SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 2-(2'-TOSYLAMINOPHENYL)BENZIMIDAZOLE AND ITS SUBSTITUTED DERIVATIVES

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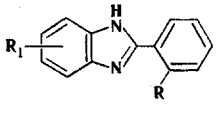
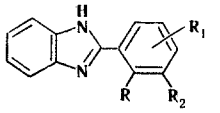
Tosylamino-substituted 2-arylbenzimidazoles have blue or green fluorescence in the crystalline state and in toluene at room temperature. The effect of the substituents on the position of the absorption and fluorescence bands and on the strength of the intramolecular hydrogen bond was investigated. An anomalously large Stokesian shift within the limits 8800-11450 cm^{-1} is characteristic for compounds that contain an o-tosylamino group.

We have previously described 2-(2'-tosylaminophenyl)benzimidazoles Ia-d, which contain substituents in the 4(5) position of the benzimidazole fragment [1]. A study of the spectral-luminescence properties of these compounds demonstrated the presence in them of an anomalously large Stokesian shift of the fluorescence spectrum and a substantial dependence of the spectral characteristics on the electronic nature of the incorporated substituents.

The subject of the present communication is the synthesis and study of the spectral-luminescence properties of 2-(2'-tosylaminophenyl)benzimidazoles IIa-c, which contain substituents in the phenyl fragment of the molecules:



Ia-d

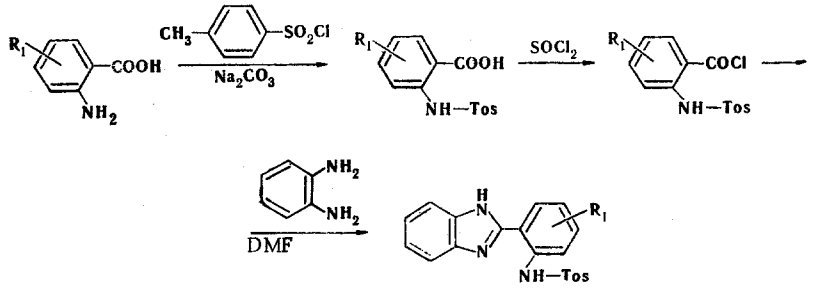


IIa-h

I a R=NH-Tos*, R_1=H; b R=NH-Tos, R_1=Cl; c R=NH-Tos, R_1=CH_3; d R=NH-Tos, R_1=NO_2; II a R=NH-Tos, R_1=4-Br, R_2=H; b R=NH-Tos, R_1=5-Br, R_2=H; c R=NH-Tos, R_1=4-NH_2, R_2=H; d R=NH-Tos, R_1=5-NH_2, R_2=H; e R=NH-Tos, R_1=4-NO_2, R_2=H; f R=NH-Tos, R_1=5-NO_2, R_2=H; g R=R_1=H, R_2=NH-Tos; h R=R_2=H, R_1=NH-Tos

For comparison, we also synthesized IIg,h, which contain a tosylamino group in the meta and para positions of the phenyl ring and do not contain a hydrogen bond.

Compounds II were synthesized by our previously described method [1] in conformity with the scheme.



*Tos = $SO_2C_6H_4CH_3$.

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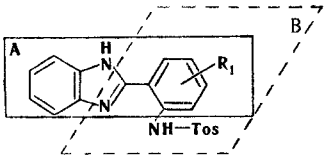
TABLE 1. Spectral Characteristics of 2-Tosylamino-Substituted 2-Arylbenzimidazoles

Compound	Absorption in toluene, λ_{max}, nm	Luminescence		$\Delta\nu$, cm^{-1}
		λ_{max} in toluene, nm	λ_{max} in powders, nm	
Ia	300,320	495	465	11250
Ib	305,325	500	475	10770
Ic	305,320	505	475	11450
Id	325,340	—	—	—
IIa	305,330	515	485	10900
IIb	305,320	505	475	11450
IIc	305,330	465	455	8000
IId	305,340	—	—	—
IIe	325,370	575	—	9600
IIf	305,315	—	—	—
IIg	310	—	455	—
IIh	310	—	455	—

A comparison of the absorption spectra of substituted 2-(2'-tosylaminophenyl)benzimidazoles I and II shows that the substituent effect is manifested more markedly for II than for I (Table 1). Two bands that differ little with respect to their intensities are displayed distinctly in the absorption spectra of II. As in the case of I, the short-wave band is similar in position and intensity to the band of 2-phenylbenzimidazole, and we assigned it to an electron transition localized on chromophore A, which is π-isoelectronic with respect to stilbene [1]. One might have expected that this band would be sensitive



only to the effect of substituents conjugated with the chromophore responsible for its origin, i.e., those in the 4(5) or 4' positions. In fact, the nitro group has the greatest effect when it is in the positions indicated above (Id and IIe). A comparison of the spectra of I and II with the spectra of IIg and IIh shows that only one absorption band is observed in the spectra of the latter. The development of a long-wave band is consequently not only a consequence of the presence of a tosylamino group but is also due to the position of this group.

In conformity with the opinions expressed in the literature [2-5], we assume that the long-wave absorption band is due to intramolecular charge transfer from the nitrogen atom of the tosylamino group to the heterocyclic C=N group. This transition is localized on chromophore B, which includes a ring with an intramolecular hydrogen bond. The role of the hydrogen bond reduces to an increase in the polarization of the system, which facilitates charge transfer. The validity of the interpretation of the absorption bands presented above is confirmed by their similarity to the absorption spectrum of N-(2-tosylaminobenzylidene)aniline, which is π-isoelectronic with respect to 2-(2'-tosylaminophenyl)-benzimidazole. Two bands with maxima at 320 and 332 nm are observed in the absorption spectrum of the former [6]. An additional confirmation of the correctness of regarding the long-wave absorption band of Ia-d and IIa-f as a band of transfer of charge localized on chromophore B is the dependence of its position on the character of the effect of the substituents. The substituents in the 4' position of the phenyl ring (IIa,c,e) and in the 4(5) position of the benzimidazole fragment (Ib-d) are not conjugated with the tosylamino group and may affect the ease of charge transfer only by means of a change in the electron density on the nitrogen atom of the C=N group. An inductive effect on the tosylamino group from the 4' position is also possible. The long-wave band of chromophore B is shifted bathochromically in the absorption spectra of all of these compounds, regardless of the electronic nature of the substituent. For example, the nitro group by decreasing the basicity of the heteroring nitrogen atom weakens the intramolecular hydrogen bond giving rise to a significant bathochromic shift of the long-wave band (20 and 50 nm, respectively, for Id and IIe relative to Ia). This effect is not so great in the case of other substituents, and the red shift of the long-wave band is therefore smaller.

TABLE 2. Characteristics of IIa-h

Compound	mp, °C	S found, %	Empirical formula	S calc., %	Yield, %
IIa	241—242	7,2	$C_{20}H_{16}BrN_3O_2S$*	7,2	27
IIb	234—235	7,2	$C_{20}H_{16}BrN_3O_2S$*	7,2	33
IIc	262	8,2	$C_{20}H_{18}N_4O_2S$	8,5	42
IId	260—262	8,2	$C_{20}H_{18}N_4O_2S$	8,5	35
IIe	314	7,6	$C_{20}H_{16}N_4O_4S$	7,8	45
IIf	292—293	7,9	$C_{20}H_{16}N_4O_4S$	7,8	40
IIg	253—255	8,8	$C_{20}H_{17}N_3O_2S$	8,8	55
IIh	289—290	8,8	$C_{20}H_{17}N_3O_2S$	8,8	60

*Found: Br 18.0%. Calculated: Br 18.1%.

Substituents in the 5' position (IIb,d,f) are conjugated with the tosylamino group and by affecting the electron density on the nitrogen atom of this group facilitate or hinder charge transfer. Taking this explanation into account, the bathochromic effect exerted by the amino group (IId) and the hypsochromic effect of the nitro group (IIf) become understandable. Similar character of the effect of substituents on the position of the long-wave band was also noted in the spectra of substituted N-(2-tosylaminobenzylidene)aniline [7] and 2-(2'-tosylaminophenyl)benzoxazole [8].

The overwhelming majority of the substituted 2-(2'-tosylaminophenyl)benzimidazoles fluoresce at room temperature in solutions and in the crystalline state; an anomalously large Stokesian shift (8800-11500 cm^{-1}), the reason for which, in our opinion, is the energy expended in migration of the proton along the coordinates of the hydrogen bond in the ground and excited nonequilibrium states, is observed in this case. The fluorescence spectra are characterized by one band with a distinctly expressed maximum. Depending on the structures of IIa-f, the position of the emission maxima of toluene solutions of these compounds range from 465 to 575 nm, and the quantum yields range from 0.1 to 0.25.

Retention of fluorescence in the case of IIe (λ_{max} of the long-wave absorption band is found at 370 nm) is interesting. The Lippert rule, in accordance with which only those nitro compounds with long-wave absorption bands that are shifted bathochromically to above 500 nm can fluoresce [9], is not adhered to in this case. As in [10], we assume that the singlet $S_{\pi,\pi}$ level that develops owing to migration of the proton in the excited state is lower than the $T_{n,\pi}$ level and that quenching of the fluorescence becomes impossible. At the same time, in the case of Id and IIf, the long-wave absorption bands of which are located in a shorter-wave region than those of IIe, a relative orientation of the levels favorable for retention of fluorescence is not achieved. The ability of IIe to fluoresce provides us with the possibility of estimating the extent to which the lower excited level is lowered owing to migration of the proton. In this case this value, which corresponds to strengthening of the hydrogen bond in the excited state, is 20 kcal/mole.

The fluorescence maximum is shifted bathochromically as the intramolecular hydrogen bond becomes weaker in the ground equilibrium state, and an increase in the Stokesian shift as compared with unsubstituted 2-(2'-tosylaminophenyl)benzimidazole (IIa,e) is observed. Strengthening of the intramolecular hydrogen bond under the influence of, for example, the amino group shifts the fluorescence maximum hypsochromically, while the Stokesian shift displays a tendency to decrease (IIc). The decrease in the Stokesian shift as the intramolecular hydrogen bond becomes stronger constitutes evidence that a decrease in the energy expended in migration of the proton is observed in the excited state.

Compounds IIg,h, which do not contain an intramolecular hydrogen bond, do not fluoresce in solutions at room temperature.

EXPERIMENTAL

The substituted anthranilic acids necessary for the synthesis were obtained by known methods: 4-bromo [11], 5-bromo [12], 4-nitro [13], and 5-nitro [14]. The yields, melting points, and results of elementary analysis of IIa-h are presented in Table 2.

The absorption spectra of 2-(2'-tosylaminophenyl)benzimidazole and its substituted derivatives in toluene ($3 \cdot 10^{-5}$ M solutions) were measured with an SF-4 spectrophotometer.

A setup consisting of a ZMR-3 mirror monochromator, an FÉU-18 optical emission detector, and an M-95 microammeter was used to investigate the fluorescence spectra of toluene solutions ($c = 10^{-3}$ M) and powders. Photoluminescence was excited with an SVDSh-500 lamp, from the spectrum of which the exciting light with a wavelength of 313 nm was isolated with a DMR-4 quartz monochromator. The spectra obtained were corrected with allowance for the spectral sensitivity of the setup. The absolute fluorescence quantum yields were determined by the equal-absorption method [15].

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VINYLATION OF 3-PYRIDAZONES

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The vinylation of 3-pyridazones through a step involving the production of 2-hydroxy- and 2-chloroethyl-substituted compounds with subsequent dehydrochlorination, as well as vinylation by means of vinyl acetate, in all cases leads only to N-vinyl derivatives.

Depending on the direction of reactions of compounds with a pyridazine ring that display lactam–lactim tautomerism, one can obtain isomers that differ with respect to their properties. Their pesticidal [1] and pharmacological [2] activity provides a basis for the assumption that the unsaturated derivatives of such substances are promising products in the creation of preparations with prolonged action. They are also of interest for the chemistry of high-molecular-weight compounds [3]. The aim of the present research was therefore to study the direction of vinylation reactions of pyridazone and its derivatives.

The synthesis of unsaturated pyridazine derivatives by vinylation of pyridazines with acetylene under pressure has been reported [4]. Vinylation with vinyl acetate or vinyl alkyl ethers in the presence of divalent mercury salts is also possible. Vinyl derivatives

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