NITRO-SUBSTITUTED 2-PHENYL- AND 2-(2-TOSYLAMINOPHENYL)-4H-3,1-BENZOXAZIN-4-ONE

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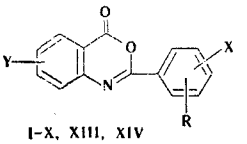
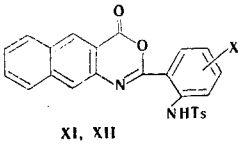
Nitro-substituted 2-phenyl- and 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-ones were synthesized. The UV, IR, and luminescence spectra were studied. The position of the nitro group affects the strength of the intramolecular hydrogen bond (IHB). The luminescence properties of nitro-substituted 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-ones are associated with the strength of the IHB. The luminescence maximum is shifted to the short-wave region as the IHB becomes stronger.

We have previously [1-3] synthesized chloro-, bromo-, and methoxy-substituted 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-ones. A study of the IR spectra of these compounds demonstrated that the strength of the intramolecular hydrogen bond (IHB) depends to a considerable degree on the character and position of the substituents. The IHB also affects the luminescence properties. In a series of methoxy-substituted compounds, the luminescence maximum is shifted to the short-wave region as the IHB becomes stronger. In order to further study the effect of substituents on the electronic spectra of compounds of this series, we synthesized benzoxazinones (II-V) and naphthoxazinones (XI and XII) containing nitro groups in various positions. For comparison, we synthesized a number of nitro-substituted 2-phenyl-4H-3,1-benzoxazin-4-ones without IHB (VII-X). In the present paper, we present data on the IR and electronic spectra of the compounds obtained.



I-X, XIII, XIV



XI, XII

I-V R=NHTs; XIII R=3-NHTs; XIV R=4-NHTs; II, VII, XI X=5-NO_2; III, VIII, XII X=4-NO_2; IV, IX Y=7-NO_2; V, X Y=6-NO_2

IR Spectra. The ν_{NH} frequencies of nitro-substituted compounds are presented in Table 1. The strength of the IHB depends on two factors: the lability of the hydrogen of the tosylamino group and the basicity of the heterocyclic nitrogen. Compound II has a stronger IHB than I, which is associated with an increase in the lability of the hydrogen of the tosylamino group. Weakening of the IHB occurs in IV because of the decrease in the basicity of the heterocyclic nitrogen under the influence of the negative inductive effect of the nitro group. In addition, the nitro group, which is in conjugation with the keto group of the heteroring, intensifies its acceptor effect as a result of which the electronic density of the heteroring as a whole and, consequently, of the nitrogen is reduced. The nitro group in V is conjugated with the heterocyclic nitrogen, which leads to a decrease in its basicity. In addition, the effect of the keto group on the heteroring increases under the influence of the inductive effect of the nitro group. For these reasons, the IHB in V is markedly weakened. A similar effect might have been expected for III. However, even a slight strengthening of the IHB is observed for III. This is explained by two effects of the nitro

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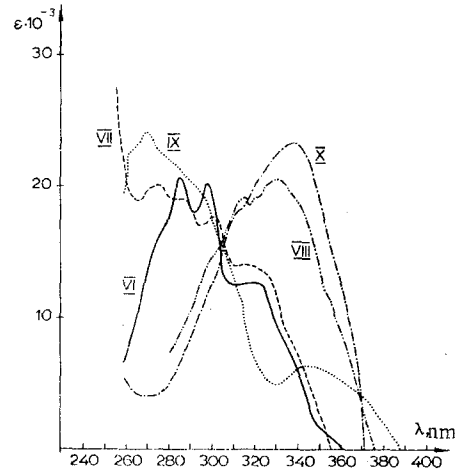


Fig. 1. Absorption spectra of VI-X.

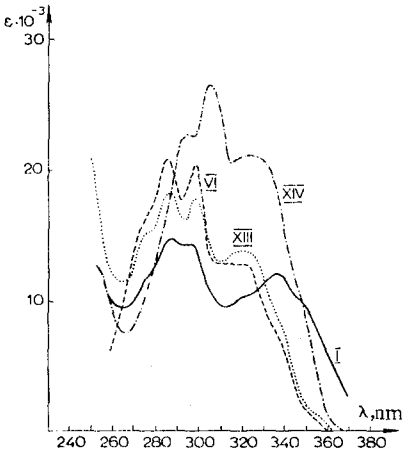


Fig. 2. Absorption spectra of I, VI, XIII, and XIV.

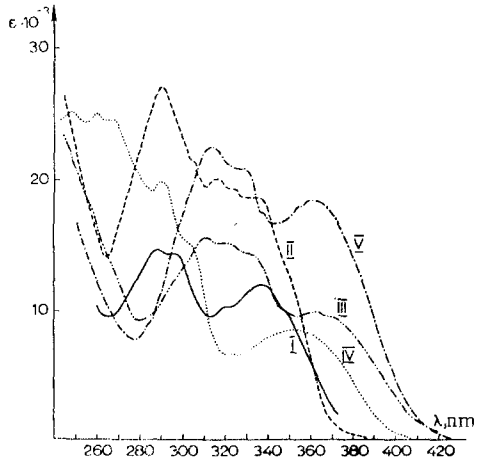


Fig. 3. Absorption spectra of I-V.

group that oppositely affect the strength of the IHB – a decrease in the basicity of the heterocyclic nitrogen and an increase in the lability of the hydrogen of the tosylamino group. It is apparent from a comparison of ν_{NH} of compounds without IHB (XIII and XIV) and those with IHB (I-V) that the shift ($\Delta\nu_{NH}$) as a result of the formation of IHB does not exceed 360 cm^{-1}, which attests to a rather weak IHB.

UV Spectra. The absorption spectrum of 2-phenyl-4H-3,1-benzoxazin-4-one (VI, Fig. 1) consists of two bands – an intense band with a crude vibrational structure at 280-305 nm ($\varepsilon \sim 20{,}000$) and a long-wave band at 310-330 nm ($\varepsilon \sim 13{,}750$). It is seen from Fig. 1 that a nitro group that is not conjugated with the heterocyclic nitrogen atom (VII and IX) causes only slight changes in the position and intensity of the 280-305 nm band. The second band in the spectrum of VII is close to the long-wave band of VI, while the second band in the spectrum of IX undergoes a considerable bathochromic shift (~20 mm) and decrease in intensity ($\varepsilon \sim 6000$). Since the nitro group in IX is conjugated with the keto group of the heteroring, the band at 310-330 nm is probably associated with a transition localized in the benzoxazinone ring. The band at 280-305 nm in the spectra of VIII and X, in which the nitro group is conjugated with the heterocyclic nitrogen, undergoes a pronounced bathochromic shift (~40-50 nm) and is more intense and overlaps the long-wave band.

The introduction of a tosylamino group (I) into the ortho position of the 2-phenyl ring causes the development of a new band at 330-350 nm ($\varepsilon \sim 11{,}000$). The two shorter-wave bands of I coincide in position with the absorption bands characteristic for the absorption spectrum of IV, but their intensities are reduced. The development of a new band in the absorption spectrum of I is associated with the presence of an IHB in it. In fact, compounds without IHB (VI, XIII, and IV) do not have such an absorption band (Fig. 2).*

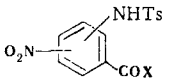
On comparing the absorption spectra of IV with those of I and XIII, it is seen that the introduction of a tosylamino group does not affect the position of the absorption bands at 280-325 nm. The tosylamino group in XIII is not conjugated with the overall π system of the molecule. The coincidence of the intensities of the absorption bands of I and XIII at 280-325 nm therefore attests to the absence of conjugation of the tosylamino group, and the absorption intensity in this region is almost doubled in the spectra of XIV, where there is no hindrance to conjugation. Since the effects of o- and p-substituents are usually close, the anomalously low intensity of the absorption of I as compared with XIV can be explained by the steric hindrance that develops when a tosylamino group is introduced into the o-position of the 2-phenyl ring. The presence of steric hindrance, which brings about the formation of a nonplanar ring with an IHB, explains the relatively small shift ($\Delta\nu_{NH}$) for I as compared with XIII, which was mentioned above.

*The bathochromic shift of the absorption bands that is observed when a p-tosylamino group is introduced (XIV) is similar to the effect of a p-methoxy group [4].

TABLE 1. IR Spectra and Luminescence Spectra of II-V and XI-XIV

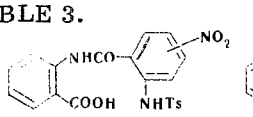
Spectral characteristics	Compound								
	I	II	III	IV	V	XI	XII	XIII	XIV
λ_{max}, nm	535	520	564	—	566	530	572	—	—
I/I_0	100	38,6	58,2	—	43,6	32,3	38,6	—	—
ν_{NH}, cm^{-1}	3071	3024	3063	3099	3091	—	—	3385	3394

TABLE 2.

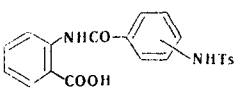


X	Substituent position: NHTs	Substituent position: NO_2	Mp, °C (crystallization solvent)	Empirical formula	Found, % C	Found, % H	Found, % N	Found, % S	Calc., % C	Calc., % H	Calc., % N	Calc., % S	Yield, %
OH	2	4	213—214 (35% alcohol)	$C_{14}H_{12}N_2O_6S$	50,0	3,9	—	9,6	50,0	3,6	—	9,5	73
OH	3	—	167,5—168,5 (dioxane)	$C_{14}H_{13}NO_4S$	57,6	5,0	4,6	11,2	57,7	4,5	4,8	11,0	94
OH	4	—	231,5—232,5 (10% CH_3OH)	$C_{14}H_{13}NO_4S$	57,8	4,4	4,8	10,9	57,7	4,5	4,8	11,0	42
Cl	2	4	162—163(benzene)	$C_{14}H_{11}ClN_2O_5S$	47,5	3,2	—	8,8	47,4	3,1	—	9,0	54
Cl	2	5	140,5—141,5 (25% (benzene—heptane)	$C_{14}H_{11}ClN_2O_5S$	47,2	3,1	7,9	8,9	47,4	3,1	7,9	9,0	88,3
Cl	3	—	117,1—117,6 (benzene)	$C_{14}H_{12}ClNO_3S$	54,2	3,9	4,7	10,5	54,3	3,9	4,5	10,4	93
Cl	4	—	129—129,5 (benzene - heptane)	$C_{14}H_{12}ClNO_3S$	53,9	3,7	4,2	10,1	54,3	3,9	4,5	10,4	62

TABLE 3.



A



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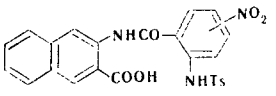


C

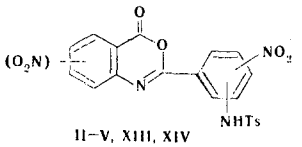
Formula	Substituent position	Mp, °C (crystallization solvent)	Empirical formula	Found, % C	Found, % H	Found, % N	Found, % S	Calc., % C	Calc., % H	Calc., % N	Calc., % S	Yield, %
A	4	252—253 (dioxane)	$C_{21}H_{17}N_3O_7S$	55,4	3,7	9,3	7,3	55,4	3,8	9,2	7,0	70,3
A	5	250,1—251 (CH_3COOH)	$C_{21}H_{17}N_3O_7S$	55,7	4,0	9,4	6,7	55,4	3,8	9,2	7,0	81,3
A	(4)*	241,2(dec., alcohol)	$C_{21}H_{17}N_3O_7S$	54,9	3,9	8,9	6,7	55,4	3,8	9,2	7,0	42
A	(5)*	233—234 (dioxane)	$C_{21}H_{17}N_3O_7S$	55,0	3,7	8,9	6,9	55,4	3,8	9,2	7,0	70,9
B	3	220—220,5 (50%alcohol)	$C_{21}H_{18}N_2O_5S$	61,4	4,5	6,7	7,9	61,5	4,4	6,8	7,8	50
B	4	229,5—230 (CH_3COOH)	$C_{21}H_{18}N_2O_5S$	61,1	4,1	6,5	7,6	61,5	4,4	6,8	7,8	41,4
C	4	268—268,5(dioxane)	$C_{25}H_{19}N_3O_7S$	59,0	3,4	8,3	6,2	59,4	3,8	8,3	6,3	67,3
C	5	270,5—271 (CH_3COOH)	$C_{25}H_{19}N_3O_7S$	59,1	3,6	8,6	6,1	59,4	3,8	8,3	6,3	43,4

*Nitro group only in the ring with a free COOH group.

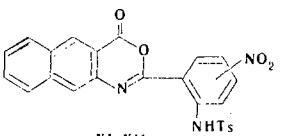
The nitro group in the absorption spectra of II-V has the same effect on the position and intensity of the short-wave bands as in VII-X. Like the short-wave bands, the longest-wave band which is characteristic for compounds with IHB, undergoes a considerable bathochromic shift in compounds in which the nitro group is conjugated with the heterocyclic nitrogen (III and V). The long-wave band in the spectrum of II, in which this sort of conjugation is absent, is shifted hypsochromically and is expressed only as a shoulder on the adjacent band. A similar effect might have been expected in the absorption spectrum of IV. A comparison of the spectra of IX and IV makes it possible to conclude that the maximum at 354 nm observed for IV can be considered to be the result of the superimposition of the longest-wave band and the bathochromically shifted shorter-wave band.

Luminescence Spectra. The maxima and relative intensities of the luminescence spectra of I-V, XI, and XII are presented in Table 1. Nitro compounds without IHB (VII-X) do not fluoresce. Compounds with IHB have rather intense luminescence, with the exception of IV, in which the nitro group is conjugated with the heterocyclic keto group. Just as in methoxy-substituted compounds, the position of the luminescence maximum of nitro compounds depends on the strength of the IHB. Strengthening of the IHB entails a hyp-

TABLE 4.



II–V, XIII, XIV



XI, XII

Compound	Substituent position*		Mp, °C†	Empirical formula	Found, %				Calc., %				Yield, %
	$NHTs$	NO_2			C	H	N	S	C	H	N	S	
II	2	5	247,5—248	$C_{21}H_{15}N_3O_6S$	57,6	3,6	9,8	7,4	57,7	3,5	9,6	7,3	78
III	2	4	244—244,5	$C_{21}H_{15}N_3O_6S$	57,6	3,3	9,2	7,8	57,7	3,5	9,6	7,3	98
IV	2	(7)	239,5—239,8	$C_{21}H_{15}N_3O_6S$	57,7	3,5	9,3	7,4	57,7	3,5	9,6	7,3	82
V	2	(6)	224,5—225,5	$C_{21}H_{15}N_3O_6S$	57,4	3,8	9,7	7,0	57,7	3,5	9,6	7,3	80
XI	—	5	287—287,5	$C_{25}H_{17}N_3O_6S$	61,4	3,4	8,5	6,7	61,6	3,5	8,6	6,6	85
XII	—	4	269,7—270	$C_{25}H_{17}N_3O_6S$	61,6	3,7	8,4	6,8	61,6	3,5	8,6	6,6	98
XIII	3	—	214,3—214,6	$C_{21}H_{16}N_2O_4S$	64,1	4,1	7,2	8,2	64,3	4,1	7,1	8,2	95
XIV	4	—	194—194,5	$C_{21}H_{16}N_2O_4S$	64,3	4,1	6,9	8,1	64,3	4,1	7,1	8,2	98

* The position during substitution in the benzoxazine ring is indicated in parentheses.

† Compounds IV and V were recrystallized from dichloroethane and dioxane respectively, while the remaining compounds were recrystallized from acetic anhydride.

sochromic shift of the maximum, while weakening of the IHB involves a bathochromic shift of the luminescence maximum. An additional bathochromic shift is observed on annelation of the benzene ring (XI and XII). In contrast to the methoxy-substituted compounds, the luminescence intensity in a series of nitro compounds is practically independent of the strength of the IHB.

EXPERIMENTAL

The synthesis of nitro-substituted 2-(2-toxylaminophenyl)-4H-3,1-benzoxazin-4-ones, -(2-tosylaminophenyl)-4H-naphth[2,3-d]-1,3-oxazin-4-ones, and 2-(3- or 4-tosylaminophenyl)-4H-3,1-benzoxazin-4-ones was accomplished via the method presented in [3] for the preparation of halo-substituted derivatives. The melting points, yields, and results of the analyses of the substances obtained are presented in Tables 2 and 3. The acylation of 4-nitroanthranilic acid with N-tosylanthranyl chloride and the acylation of anthranilic and 2,3-aminonaphthoic acid with 4-nitro-N-tosylanthranyl chloride were carried out in absolute dioxane.

5-Nitro-N-tosylanthranilic Acid. A 5 ml sample of nitric acid (sp. gr. 1.5) was added with stirring at 65-70° in the course of 1 h to 11.2 g (0.04 mole) of N-tosylanthranilic acid in 340 ml of glacial acetic acid, and the mixture was stirred for 15 min and poured into 1.5 liter of water. The resulting precipitate was crystallized twice from glacial acetic acid to give a product with mp 196-197°. Calculated: C 50.0; H 3.6; N 8.3; S 9.5%. $C_{14}H_{12}N_2O_6S$. Found: C 49.6; H 4.0; N 8.4; S 9.3%. The position of the nitro group was proved by hydrolysis of the compound in concentrated sulfuric acid to the nitroanthranilic acid, which was identical to a sample of 5-nitroanthranilic acid obtained by an independent method [5]. 5-Nitroanthranilic acid could not be tosylated.

Nitro-substituted 2-phenyl-4H-3,1-benzoxazin-4-ones were obtained by methods described in the literature: VI [6], VII [7], VIII [8], IX [9], and X [10].

The IR spectra were measured with a UR-10 spectrometer with an LiF prism at 2600-3600 cm^{-1}. The compounds were investigated in the form of saturated solutions in tetrachloroethylene with a cuvette thickness of 1 cm. The accuracy in the frequency measurements was ± 10 cm^{-1}. The UV spectra of dichloroethane solutions (c $1 \cdot 10^{-4}$ to $0.5 \cdot 10^{-4}$ M) were recorded at room temperature with an SF-4A spectrophotometer.

The luminescence spectra of $1 \cdot 10^{-4}$ to $0.5 \cdot 10^{-4}$ solutions in dichloroethane at 77°K were investigated with an ISP-51 spectrograph with an FÉP-1 adapter. Excitation was provided by a PRK-4 lamp (365 nm). An FÉU-17 served as the radiation detector.

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LITERATURE CITED

1. All-Union Scientific-Research Institute of Chemical Reagents and Ultrahigh Purity Chemical Substances, British Patent No. 1,070,326 (1964); Chem. Abstr., 68, 59,592 (1968).
2. B. M. Bolotin, M. V. Loseva, V. G. Brudz', and N. I. Chernova, USSR Author's Certificate No. 230,353 (1968); Byull. Izobr., No. 34, 75 (1968).
3. M. V. Loseva, B. M. Bolotin, and B. M. Krasovitskii, Khim. Geterotsikl. Soedin., 1597 (1970).
4. M. V. Loseva, B. M. Bolotin, and B. M. Krasovitskii, Khim. Geterotsikl. Soedin., 1028 (1971).
5. A. M. Lukin and G. S. Petrova, Chemical Reagents and Preparations [in Russian], Vol. 1, Moscow (1960), p. 57.
6. D. I. Bain and R. K. Smalley, J. Chem. Soc. (C), 1593 (1968).
7. C. L. Arons and R. E. Marks, J. Chem. Soc., 1627 (1956).
8. D. T. Zentmyer and E. C. Wagner, J. Org. Chem., 14, 967 (1949).
9. S. S. Joshi and I. R. Gambhir, J. Org. Chem., 26, 3714 (1961).
10. E. B. Womack and N. Campball, J. Chem. Soc., 1402 (1938).