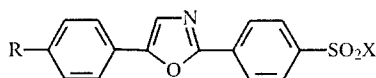


# 4-(5-ARYL-2-OXAZOLYL)BENZENESULFONIC ACID DERIVATIVES CONTAINING A DIMETHYLAMINO GROUP

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*Condensation of 4-chlorosulfonyl- and 4-fluorosulfonyl-benzoyl chlorides with p-dimethylamino- $\alpha$ -aminoacetophenone followed by cyclodehydration of the resulting amides leads to the formation of 4-(5-dimethylamino-phenyl-2-oxazolyl)benzenesulfonyl halides, and the corresponding sulfonic ester, sulfomorpholide, sulfonamide, and sodium salt are synthesized from them. The spectral and luminescence properties of the compounds synthesized have been studied in toluene, ethanol, and DMF. The ability of the sulfonyl group to transmit the electronic effects of the substituents on it to the overall molecular  $\pi$ -electron system of 2,5-diaryloxazole has been demonstrated. Solvation fluorochromia has been detected in polar solvents. In some of the compounds studied the Stokes shift exceeds 200 nm.*

In our previous study [1] on the spectral and luminescence properties of 4-(5-aryl-2-oxazolyl)benzenesulfonic acid derivatives of type A



A

R = H, OMe, Ph; X = Cl, F, OMe, NH<sub>2</sub>

we put forward the suggestion that the sulfonyl group is able to transmit the electronic effects of the substituents introduced into it to the overall molecular  $\pi$ -electron system of 2,5-diaryloxazole. In order to support this hypothesis we synthesized a number of compounds (I-VI) containing the dimethylamino group — a strong electron-donating substituent — at the para position of the 5-phenyl group.

The synthesis was carried out by reaction of p-dimethylamino- $\alpha$ -aminoacetophenone hydrochloride with 4-chlorosulfonyl- or 4-fluorosulfonyl-benzoyl chlorides followed by cyclization of the resulting amides (VII, VIII) in phosphorus oxychloride. The halosulfonyl derivatives I and II thus obtained were converted to the ester III, morpholide IV, amide V, or sodium salt VI on treatment with methanol, morpholine, ammonia, or sodium hydroxide, respectively.

The spectral and luminescence characteristics of the compounds synthesized are given in Table 1, and data on the previously obtained 5-(4-dimethylaminophenyl)-2-(4-difluoromethylsulfonylphenyl)oxazole (IX) [2] and 5-(4-dimethylamino-phenyl)-2-phenyloxazole (X) [3] are listed for comparison.

As expected, the introduction of a strong donating substituent — the dimethylamino group — into the 5-phenyl group caused considerable polarization of the molecular  $\pi$ -electron system, and as a result there was a shift to longer wavelength of the bands in the electronic spectra of these compounds compared to the previously reported products [1].

Variation of the substituent X in the sulfonyl residue of the molecule also quite clearly manifests itself in the spectra. Comparison of the electronic absorption spectra of compounds I-VI and IX in toluene shows that the electron-withdrawing

TABLE 1. Spectral and Luminescence Characteristics of Compounds I-VI, IX, and X

Com- pound	Absorption, $\epsilon$ , $\lambda_{\max}$ , nm ( $\epsilon \cdot 10^{-3}$ )			Fluorescence, $\lambda_{\max}$ , nm ( $\eta$ )		
	toluene	ethanol	DMF	toluene	ethanol	DMF
I	295 (18,5) 410 (20,0)	285 (17,2) 380 (18,6)	275 (16,2) 360 (32,4)	—	520 (0,1) 560 shld.	495 (0,5) 570 shld.
II	290 (19,8) 400 (24,4)	290 (22,0) 400 (22,6)	290 (21,9) 405 (23,9)	513 (0,56)	660 w. lum.	660 w. lum.
III	285 (18,2) 385 (26,9)	285 (20,0) 385 (24,5)	285 (20,0) 387 (25,8)	485 (0,5)	600 (0,27)	580 (0,67)
IV	380 (29,5)	255 (19,8) 380 (25,8)	—	475 (0,54)	590 (0,99)	—
V	280 (fluct) 375 (fluct)	280 (17,0) 370 (22,0)	280 (16,3) 375 (24,1)	465 (0,54)	567 (0,43)	567 (0,90)
VI	—	275 (15,4) 360 (27,0)	—	—	505 (0,59)	—
IX	398 (18,8)	288 398	398	505 (0,52)	640	655
X	348 (29,0)	347 (30,0)	—	417 (0,6)	470 (0,6)	—

TABLE 2. Physicochemical Properties of Compounds I-VI

Com- pound	Empirical formula	mp, °C	IR spectrum, $\text{cm}^{-1}$			Yield, %
			$\nu_{\text{C=N}}$	$\nu^{\text{s}}_{\text{S=O}}$	$\nu^{\text{as}}_{\text{S=O}}$	
I	C <sub>17</sub> H <sub>15</sub> ClN <sub>2</sub> O <sub>3</sub> S	173...174	1610	1180	1390	52
II	C <sub>17</sub> H <sub>15</sub> FN <sub>2</sub> O <sub>3</sub> S	212...213	1605	1212	1400	58
III	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>4</sub> S	168...169	1610	1190	1359	70
IV	C <sub>21</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub> S	223...224	1610	1175	1340	75
V	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S	245...246	1610	1157	1320	65
VI	C <sub>17</sub> H <sub>15</sub> N <sub>2</sub> O <sub>4</sub> SNa	> 300	1610	1055	1185	50

the quantum yield decreases. At the same time the absorption spectra are virtually unchanged in comparison with the spectra in toluene. It is clear that in ethanol a hydrogen bond is formed between the molecules of the compound in an excited state and the solvent molecules [5].

It should be noted that compound I, which contains the SO<sub>2</sub>Cl group, fluoresces in polar solvents but not in toluene. Fluorescence quenching by the SO<sub>2</sub>Cl group was recorded previously [1] in compounds of a similar structure but not containing a dimethylamino group. Quantum-chemical calculations [4] showed that for sulfonyl chlorides the main channel of deactivation of the electronically excited state is intersystem crossing. Polar solvents considerably reduce the energy of the S<sub>1</sub>( $\pi\pi^*$ ) level of compound I, which makes it possible for fluorescence to occur.

## EXPERIMENTAL

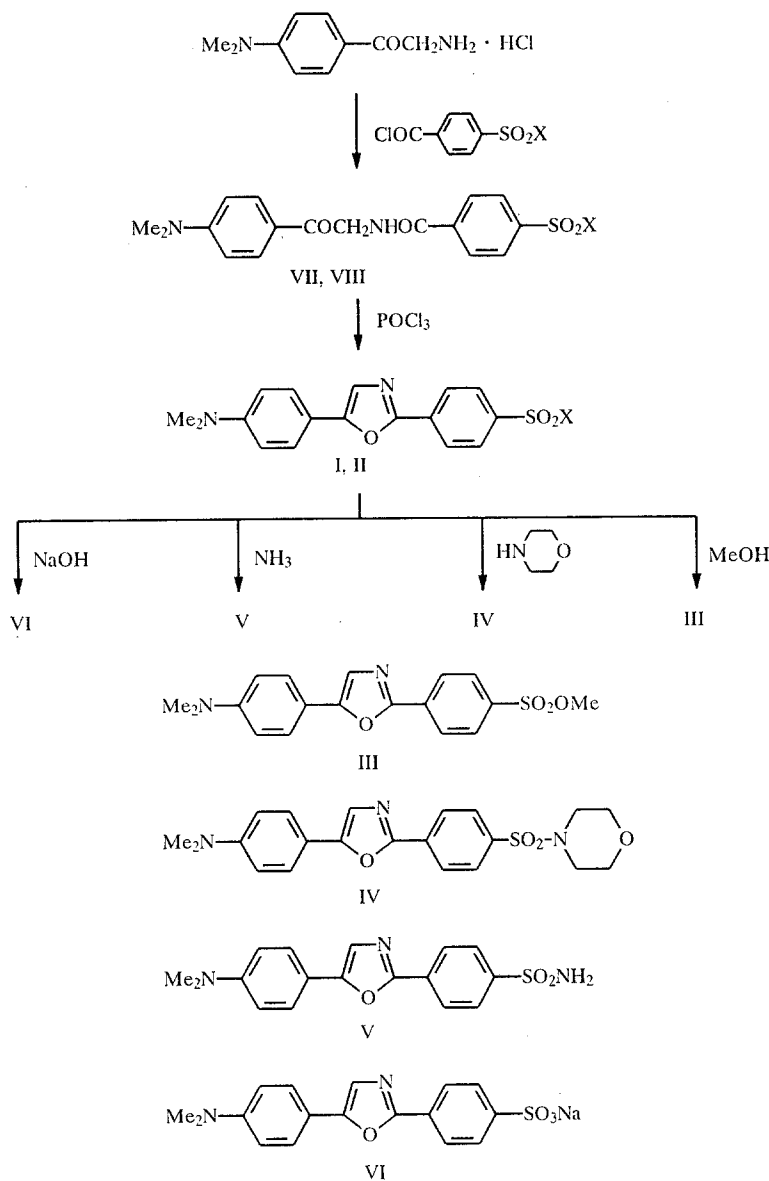
IR spectra were recorded on a Specord-75 IR instrument as KBr disks. The absorption spectra were recorded on a Specord M-40 instrument. Luminescence spectra were recorded on equipment consisting of a ZMR-3 reflecting monochromator, FÉU-18 optical radiation detector, and M-95 microammeter. Photoluminescence was induced with a SVDSH-500 lamp, from whose spectrum light of wavelength 365 nm was selected by a DMR-4 quartz monochromator. The absolute quantum yields of fluorescence were determined by the equal absorption method of [6].

The properties of the compounds prepared are given in Table 2.

The elemental analysis data for Cl (F), N, and S corresponded to the calculated values.

**4-(5-Dimethylaminophenyl-2-oxazolyl)benzenesulfonyl Chloride (I) and 4-(5-Dimethylaminophenyl-2-oxazolyl)benzenesulfonyl Fluoride (II).** To a solution mixture of 15 mmoles of the respective halosulfonylbenzoyl chloride in 50

substituents Cl, F, and CHF<sub>2</sub> give rise to a more pronounced shift to longer wavelength than the donor substituents OCH<sub>3</sub>, morpholinyl, and NH<sub>2</sub>. These effects can be seen even more clearly when the fluorescence spectra are compared.



Thus, compounds II, VI, and IX, which contain the withdrawing groups SO<sub>2</sub>F and SO<sub>2</sub>CHF<sub>2</sub>, fluoresce in the green region of the spectrum, while compounds III-V with donor substituents fluoresce in the blue region. In the latter case the relationship between the position of the fluorescence maximum and the donating capacity of the substituent is very clear. On the basis of these data it may be asserted that the sulfonyl group is not an insulating bridge but is quite effectively involved in the overall molecular  $\pi$ -electron system of the 2,5-diaryloxazole and transmits to this system the electronic effects of the substituents attached to it. We came to a similar conclusion in [4] on the basis of quantum-chemical calculations carried out on the same molecular structures. According to these calculations, the long-wavelength band in the adsorption spectra of sulfonyl-substituted oxazoles is derived from a  $\pi\pi^* S_0 \rightarrow S_1^*$  transition. In this case the SO<sub>2</sub>X group participates in conjugation with the electron system of the 2,5-diaryloxazole through a significant contribution of the 3s and 3p<sub>z</sub> of the sulfur atom and the 2p<sub>z</sub> orbitals of the oxygen atoms. Thus, the substituent effect is transmitted not only via the  $\pi$ -system but also via the  $\sigma$ -bonds, which is due to the nonplanar structure of the sulfonyl group.

The compounds studied exhibit a positive solvation fluorochromia effect on changing to more polar solvents. While the absorption spectra change only slightly on going from toluene to ethanol and DMF, the maxima of the fluorescence spectra are shifted by 100 nm or more to longer wavelength. The previous trend is maintained — substituents that intensify the withdrawing properties of the sulfonyl group (I, II, IX) have a stronger effect on the spectra than those that weaken its acceptor capacity (III-V). In ethanol the fluorescence spectra for all compounds are in the form of a broad structureless band, and in almost all cases

ml of benzene and 1 mmole of p-dimethylamino- $\alpha$ -aminoacetophenone hydrochloride in 150 ml of water was added dropwise at 2-5°C and with vigorous agitation a 10% solution of NaHCO<sub>3</sub> until a weak alkaline reaction was given with litmus. The precipitate of amides VII or VIII which formed after 2 h standing were filtered off, dried, and refluxed for 1 h in a fivefold excess (by weight) of phosphorus oxychloride. The reaction mixture was cooled, poured onto ice, dried, and crystallized from benzene.

**Methyl 4-(5-Dimethylaminophenyl-2-oxazoly)benzenesulfonate (III).** To a suspension of 1 mmole of acid chloride I in a tenfold excess of methanol was added dropwise with vigorous agitation an equimolar quantity of a 10% solution of NaOH, and the mixture was left to stand for 1 h and then poured into water. The precipitate of III was filtered off, washed with water, dried, and recrystallized from toluene.

**4-(5-Dimethylaminophenyl-2-oxazoly)benzenesulfomorpholide (IV).** Compound I (1 mmole) was dissolved in dioxane on heating, excess morpholine was added, and the mixture was refluxed for 0.5 h. After cooling, the reaction mixture was poured into water, and the precipitate of IV was filtered off, dried, and crystallized from a heptane–benzene (1:1) mixture.

**4-(5-Dimethylaminophenyl-2-oxazoly)benzenesulfonamide (V).** This was obtained in a similar manner to compound IV from 1 mmole of acid chloride I and ammonia. The product was crystallized from isopropyl alcohol.

**Sodium 4-(5-Dimethylaminophenyl-2-oxazoly)benzenesulfonate (VI).** Compound I (1 mmole) was refluxed in a tenfold quantity of 10% NaOH for 1 h. After cooling, the precipitate of VI was filtered off, washed with cold water, and crystallized from water.

## REFERENCES

1. B. M. Krasovitskii, V. M. Shershukov, I. A. Fedyunyaeva, T. A. Distanova, and A. L. Shakhnovich, *Zh. Org. Khim.*, **24**, 1298 (1988).
2. B. M. Krasovitskii, V. M. Shershukov, and L. M. Yagupol'skii, *Khim. Geterotsikl. Soedin.*, No. 8, 1042 (1982).
3. B. M. Krasovitskii, I. A. Fedyunyaeva, V. M. Shershukov, and L. D. Patsenker, *Luminescent Organic Materials: Collection of Scientific Transactions* [in Russian], VNI Monokristallov, Khar'kov (1989), No. 24, p. 57.
4. G. V. Maier, V. M. Shershukov, O. K. Bazyl', A. A. Karypov, V. Ya. Artyukhov, and I. A. Fedyunyaeva, *Zh. Prikl. Spektrosk.*, **55**, 576 (1991).
5. O. V. Sverdlova, *Electronic Spectra in Organic Chemistry* [in Russian], Khimiya, Moscow (1983), p. 170.
6. A. S. Cherkasov, *Zh. Fiz. Khim.*, **29**, 2209 (1955).