzene (IIIb) was synthesized by the condensation of 6-diethylamino-2-methylbenzoxazole with terephthalic aldehyde in DMF in the presence of KOH [1].

The maximums of the long-wave absorption bands of the compounds (Ib-d), (IIb), and (IIIb), containing dialkylamino groups, responsible for the luminescence are situated in the region of 345-460 nm (cf. Table 1). The introduction of the dialkylamino group at the position 6 of the benzoxazole fragment of 2-phenylbenzoxazole leads to a bathochromic shift of the absorption band of compound (Ib) by comparison with the unsubstituted compound (Ia) in DMF amounting to 64 nm; the influence of the analogous substituent at the position 4 of the phenyl fragment is significantly weaker, and the bathochromic shift of the absorption maximum of compound (Ic) comprises 44 nm by comparison with (Ia) in DMF. A still larger bathochromic

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Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 238-241, February, 1993. Original article submitted October 21, 1992.

TABLE 1. Characteristics of Aryl- and Styrylbenzoxazoles*

| Compound | R | $R^1$ | Empirical formula | mp, °C | Solvent | Absorption | | Luminescence | | $\Delta\nu_s$, см$^{-1}$ | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $\lambda_{max}$, nm | log ε | $\lambda_{max}$, nm | $\varphi$ | | |
| Ia | H | H | | | DMF | 301 | | | | | |
| | | | | | benzene | 299 | | 339 | | 3950 | |
| Ib | $NEt_2$ | H | $C_{17}H_{18}N_2O$ | 77...78 | DMF | 365 | 4,42 | 470 | 0,85 | 6120 | 47 |
| | | | | | toluene | 358 | | 430 | 0,65 | 4680 | |
| Ic | H | $NMe_2$ | | | DMF | 345 | 4,64 | 398 | 0,70 | 3860 | |
| Id | $NEt_2$ | $NO_2$ | $C_{17}H_{17}N_3O_3$ | 191...192 | DMF | 452 | 4,00 | | | | 23 |
| | | | | | toluene | 443 | 4,10 | 595 | 0,52 | 5770 | |
| IIa | H | | | | DMF | 358, 341**, 327 | | 395**, 413 | 0,62 | 4010 | |
| IIb | $NEt_2$ | | $C_{28}H_{30}N_4O_2$ | 174...175 | DMF | 430, 310 shoulder | 4,60, 3,48 | 556 | 0,80 | 5270 | 65 |
| IIIa | H | | | | chloroform | 401 sh., 382, 366 | 4,49 , 4,78, 4,72 | 448, | 0,43 | 3860 | |
| IIIb | $NEt_2$ | | $C_{32}H_{34}N_4O_2$ | 199...201 | DMF | 457, 323 | 4,64, 4,20 | 650 | 0,55 | 6500 | 79 |

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*The compounds (Ia, c), (IIa), and (IIIa) were obtained according to [1, 6].

**The main maximum.

shift of the absorption band by comparison with the unsubstituted analogs (IIa) and (IIIa) is observed for the compounds (IIb) and (IIIb), containing two dialkylamino groups. The compound (Id), containing the electron-donor diethylamino group and the electron-acceptor nitro group, absorbs in a much higher long-wave region than the compound (Ib), and in the same spectral region as 4-diethylamino-4′-nitrostilbene, which is isoelectronic with it [8].

The investigated compounds (Ib-d), (IIb), and (IIIb), containing dialkylamino groups, show strong luminescence in the wide spectral range of 400-650 nm. The presence of the dialkylamino group at the position 6 of the benzoxazole fragment of these compounds leads to a large Stokes shift $\Delta\nu_s$ (up to 6500 $cm^{-1}$), whereas the $\Delta\nu_s$ for the analogous unsubstituted compounds (Ia), (IIa), and (IIIa) does not exceed 4010 $cm^{-1}$. The introduction of the dialkylamino group into the phenyl fragment [compound (Ic)] does not lead to an increase of the Stokes shift by comparison with the unsubstituted analog (Ia).

The increase of the Stokes shift in the monosubstituted compound (Ib) by comparison with the unsubstituted analog (Ia) is apparently explained by the electron-donor properties of the diethylamino group, facilitating the intramolecular transfer of charge from the benzoxazole fragment to the aryl group on excitation [2, 9]. It can be seen by the comparison of the spectra of the compounds (Ib) and (Id) in toluene that the Stokes shift increases for the compound (Id) containing the electron-donor diethylamino group and the electron-acceptor nitro group. This evidently indicates the presence of a significant dipole moment for the compound (Id) in the excited state; this leads to a marked bathochromic shift by comparison with the unsubstituted compound (Ia). Such an effect was noted previously for 4-diethylamino-4′-nitrostilbene [8] and for 2-(4-difluoromethylsulfonylphenyl)-5-(4-dimethylaminophenyl)oxazole [10]. This is indicated by the dependence of the luminescence of the compound (Id) on the polarity of the solvent: The luminescence of its solutions changes from blue in heptane to orange in toluene. In polar solvents such as DMF and ethanol, the intensity of the luminescence of compound (Id) decreases sharply as in the case of 4-diethylamino-4′-nitrostilbene, for which the increase of the solvent polarity leads to the long-wave shift of the luminescence bands and the decrease in the intensity of the luminescence [11].

The symmetrical disubstituted compounds (IIb) and (IIIb) are also characterized by high Stokes shifts, whereby the maximal value of the $\Delta\nu_s$ is observed for the compound (IIIb), which possesses the longest effective chain of conjugation.

The absolute quantum yields of the luminescence $\varphi$ for the compounds (Ib-d), (IIb), and (IIIb), containing dialkylamino groups, are high (0.52-0.85) and generally exceed the quantum yields of the unsubstituted compounds (IIa) and (IIIa).

Therefore, the substitution of the hydrogen atom at the position 6 of the benzoxazole fragment in the series of investigated aryl- and styrylbenzoxazoles by the dialkylamino group leads to the long-wave shift of their absorption and luminescence bands, the increase of the quantum yield, and the significant increase of the Stokes shift by comparison with the analogous unsubstituted compounds.

## EXPERIMENTAL

The electronic absorption spectra of the investigated compounds were measured on a Unicam SP-8000 spectrophotometer. The luminescence spectra were measured on equipment of the SDL-1 type assembled on the basis of the MDR-1 monochromator. The luminescence was excited by light of the DKSSh-1000 lamp, separated by the MDR-3 monochromator. The spectra were corrected for the spectral sensitivity of the instrument. The Stokes shift was determined as the difference of the strongest long-wave absorption maximum and the main luminescence maximum. The quantum yields of the luminescence were determined by a relative method; the standard utilized was the ethanolic solution of 3-aminophthalimide ($\varphi = 0.6$ [12]).

The compounds (Ib, d), (IIb), and (IIIb) were synthesized for the first time by methods analogous to those described in the works [1, 6].

The data of the elemental analysis for C, H, and N for these compounds correspond with the calculated data.

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