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

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o-TOSYLAMINO-SUBSTITUTED 2-ARYLBENZIMIDAZOLES

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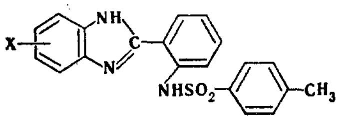
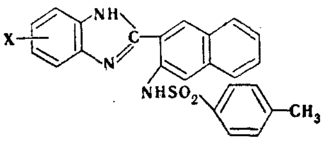
A number of o-tosylamino-substituted 2-arylbenzimidazoles were synthesized, and the effect of substituents on the position of the absorption bands of toluene solutions of the products was investigated. Except for the compound containing a nitro group, the investigated compounds fluoresce in the solid 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)-quinazolones [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).



I



II

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 [λ_{max} 300 nm (ε 12,000)] is similar with respect to its position and structure to the absorption

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All-Union Scientific-Research Institute of Simple Crystals, Scintillation Materials, and Ultrapure Chemical Substances, Khar'kov. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5 pp. 673-675, May, 1976. Original article submitted April 28, 1975.

TABLE 1. Spectral Characteristics of o-Tosylamino-Substituted 2-Arylbenzimidazoles

Compound	X	Absorption λ_{max}, nm	Fluorescence λ_{max}, nm		η in toluene
			toluene	crystals	
Ia	H	300, 320	495	465	0,39
Ib	Cl	305, 325	500	475	0,20
Ic	CH_3	305, 320	505	475	0,16
Id	NO_2	325, 340	Does not luminesce		—
IIa	H	320, 335*	Weak reddish luminescence	535	—
IIb	Cl	325, 340*	—	570	—
IIc	CH_3	325, 340*	—	572	—

*Inflection.

band of 2-phenylbenzimidazole [9] and can be assigned to an electron transition localized on the chromophore, which is π-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 (π-isoelectronic with respect to stilbene) chain and therefore affect the transition localized on this chromophore. The same substituents in the 2-(2-tosylaminophenyl)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 (λ_{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

TABLE 2. o-Tosylamino-Substituted 2-Arylbenzimidazoles

Compound	mp, °C	Empirical formula	Found, %		Calc., %		Yield, %
			S	Cl	S	Cl	
Ia	137	$C_{20}H_{17}N_3O_2S$	8,9	—	8,8	—	63
Ib	197—198	$C_{20}H_{16}ClN_3O_2S$	8,2	8,9	8,1	8,8	35
Ic	161	$C_{21}H_{19}N_3O_2S$	8,6	—	8,5	—	55
Id	215	$C_{20}H_{16}N_4O_4S$	7,8	—	7,8	—	35
IIa	226—227	$C_{24}H_{19}N_3O_2S$	7,6	—	7,7	—	58
IIb	235—236	$C_{24}H_{18}ClN_3O_2S$	7,2	7,7	7,1	7,8	50
IIc	221—222	$C_{25}H_{21}N_3O_2S$	7,4	—	7,5	—	49

ZMR-3 mirror monochromator, an FÉU- 18 optical radiation detector, and an M-95 microammeter was used to investigate the fluorescence spectra of toluene solutions (10^{-3} M) and powders; the photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which light with wavelength 313 nm was isolated with a DMR-4 quartz monochromator. The spectra thus obtained were scaled with allowance for the spectral sensitivity of the apparatus. The absolute fluorescence quantum yields were determined by the equal absorption method [11].

Synthesis of o-Tosylamino-substituted 2-Arylbenzimidazoles. A 3.1-g (0.01 mole) sample of tosylanthranylyl chloride or 3.6 g (0.01 mole) of 2.3-tosylaminonaphthoyl chloride was added at 50° in the course of 10 min to a solution of 0.01 mole of substituted o-phenylenediamine in 50 ml of DMF, and the mixture was refluxed for 3 h. It was then cooled to room temperature and poured into 800 ml of a mixture of water and ice. After 30 min, the liberated oil was converted to a crystalline precipitate, which was removed by filtration, washed with 250 ml of hot water, and crystallized from a suitable solvent. The melting points and results of elementary analysis of the newly synthesized compounds are presented in Table 2.

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