4H-3,1-BENZOXAZIN-4-ONES

METHOXY-SUBSTITUTED 2-(2-ARENESULFONYLAMINOPHENYL)-4H-3,1-BENZOXAZIN-4-ONES

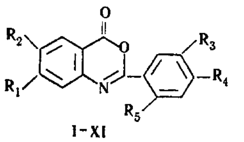
M. V. Loseva, B. M. Bolotin,
and B. M. Krasovitskii

UDC 547.867.2.07

Methoxy-substituted 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-one and 2-phenyl-4H-3,1-benzoxazin-4-one were synthesized. Their UV, IR, and luminescence spectra were studied. The position of the methoxy group affects the strength of the intramolecular hydrogen bond (IHB). The luminescence properties of methoxy-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 with strengthening of the IHB, and the luminescence intensity increase simultaneously.

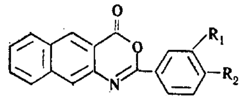
2-(2-Arenesulfonylaminophenyl)-4H-3,-benzoxazin-4-ones [1], their naphthyl analogs [2], and substituted benzoxazinones that contain chlorine and bromine in various positions [3] have intense luminescence. Benzoxazinones and naphthoxazinones containing methoxy groups in various positions (IV-VII and XIII-XIV) were synthesized in order to further study the effect of substituents on the electronic spectra of compounds of this series. A number of methox-substituted 2-phenyl-4H-3,1-benzoxazin-4-ones (VIII-XI) were synthesized for comparison.

In this paper we present data on the IR, UV, and luminescence spectra of the following compounds:



I-XI

I $R_1 = R_2 = R_3 = R_4 = R_5 = H$;
II $R_1 = R_2 = R_3 = R_4 = H$, $R_5 = o\text{-}N(CH_3)SO_2C_6H_4CH_3$;
III $R_1 = R_2 = R_3 = R_4 = H$, $R_5 = o\text{-}NHSO_2C_6H_4CH_3$;
IV $R_1 = R_2 = R_4 = H$, $R_3 = OCH_3$, $R_5 = o\text{-}NHSO_2C_6H_4CH_3$;
V $R_1 = R_2 = R_3 = H$, $R_4 = OCH_3$, $R_5 = o\text{-}NHSO_2C_6H_4CH_3$;
VI $R_1 = R_3 = R_4 = H$, $R_2 = OCH_3$, $R_5 = o\text{-}NHSO_2C_6H_4CH_3$;
VII $R_1 = OCH_3$, $R_2 = R_3 = R_4 = H$, $R_5 = o\text{-}NHSO_2C_6H_4CH_3$;
VIII $R_1 = R_2 = R_4 = R_5 = H$, $R_3 = OCH_3$;
IX $R_1 = R_2 = R_3 = R_5 = H$, $R_4 = OCH_3$;
X $R_1 = R_3 = R_4 = R_5 = H$, $R_2 = OCH_3$; XI $R_1 = OCH_3$, $R_2 = R_3 = R_4 = R_5 = H$



XII-XIV

XII $R_1 = R_2 = H$, $R_3 = o\text{-}NHSO_2C_6H_4CH_3$;
XIII $R_1 = OCH_3$, $R_2 = H$, $R_3 = o\text{-}NHSO_2C_6H_4CH_3$;
XIV $R_1 = H$, $R_2 = OCH_3$, $R_3 = o\text{-}NHSO_2C_6H_4CH_3$

IR Spectra. The intense, yellow-green luminescence of 2-(2-arenesulfonylaminophenyl)-4H-3,1-benzoxazin-4-ones is caused by an intramolecular hydrogen bond (IHB), since the luminescence maximum of I and II, in which formation of an IHB is impossible, is situated in the near UV [4]. Since methoxy-substituted 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-ones also luminesce in the yellow-green region, we commenced a study of them from an elucidation of the effect of a methoxy group on the position of the N−H band (γ_{N-H}) in the IR spectra (Table 1). A methoxy group in the 2-position of the phenyl ring, through its strong electron-donor properties, has a twofold effect on the strength of the IHB: it reduces the lability of

---

All-Union Scientific-Research Institute of Chemical Reagents and Especially Pure Chemical Substance, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1028-1032, August, 1971. Original article submitted July 20, 1970.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for $15.00.

TABLE 1. Maxima in the Luminescence Spectra and Absorption Frequencies of the N−H Bond of Methoxy-Substituted 2-(2-Tosylaminophenyl)-4H-3,1-benzoxazin-4-ones

Compound	λ_{max}, nm			ν_{N-H}, cm^{-1}
	Dichloroethane	Dioxane	Dimethylformamide	
III	535, 111	529, 81	529, 92	3070
IV	561, 97	558, 76	560, 82	3085
V	496, 172	488, 157	495, 131	3035
VI	525, 155	521, 131	512, 138	3065
VII	529, 136	521, 130	525, 97	3060
XII	550, 97	548, 93	534, 77	3075
XIII	569, 91	565, 67	563, 63	
XIV	501, 66	500, 92	484, 58	

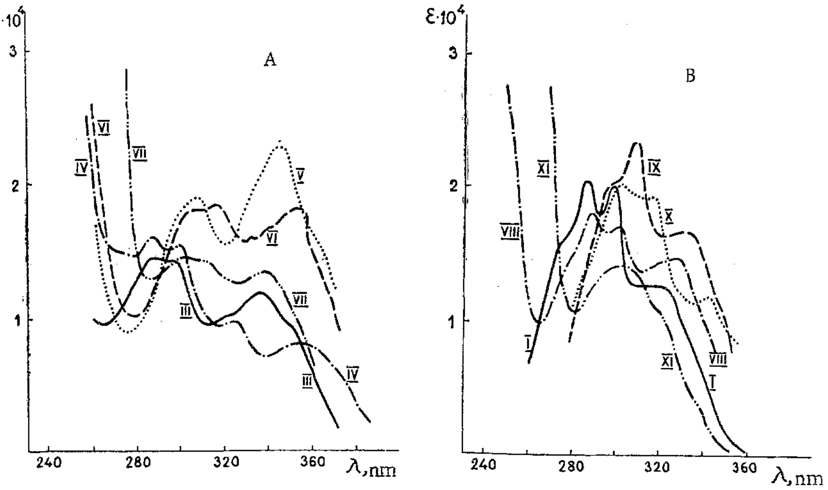


Fig. 1. Absorption spectra of methoxy-substituted 2-phenyl-4H-3,1-benzoxazin-4-ones (A) and 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-ones (B).

the hydrogen of the tosylamino group and thereby weakens the IHB (IV, γ_{N-H}3085 cm^{-1}); it increases the basicity of the heterocyclic nitrogen, which promotes strengthening of the IHB (V, γ_{N-H}3035 cm^{-1}) in comparison with unsubstituted III (γ_{N-H}3070 cm^{-1}). In VI, γ_{N-H} is 3065 cm^{-1}; i.e., the methoxy group has practically no effect on the strength of the IHB. This is probably associated with the fact that, by raising the basicity of the heterocyclic nitrogen, the methoxy group simultaneously intensifies the electron-acceptor effect of the carbonyl group through its own negative inductive effect. The slight strengthening of the IHB in VII (γ_{N-H}3060 cm^{-1}) can be explained by the interaction of the methoxy and carbonyl groups. The electron-acceptor effect of the carbonyl group is reduced in the process, and the electron density on the heterocyclic nitrogen is consequently increased.

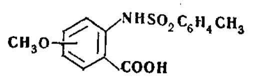
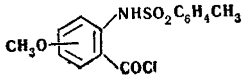
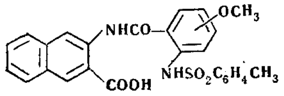
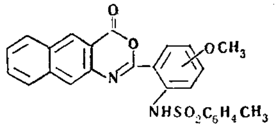
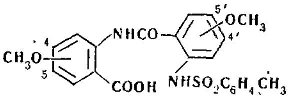
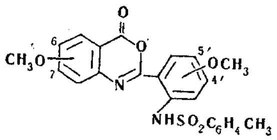
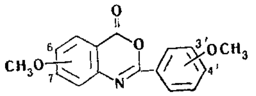
UV Spectra. At 270-325 nm, I and III have identical absorption bands (Fig. 1). In addition, III has a long-wave band (λ_{max}338 nm). The development of this band is apparently associated with the presence of an IHB in III [4]. This assumption is based on the fact that II, in which the formation of an IHB is impossible, does not absorb in this wavelength region, and its spectrum is similar to that of I.

It is known from the literature that the appearance of a longer-wave band than is the case with an analogous compound without an IHB [5,6] is characteristic for compounds of the III type that contain a six-membered IHB ring, which assumes the inclusion of the vacant 2p orbitals of hydrogen into the overall π-electron system of the molecule with the formation of a quasi-aromatic ring.

The methoxy group in the spectra of IV-VII induces a bathochromic shift of the long-wave band, which is greatest for IV, and slight for VII.

In comparing the spectra of I and III, IV and VIII, V and IX, and VI and XI, it is apparent that the position of the absorption bands of each pair of compounds at 270-330 nm coincides. This indicates that the

TABLE 2. Characteristics of Methoxy-Substituted Benz- and Naphthoxazinones and Intermediates

Position of CH3O	mp	Purification solvent	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
1	2	3	4	5	6	7	8	9	10	11
										
4	223—224	EtOH+H$_2$O	$C_{15}H_{15}NO_5S$	55,73	4,81	4,45	56,06	4,71	4,36	74,5
5	185—186	AcOH+H$_2$O	$C_{15}H_{15}NO_5S$	55,98	4,99	4,56	56,06	4,71	4,36	69
										
4	157,5—158,5	Hexane—benzene 1 : 1	$C_{15}H_{14}ClNO_4S$	53,09	4,22	4,15	53,02	4,15	4,12	78
5	120—120,7	Benzene	$C_{15}H_{14}ClNO_4S$	53,10	4,65	3,82	53,02	4,15	4,12	81
										
4′	225,5—226	AcOH	$C_{26}H_{22}N_2O_6S$	63,49	4,78	5,76	63,66	4,52	5,71	90
5′	239,5—240	AcOH	$C_{26}H_{22}N_2O_6S$	63,85	4,83	5,84	63,66	4,52	5,71	46
										
4′	245,5—246,5	AcOH	$C_{26}H_{20}N_2O_5S$	65,67	4,14	5,80	66,08	4,27	5,93	76
5′	251—252	AcOH	$C_{26}H_{20}N_2O_5S$	65,89	4,47	5,88	66,08	4,27	5,93	98
										
5′	201—202	AcOH	$C_{22}H_{20}N_2O_6S$	59,64	4,58	6,65	59,99	4,57	6,36	57
4′	202,5—204	AcOH	$C_{22}H_{20}N_2O_6S$	59,90	4,61	6,48	59,99	4,57	6,36	43
5	199—200	AcOH	$C_{22}H_{20}N_2O_6S$	59,73	4,79	6,27	59,99	4,57	6,36	75
4	214—215	AcOH	$C_{22}H_{20}N_2O_6S$	59,85	4,59	6,59	59,99	4,57	6,36	47
										
5′	174,5—175	AcOH	$C_{22}H_{18}N_2O_5S$	62,63	4,16	6,84	62,52	4,29	6,63	82
4′	249—250	AcOH	$C_{22}H_{18}N_2O_5S$	62,79	4,54	6,27	62,52	4,29	6,63	50
6	210,5—211,5	AcOH	$C_{22}H_{18}N_2O_5S$	62,00	4,15	6,61	62,52	4,29	6,63	79
7	218—219	AcOH	$C_{22}H_{18}N_2O_5S$	62,62	4,34	6,82	62,52	4,29	6,63	42
										
3′	122—123	EtOH	$C_{15}H_{11}NO_5$	70,91	4,39	5,23	71,13	4,37	5,53	94
4′	156,5—157[8]	—	$C_{15}H_{11}NO_3$	—	—	—	—	—	—	—
6	146,5—147,5	EtOH	$C_{15}H_{11}NO_3$	71,19	4,50	5,82	71,13	4,37	5,53	87
7	150,7—151,3	EtOH	$C_{15}H_{11}NO_3$	71,09	4,50	5,45	71,13	4,37	5,53	48

formation of an IHB does not affect their absorption at 270-330 nm.

Luminescence Spectra. All of the methoxy-substituted benz- and naphthoxazinones have intense luminescence in the yellow-green region is associated with the presence of IHB in them. The strength of the IHB affects the position of the luminescence maximum of methoxy-substituted 2-(2-tosylaminophenyl)-4H-3,1-benzoxazin-4-ones: the stronger the IHB, the more the maximum is shifted to the short-wave region, and the higher the intensity of the luminescence (Table 1).

The same dependence as for III-V is observed in the effect of substituents on the UV and luminescence spectra in a number of methoxy-substituted naphthoxazinones (XII-XIV).

EXPERIMENTAL

The synthesis of methoxy-substituted 2-(2-tosylaminophenyl)-4H-3,1-benzoazin-4-ones and 2-(2-tosylaminophenyl)-4H-naphth[2,3-d][1,3]oxazin-4-ones was accomplished by a method similar to that presented in [3] for the preparation of halogen-substituted derivatives. The melting points, analyses, yields, and solvents used to purify the products are presented in Table 2. A number of methoxy-substituted 2-phenyl-4H-3,1-benzoxazin-4-ones were obtained via a scheme similar to that described in [7] (Table 2).

The IR spectra were obtained with a UR-10 spectrometer with an LiF prism at 2600-3600 cm^{-1}. The compounds were investigated as 0.003-0.01 M solutions in tetrachloroethylene; the cuvette thickness was 1 cm, and the accuracy in the measurements was ± 10 cm^{-1}.

The UV spectra of dichlorethane solutions ($1 \cdot 10^{-4}$ to $0.5 \cdot 10^{-4}$ M) were recorded at room temperature (cuvette thickness 1 cm) with a Hitachi automatic spectrophotometer.

The luminescence spectra of solutions ($2.5 \cdot 10^{-3}$ to $0.75 \cdot 10^{-3}$ M) in dichloroethane, dioxane, and dimethylformamide at 77 deg K were investigated with an ISP-51 spectrograph with an FÉP-1 adapter. The spectra were excited with a PRK-4 lamp (365 nm). An FÉU-17 photomultiplier served as a radiation detector. The spectra were corrected for the spectral sensitivity of the apparatus.

The authors thank Yu. S. Ryabokobylko and A. O. Zisman for measuring the absorption spectra in the IR and UV regions.

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 Authors' Certificate No.230,353 (1968); Byull. Izobr., No. 34, 75 (1968).
3. M. V. Loseva, B. M. Krasovitskii, and B. M. Bolotin, Khim. Geterotsikl. Soedin., 1957 (1970).
4. B. M. Bogotin, Yu. S. Ryabokobylko, D. A. Drapkina, and V. G. Brudz', Khim. Reaktivy i Preparaty. Trudy IREA, 27, 289 (1965).
5. N. Ebara, Bull. Chem. Soc. Japan, 34, 1151 (1961).
6. R. Passerini, J. Chem. Soc., 2256 (1954).
7. D. I. Bain and R. K. Smalley, J. Chem. Soc. (C), 1593 (1968).
8. C. L. Arcus and R. E. Marks, J. Chem. Soc., 1627 (1956).