HALOGEN-SUBSTITUTED 2-(2'-ARENESULFONYLAMINOPHENYL)-4H-1,3-BENZOXAZ-4-ONES

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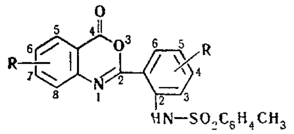
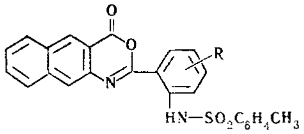
Chloro- and bromo-substituted 2-(2'-tosylaminophenyl)-4H-1,3-benzoxaz-4-ones and 2-(2'-tosylaminophenyl)-4H-naphtho[2,3-d]-1,3-oxaz-4-ones, their absorption spectra at room temperature, and their luminescence spectra at 77 deg K are described.

We have previously shown that 2-(2'-arenesulfonylaminophenyl)-4H-1,3-benzoxaz-4-ones [1] and their naphthyl analogs [2] have intense luminescence and that the nature of the acyl residue appreciably affects the position of the luminescence maximum [3].

In order to elucidate the effect of substituents on the luminescence properties, we synthesized a number of 2-(2'-tosylaminophenyl)-4H-1,3-benzoxaz-4-ones and 2-(2'-tosylaminophenyl)-4H-naphth[2,3-d] [1, 3]-oxaz-4-ones with substituents at various positions.

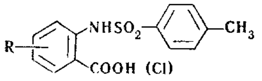




This communication is devoted to an investigation of halogen-substituted benzoxazones and naphthoxazones (R = Cl, Br).

The halogen-substituted N-tosylanthranilic acids and their acid chlorides (Table 1) were obtained by the method recommended for unsubstituted N-tosylanthranilic acid [4]. It should be noted that the acid chlorides synthesized are unstable and are partially converted to benzoxazoles on prolonged storage. The 2-(N-Tosylanthranoylamino)-3-naphthoic and tosylanthranoylanthranilic acids were obtained by acylation of 2-amino-3-naphthoic, anthranilic, or substituted anthranilic acids with the acid chlorides of the appropriate N-tosylanthranilic acids in glacial acetic acid [5] (Tables 2 and 3).

TABLE 1. Substituted Tosylanthranilic Acids and Their Acid Chlorides



Compound	R	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
I	5-Br	201[a]	$C_{14}H_{12}BrNO_4S$	45,28	3,15	3,60	45,42	3,26	3,78	83
II	4-Br	203[a]	$C_{14}H_{12}BrNO_4S$	45,60	3,55	3,56	45,42	3,26	3,78	87
III	5-Cl	206[b]	$C_{14}H_{12}ClNO_4S$	51,96	4,10	4,42	51,64	3,71	4,29	61
IV	4-Cl	203[b]	$C_{14}H_{12}ClNO_4S$	52,00	3,43	4,24	51,64	3,71	4,29	52
V	5-Br	123[c]	$C_{14}H_{11}BrClNO_3S$	43,36	2,83	3,68	43,26	2,85	3,60	51
VI	4-Br	122[c]	$C_{14}H_{11}BrClNO_3S$	43,34	3,12	3,69	43,26	2,85	3,60	89
VII	5-Cl	138[d]	$C_{14}H_{11}Cl_2NO_3S$	48,56	3,53	3,87	48,85	3,22	4,06	72
VIII	4-Cl	155[e]	$C_{14}H_{11}Cl_2NO_3S$	49,10	3,55	3,82	48,85	3,22	4,06	77

[a, e] From benzene. [b] From alcohol–water. [c] From heptane. [d] From hexane–benzene.

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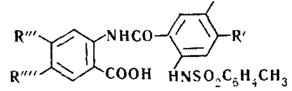
TABLE 2. Substituted Tosylanthranoylanthranilic Acids

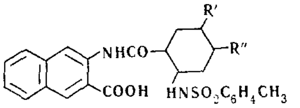


Compound	R′	R″	R‴	R⁗	Mp, °C	Empirical formula	S, % Found	S, % Calc.	Yield, %
IX	Br	H	H	H	223[a]	$C_{21}H_{17}BrN_2O_5S$	6,24	6,55	64
X	H	Br	H	H	216[a]	$C_{21}H_{17}BrN_2O_5S$	6,59	6,55	72
XI	H	H	Br	H	212[b]	$C_{21}H_{17}BrN_2O_5S$	6,99	6,55	97
XII	H	H	H	Br	214[b]	$C_{21}H_{17}BrN_2O_5S$	6,25	6,55	85
XIII	Cl	H	H	H	241[a]	$C_{21}H_{17}ClN_2O_5S$	7,48	7,21	47
XIV	H	Cl	H	H	219[a]	$C_{21}H_{17}ClN_2O_5S$	7,65	7,21	73
XV	H	H	Cl	H	197[a]	$C_{21}H_{17}ClN_2O_5S$	7,18	7,21	73
XVI	H	H	H	Cl	220[a]	$C_{21}H_{17}ClN_2O_5S$	7,43	7,21	45

[a] From acetic acid.

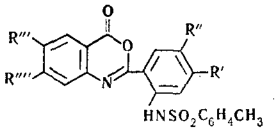
[b] From alcohol–water.

TABLE 3. Substituted 2-(N-Tosylanthranoylamino)-3-naphthoic Acids



Compound	R′	R″	Mp, °C (from acetic acid)	Empirical formula	S, % Found	S, % Calc.	Yield, %
XVII	Br	H	265	$C_{25}H_{19}BrN_2O_5S$	6,05	5,94	55
XVIII	H	Br	252	$C_{25}H_{19}BrN_2O_5S$	6,20	5,94	72
XIX	Cl	H	262	$C_{25}H_{19}ClN_2O_5S$	6,38	6,48	67
XX	H	Cl	266	$C_{25}H_{19}ClN_2O_5S$	6,70	6,48	50

TABLE 4. Substituted 2-(2′-Tosylaminophenyl)-4H-1,3-benzoxaz-4-ones

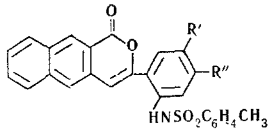


Compound	R′	R″	R‴	R⁗	Mp (from acetic acid)	Empirical formula	Found, % C	Found, % H	Found, % N	Found, % S	Calc., % C	Calc., % H	Calc., % N	Calc., % S	Yield, %
XXI	Br	H	H	H	219	$C_{21}H_{15}BrN_2O_4S$	53,58	3,29		7,17	53,51	3,21		6,80	78
XXII	H	Br	H	H	220	$C_{21}H_{15}BrN_2O_4S$	53,71	3,09		6,70	53,51	3,21		6,80	97,5
XXIII	H	H	Br	H	216	$C_{21}H_{15}BrN_2O_4S$	53,25	3,41		7,11	53,51	3,21		6,80	64
XXIV	H	H	H	Br	216	$C_{21}H_{15}BrN_2O_4S$	53,22	3,74		6,88	53,51	3,21		6,80	52
XXV	Cl	H	H	H	234	$C_{21}H_{15}ClN_2O_4S$	59,17	3,53	6,45		59,08	3,54	6,56		62
XXVI	H	Cl	H	H	221	$C_{21}H_{15}ClN_2O_4S$	59,36	3,76	6,71		59,08	3,54	6,56		74
XXVII	H	H	Cl	H	217	$C_{21}H_{15}ClN_2O_4S$	58,91	3,65	6,37		59,08	3,54	6,56		84
XXVIII	H	H	H	Cl	216	$C_{21}H_{15}ClN_2O_4S$	59,13	3,48	6,24		59,08	3,54	6,56		43

The compounds obtained were converted to benzoxazones by heating with thionyl chloride via the method in [6] (Tables 4 and 5).

All of the synthesized benzoxazones absorb in the UV region of the spectra. Like unsubstituted 2-(2′-tosylaminophenyl)-4H-1,3-benzoxaz-4-one, their spectra consist of three bands with maxima at 220–250, 280–300, and 340–355 mm. The position and intensity of the first two bands remain virtually constant on passing from one compound to the other. The position of the substituents in the benz- and naphthoxazones and replacement of chlorine by bromine do not affect the character of these bands and the position of the

TABLE 5. Substituted 2-(2-Tosylaminophenyl)-4H-naphth[2,3-d]-[1,3]oxaz-4-ones



Compound	R′	R″	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	N	C	H	N	
XXIX	Br	H	287[a]	$C_{25}H_{17}BrN_2O_4S$	57,68	3,15	5,43	57,59	3,28	5,37	65
XXX	H	Br	286[b]	$C_{25}H_{17}BrN_2O_4S$	57,37	3,29	5,39	57,59	3,28	5,37	71
XXXI	Cl	H	266[b]	$C_{25}H_{17}ClN_2O_4S$	62,85	3,56	5,68	62,95	3,59	5,87	55
XXXII	H	Cl	267a	$C_{25}H_{17}ClN_2O_4S$	62,98	3,69	5,67	62,95	3,59	5,87	61

[a] From acetic acid

[b] From dioxane.

TABLE 6. Absorption and Luminescence Spectra of Halogen-Substituted 2-(2'-Tosylaminophenyl)-4H-1,3-benzoxaz-4-ones and 2-(2'-Tosylaminophenyl)-4H-naphth[2,3-d][1,3]oxaz-4-ones

Compound	R	Absorption in DCE		Luminescence, λ_{max}, nm		
		λ_{max}, nm	ε	DCE	Dioxane	DMFA
	H	336	15000	534	529	529
XXVII	6-Cl	344	11950	544	521	532
XXIII	6-Br	345	10160	542	525	536
XXVIII	7-Cl	345	14210	550	547	542
XXIV	7-Br	346	13750	543	524	536
XXVI	5′-Cl	345	10090	549	522	542
XXII	5′-Br	346	12220	547	523	542
XXV	4′-Cl	339	17320	533	537	523
XXI	4′-Br	346	9060	542	528	546
XXXI	H	349	17450	550	546	547
XXIX	5′-Cl	352	16330	565	556	559
XXXII	5′-Br	352	15440	563	544	557
XXX	4′-Cl	351	25170	551	548	522
	4′-Br	354	14700	562	545	557

Note: DCE: dichloroethane; DMFA: dimethylformamide.

absorption maximum. An exception is observed on passing from benzoxazones to naphthoxazones. In this case, the intensity of the second band increases sharply. The long wave band is the most sensitive to the substituent effect (Table 6). The introduction of halogens into different positions of the benzoxazone molecule causes a bathochromic shift of the maximum of this band by 8-10 nm. Chlorine in the 4'-position has the smallest effect (+ 3 nm).

The very development of a long-wave band is apparently associated with the presence of a strong intramolecular hydrogen bond (IHB) in these compounds.* Compounds in which the formation of an IHB is impossible – 2-phenyl- and 2-[2'-(N-methyl-N-tosylamino)phenyl]-4H-1,3-benzoxaz-4-one – do not absorb in this region of the spectrum.

All of the halogen-substituted benz- and naphthoxazones have intense luminescense in the crystal state and in frozen solutions. In comparison with 2-(2'-tosylaminophenyl)-4H-1,3-benzoxaz-4-one, frozen solutions of the chloro- and bromobenzoxazones in dichloroethane have a bathochromically shifted luminescense maximum. No definite regularities associated with the position of the halogen are observed in the majority of cases, but chlorine in the 4' position causes the smallest shift.

The nature of the solvent appreciably affects the position of the absorption maximum. In comparison with a dichloroethane solution, the maxima in dioxane and dimethylformamide are shifted hypsochromically. This fact can be explained by interaction of the solvent with the compound, resulting in weakening of the IHB. Triethylamine has a particularly strong effect: solutions in it have blue luminescence. Since 2-phenyl- and

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*The markedly diffuse NH vibrations band, which is shifted to lower wave numbers in the IR spectra attests to the existence of a strong IHB.

2-[2'-(N-methyl-N-tosylamino)phenyl]-4H-1,3-benzoxaz-4-one, for which the formation of an IHB is impossible, also luminescence in the blue region of the spectrum, it can be assumed that the pronounced hypsochromic shift of the luminescence maximum in triethylamine is due to rupture of the IHB.

EXPERIMENTAL

Substituted N-Tosylanthranilic Acids (I-IV). The substituted anthranilic acid (0.02 mole) was added in three portions with stirring to a solution (heated to 60 deg C) of 5.65 g (0.05 mole) of calcined sodium carbonate in 60 ml of water. p-Toluenesulfonyl chloride [4.71 g (0.0248 mole)] was then added to it at the same temperature in the course of 20 min. The reaction mixture was then held at 60-70 deg for 30 min, cooled to room temperature, and neutralized to pH 4 with 6 N hydrochloric acid. The product was crystallized from a suitable solvent (Table 1).

Substituted Tosylanthranoyl Chlorides (V-VIII). A mixture of 0.007 mole of substituted tosylanthranilic acid, 8.3 g (0.007 mole) of thionyl chloride, and 50 ml of benzene was refluxed for 1-1.5h. The acid dissolved completely in the process. The benzene and excess thionyl chloride were removed in vacuo, and the residue was recrystallized (Table 1).

Substituted Tosylanthranoylanthranilic and 2-(N-Tosylanthroylamino)-3-naphthoic Acids (IX-XX). The acid chloride (0.11 mole) of the appropriate tosylanthranilic acid was added in several portions to a mixture of 0.01 mole of amino acid and 0.01 mole of anhydrous sodium acetate in 20 ml of glacial acetic acid at 50-60 deg. The mixture was stirred for 2 h, and the resulting precipitate was recrystallized (Tables 2 and 3).

2-(2'-Tosylaminophenyl)-4H-1,3-benzoxaz-4-one and 2-(2'-Tosylaminophenyl)-4H-naphth[2,3-d][1,3]oxaz-4-ones. A mixture of 0.1 mole of tosylanthranoylanthranilic acid or 2-(N-tosylanthranoylamino)3-napthoic acid and 1 mole of thionyl chloride was refluxed for 30 min. After cooling the reaction mass, the benzoxazone was precipitated with heptane or hexane and recrystallized (Tables 4 and 5).

The absorption spectra were investigated at room temperature with an SF-4 spectrophotometer with dichloroethane as the solvent.

The luminescence spectra were determined at 77 deg K with an ISP-51 spectrograph with an FEP-1 adapter. Excitation was achieved with a PRK-4 lamp (365 nm). An FÉU-17 photomultiplier served as the detector. The spectra were corrected, allowing for the spectral sensitivity of the apparatus.

LITERATURE CITED

1. British Patent No. 1,070,326; Chem. Abstr. 68, 59, 592.
2. B. M. Bolotin, M. V. Loseva, V. G. Brudz', and N. I. Chernova, USSR Author's Certificate No. 230,353; Byull. Izobr., 34, 75 (1968).
3. B. M. Bolotin, Yu. S. Ryabokobylko, D. A. Drapkina, and V, G. Brudz' Khimreaktivy i Preparaty. Trudy IREA, 27, 289 (1965).
4. B. M. Bolotin, V. G. Brudz', D. A. Drapkina, and Yu. S. Ryabokobylko, Prom. khimreaktov i Osobo Chistykh Veshchestv, 4, 23 (1965).
5. L. M. Litvinenko, D. M. Aleksandrova, and G. D. Titskii, Ukr. Khim. Zh., 28, 77 (1962).
6. G. Schroeter and O. Eisleb, Ann., 367, 101 (1909).