mer VIIIb (30%). A 1.2-g sample of 2,4-dinitrophenylhydrazine in 60 ml of 20% hydrochloric acid was added to the alcohol solution, and the resulting precipitate was removed by filtration and washed with water and alcohol to give 1.05 g (70%) of acetone 2,4-dinitrophenylhydrazone. No melting-point depression was observed for a mixture of this product with an authentic sample.

Reaction of Tosyl Azide with Methyl Vinyl Ether in 2,4-Pentanedione. A mixture of 1.96 g of the azide, 1.1 ml of ether I, and 1.5 ml of 2,4-pentanedione was heated at 40° for 2 h, after which it was subjected to preparative separation on silica gel with elution by CCl_4-CHCl_3 (1:1) to give the tosylamide, with mp 137° (successively from water and toluene) and R_f 0.1, in 25% yield. PMR spectrum, δ (nitrobenzene): 2.26 (s, 3H) and 5.7 ppm (s, 2H). The PMR spectra of the fractions with R_f 0.2 and 0.4 did not contain signals of the ring system of the protons of oxazolidine and singlet signals of methyl groups of 2,4-pentanedione. The more mobile fractions contained tosyl azide (15%), which was identified from its IR spectrum, and 3-diazo-2,4-pentanedione (18%). PMR spectrum, δ (CCl_4): 2.29 ppm (s). IR spectrum (CCl_4): 1690 (C=O) and 2110 cm^{-1} (diazo group). An authentic sample of the diazo ketone obtained by the method in [8] had spectra analogous to those of the product.

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ISOMERIC DISTYRYLBENZOBISOXAZOLES

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Isomeric 2,6-distyrylbenzobisoxazoles, the UV spectra of which provide evidence of a difference in the conjugation of the styrylbenzoxazole fragments in their molecules, were synthesized by condensation of isomeric 2,6-dimethylbenzobisoxazoles with aromatic aldehydes.

The heteroanalogs of stilbene and distyrylbenzene, which contain benzoxazole structural fragments, are of considerable interest both for the study of the relationship between the structure of organic compounds and their spectral-luminescence properties and from the point of view of their application as, for example, optical bleaches [1], luminophores, and generating compounds for quantum electronics [2].

In the present communication we describe the preparation of isomeric 2,6-distyrylbenzo[1,2-d;5,4-d']- (I) and 2,6-distyrylbenzo[1,2-d; 4,5-d']bisoxazoles (II), which are heteroanalogs of distyrylbenzenes. The condensation of 2-methylbenzoxazole with aromatic aldehydes (for example, fusion with zinc chloride [3] or boric acid [4] or refluxing in methanol in the presence of alkaline agents [5]), which gives the products, in low yields, is usually employed for the synthesis of styryl-substituted benzoxazoles.

We have developed a method for the synthesis of distyrylbenzobisoxazoles I and II by condensation of 2,6-dimethylbenzo[1,2-d; 5,4-d']- (III) and 2,6-dimethylbenzo[1,2-d; 4,5-d']bisoxazole (IV), respectively, with aro-

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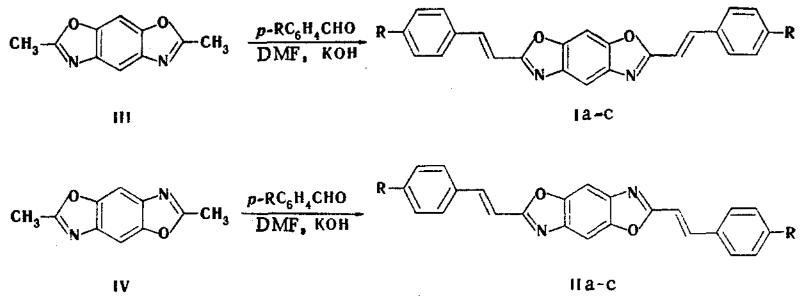
TABLE 1. Distyrylbenzobisoxazoles I and II

Compound	R	mp, °C	Empirical formula	Found, %			Calculated, %			UV spectrum in $CHCl_3$	
				C	H	N	C	H	N	λ_{max}, nm	lg ε
Ia	H	208—210	$C_{24}H_{16}N_2O_2$	78,7	4,5	7,5	79,1	4,4	7,7	332	4,69
IIa		318—319		79,5	4,9	7,8				364 380 402 sh	4,76 4,80 4,58
Ib	$C(CH_3)_3$	298—300	$C_{32}H_{32}N_2O_2$	80,7	6,3	5,6	80,6	6,8	5,9	338	4,78
IIb		358—359		89,4	6,8	6,0				368 386 408 sh	4,53 4,52 4,36
Ic	OCH_3	246—247	$C_{26}H_{20}N_2O_4$	73,5	4,5	6,5	73,6	4,7	6,6	343	4,77
IIc		294—295		73,0	5,2	6,4				380 394 412 sh	4,80 4,84 4,60

matic aldehydes in dimethylformamide (DMF) in the presence of potassium hydroxide as the catalyst.* For the benzaldehyde, p-tert-butylbenzaldehyde, and anisaldehyde that we investigated, the condensation proceeds at room temperature for 1 h and gives the products in 60-80% yields.



I, II a R=H; b R=$C(CH_3)_3$; c R=OCH_3

The individuality of I and II was confirmed by thin-layer chromatography (TLC) on aluminum oxide. Absorption bands at 970-990 cm^{-1}, which are characteristic for the deformation vibrations of the CH bonds of trans-disubstituted alkenes [7] and are absent in the spectra of starting III and IV, are present in their IR spectra. The closeness of the absorption maxima in the UV spectra of distyrylbenzobisoxazoles I (Table 1) and the corresponding styrylbenzoxazoles [4] provides evidence for disruption of the conjugation of the styrylbenzoxazole fragments in the I molecules.

The absorption maxima of distyrylbenzobisoxazoles II are shifted to the long-wave region of the spectrum as compared with isomeric I. The magnitude of the bathochromic shift (~50 nm) of the principal maxima apparently provides evidence for the presence of a single conjugation chain in the molecules of II with para-oriented C=N bonds; this is in agreement† with the available data [9] regarding the character of transmission of conjugation through the oxazole ring in the benzoxazole system.

EXPERIMENTAL

The UV spectra of the compounds were recorded with a Hitachi 356 spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

Distyrylbenzobisoxazoles I and II. A solution of 0.015 mole of the aromatic aldehyde in 2-3 ml of DMF was added with stirring to a mixture of 0.94 g (0.005 mole) of dimethylbenzobisoxazole III or IV and 2.8-4.5 g (0.05-0.08 mole) of potassium hydroxide in 30 ml of DMF, and the mixture was stirred at room temperature for 1 h. It was then decomposed with dilute hydrochloric acid, and the precipitate was removed by filtration and washed with water and a small amount of methanol. Compound Ia was purified by recrystallization from heptane, and Ib, c, and IIa-c were recrystallized from DMF.

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*The condensation of quaternary ammonium salts of III and IV with p-dimethylaminobenzaldehyde, which leads to quaternary ammonium salts of compounds of the I and II type, respectively, has been described [6].

†However, it should be noted that the long-wave absorption maxima calculated within the framework of the Pariser—Parr—Pople method for isomeric benzo[1,2-d;5,4-d']- and benzo[1,2-d;4,5-d']bisoxazoles are identical [8].

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BASICITIES AND STRUCTURES OF 4,4,6-TRIMETHYL-2-ARYLAMINO-5,6-DIHYDRO-4H-1,3-THIAZINES AND 4,4,6-TRIMETHYL-2-ARYLAMINO-5,6-DIHYDRO-4H-1,3-OXAZINES

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The relative basicities of 4,4,6-trimethyl-2-arylamino-5,6-dihydro-4H-1,3-thiazines and 4,4,6-trimethyl-2-arylamino-5,6-dihydro-4H-1,3-oxazines, which are capable of amine–imine tautomerism, and of model compounds with fixed amine and imine structures were determined by potentiometric titration in methanol. Good correlation of the pK_a values with the Hammett σ constants in the investigated reaction series was found. The inapplicability of the use of the pK_a values of model compounds for the determination of the tautomeric equilibrium constants in the case of some N-heterocyclic amines of nonaromatic character with an aryl substituent attached to the exocyclic nitrogen atom of the amidine fragment of the molecule is demonstrated.

We have previously established that 4,4,6-trimethyl-2-arylamino-5,6-dihydro-4H-1,3-thiazines (I) and 4,4,6-trimethyl-2-arylamino-4,6-dihydro-4H-1,3-oxazines (II) exist in the crystalline state in the amine form (A), which also predominates in solvents with different polarities. This conclusion was drawn on the basis of a comparison of the spectral characteristics of tautomeric I and II and model compounds – 4,4,6-trimethyl-2-(N-methyl-N-aryl)amino-5,6-dihydro-4H-1,3-thiazines (III) and 4,4,6-trimethyl-2-(N-methyl-N-aryl)amino-5,6-dihydro-4H-1,3-oxazines (IV), which have a fixed amine structure, and 3,4,4,6-tetramethyl-2-aryliminotetrahydro-1,3-thiazines (V) and 3,4,4,6-tetramethyl-2-aryliminotetrahydro-1,3-oxazines (VI), which have a fixed imine structure. In addition, in [2] we demonstrated the inapplicability of the use of the ionization constants of model compounds for the determination of the tautomeric equilibrium constants (K_t) in the 4,4,6-trimethyl-2-arylamino-4H-1,3-thiazine (VII) series because of considerable steric-electronic differences in the models and the corresponding tautomeric compounds.

TABLE 1. Relative Basicities of Aminothiazines and Aminooxazines of Reaction Series I-VI

Reaction series	Hetero-atom Y	Basicity constant $pK_a \pm 0.04$						
		a X= $=p\text{-OCH}_3$	b X= $=p\text{-C}_2\text{H}_5$	c X= $=p\text{-CH}_3$	d X= $=m\text{-CH}_3$	e X=H	f X=p-Br	g X=p-Cl
Ia,c–g	S	7,56	—	7,31	7.07	6,88	6,29	5,90
IIa–g	O	8,80	8,74	8,53	8,39	8,30	7,65	7,42
IIIa,c–g	S	8,11	—	8,02	7,92	7,79	7,25	7,05
IVa–g	O	9,35	9,24	9,08	9,10	8,94	8,52	8,36
Va, c, e	S	6,96	—	6,65	—	6,25	—	—
VIb–g	O	—	8,49	8,28	8,14	7,97	7,22	7,00

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