Electronic spectrum (isooctane), \( \lambda_{\text{max}} \), nm (log \( \varepsilon \)): 228 (4.52), 256 (4.43), 328 (4.41), and 400 (4.38). The product had \( R_f \) 0.68.

**LITERATURE CITED**


**o-TOSYLAMINO-SUBSTITUTED 2-ARYLIMIDAZOLES**

L. Sh. Afanasiadi, B. M. Bolotin, and N. F. Levchenko

A number of o-tosylamino-substituted 2-arylbenzimidazoles were synthesized, and the effect of substituents on the position of the absorption bands of toluene solutions of the products was investigated. Except for the compound containing a nitro group, the investigated compounds fluoresce in the solid state and in toluene; an anomalously large Stokesian shift is characteristic for them.

An anomalously high Stokesian shift is characteristic for the fluorescence of a considerable number of compounds with an intramolecular hydrogen bond, and this makes it possible to use some of them as organic luminophores that are colorless in daylight [1-5]. Compounds with an intramolecular hydrogen bond in which the tosylamino group acts as the proton-donor group — specifically, 2-(tosylaminophenyl)-4H-3,1-benzoxazin-4-ones [6], 2-(2-tosylaminophenyl)-4(3H)-quinazolonones [7], and 2-2(tosylaminophenyl)benzoxazoles [8] — have recently become well known.

We have synthesized and investigated o-tosylamino-substituted 2-arylbenzimidazoles I and II (X=hydrogen or functional substituents in the 5 or 6 position).

![Structure of compounds I and II](image)

The optical characteristics of these compounds are presented in Table 1.

In analogy with the above-mentioned o-tosylamino-substituted 2-arylbenzoxazoles, one may assume the presence of an intramolecular hydrogen bond in the series of compounds that we investigated.

The absorption spectra of I had two maxima at 300-340 nm, and the shortwave band [\( \lambda_{\text{max}} \) 300 nm (\( \varepsilon \) 12,000)] is similar with respect to its position and structure to the absorption

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### Table 1. Spectral Characteristics of o-Tosylamino-Substituted 2-Arylbenzimidazoles

<table>
<thead>
<tr>
<th>Compound</th>
<th>x</th>
<th>Absorption $\lambda_{\text{max}}$, nm</th>
<th>Fluorescence $\lambda_{\text{max}}$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>toluene</td>
<td>crystals</td>
</tr>
<tr>
<td>Ia</td>
<td>H</td>
<td>300.320</td>
<td>465</td>
</tr>
<tr>
<td>Ib</td>
<td>Cl</td>
<td>305.325</td>
<td>500</td>
</tr>
<tr>
<td>Ic</td>
<td>CH$_3$</td>
<td>305.320</td>
<td>505</td>
</tr>
<tr>
<td>Id</td>
<td>NO$_2$</td>
<td>325.340</td>
<td>Does not luminesce</td>
</tr>
<tr>
<td>IIa</td>
<td>H</td>
<td>320.335</td>
<td>Weak red</td>
</tr>
<tr>
<td>IIb</td>
<td>Cl</td>
<td>325.340</td>
<td>—</td>
</tr>
<tr>
<td>IIc</td>
<td>CH$_3$</td>
<td>325.340</td>
<td>—</td>
</tr>
</tbody>
</table>

*Inflection.

The band of 2-phenylbenzimidazole [9] and can be assigned to an electron transition localized on the chromophore, which is $\pi$-isoelectronic with respect to stilbene [10]. As in the case of o-tosylamino-substituted 2-arylbenzoxazoles [8], the longer-wave band is due to intramolecular charge transfer from the nitrogen atom of the tosylamino group to the nitrogen atom of the C=N group. The character of the effect of substituents on the bands serves as an additional confirmation of the correctness of this assignment of the bands. The introduction of a chlorine atom or a methyl group affects the position of the "stilbene" band and shifts it bathochromically. This is explained by the fact that the substituents are located at the end of the conjugation ($\pi$-isoelectronic with respect to stilbene) chain and therefore affect the transition localized on this chromophore. The same substituents in the 2-(2-tosylamino-phenyl)benzoxazole series, when they are introduced in the para position relative to the tosylamino group, i.e., into the chromophore responsible for the appearance of the longwave band, have practically no effect on the shortwave band, whereas the longwave band experiences an appreciable bathochromic shift.

Insofar as the nitro group is concerned, it may be noted that it gives rise to a considerable bathochromic shift of both bands. It should be stated simultaneously that, as compared with 2-(2-hydroxyphenyl)benzimidazole ($\lambda_{\text{max}}$ 365 nm in toluene), the longwave maximum of the absorption spectrum of I is shifted hypsochromically. This is probably associated with the difference in the strength of the electron-donor properties of the hydroxy and tosylamino groups, which determines the ease of intramolecular charge transfer.

Both maxima are shifted bathochromically in the absorption spectra of II because of lengthening of the conjugation chain; the longer-wave maximum appears in the form of an inflection on the curve.

All of the investigated compounds, except for the compound containing a nitro group (Id), fluoresce in the solid state and in toluene at room temperature, but the luminescence intensity of the naphthyl-substituted benzimidazoles is lower than that of the phenyl-substituted compounds. An anomalously high Stokesian shift is characteristic for o-tosylamino-substituted 2-arylbenzimidazoles, and this confirms the presence of an intramolecular hydrogen bond in these compounds [6]. Judging from the visual evaluation of the fluorescence of their weakly fluorescing toluene solutions and the fluorescence of their crystals, the Stokesian shift is considerably greater for II than for the phenyl derivatives.

The introduction of a methyl group and a chlorine atom (Ib, Ic) has little effect on the structure of the spectrum and the position of the fluorescence maximum, but the luminescence intensity decrease as compared with the unsubstituted compound.

On passing from a hydrocarbon solvent to a hydroxyl-containing solvent, the fluorescence maximum of 2-(2-tosylaminophenyl)benzimidazole undergoes a considerable hypsochromic shift (35 nm), apparently because of the competitive effect of intra- and intermolecular bonds. The fluorescence maxima of crystals of the investigated substances are shifted considerably to the shortwave regions as compared with the toluene solutions.

**EXPERIMENTAL**

The absorption spectra of solutions of the o-tosyl-substituted 2-arylbenzimidazoles in toluene ($3 \cdot 10^{-5}$ M) were measured with an SF-4 spectrophotometer. A unit consisting of a