was evaporated with a rotary evaporator. The residue was refluxed in a mixture of 10 ml of dry benzene and 2 ml of dry ethanol for 2 h, after which the mixture was cooled and filtered, and the filtrate was poured into 30 ml of hexane. The resulting precipitate was removed by filtration.

4,4'(5')-Bis(β-acryloyl)dibenzo-18-crown-6 Diethyl Ester (VII). This compound was similarly obtained from 0.2 g (0.0004 mole) of acid VI, 1 g (0.008 mole) of thionyl chloride, and 0.5 ml of dry ethanol.

Extraction of Picrates of Alkali and Alkaline Earth Metals by I-III, V, and VII-IX. A 1-ml sample of a $1 \cdot 10^{-3}$ M aqueous solution of the picrate of the corresponding metal and 0.4 ml of a $5 \cdot 10^{-3}$ M solution of the ligand in chloroform that had been previously saturated with water was stirred vigorously with a magnetic stirrer for 5 min. After centrifugation, a 0.1-ml sample of the aqueous layer was removed and treated with 2.9 ml of distilled water, and the optical density of the resulting solution was measured at 354 nm.

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SYNTHESIS AND IR SPECTRA OF SOME 2-AMINOBENZOXAZOLE DERIVATIVES

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A large number of 5-nitro-, 6-nitro-, 5-chloro-, and 6-bromo-2-aminobenzoxazoles were synthesized by the reaction of benzoxazoline-2-thiones with various amines. It was shown by IR spectroscopy that all of the compounds exist in the amino form in solution, whereas the 5-substituted compounds exist in the imino form in the solid state, and the 6-substituted compounds exist simultaneously in the two forms.

In our previous research we developed a new method for the preparation of thiourea derivatives that contain a 2-hydroxyphenyl grouping as a substituent [1, 2] by the reaction of benzoxazoline-2-thione with ammonia. These compounds proved to be interesting in a chemical respect, and this compelled us to develop a method for the preparation of derivatives of 2-aminobenzoxazole and 2-imino-3-alkylbenzoxazoline [3, 4]. We showed that 2-aminobenzoxazole derivatives exist in various tautomeric forms in the solid form and in solution [5], whereas 2-imino-3-methylbenzoxazoline derivatives have an anomalously high frequency of the azomethine group in the IR spectra [6]. In addition, some of the 2-aminobenzoxazole derivatives have the properties of stabilizers of rubber mixtures [7] and are inhibitors of metal corrosion.

We became interested in the effect of substituents in the aromatic ring of 2-aminobenzoxazoles on the state of the tautomeric equilibrium. We obtained several derivatives of 2-amino-5-nitrobenzoxazole, 2-amino-6-nitrobenzoxazole, 2-amino-5-chlorobenzoxazole, and 2-

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TABLE 1. 2-Aminobenzoxazoles III

Compound[a]	X	Y	R^1	R^2	mp, °C	N, %		Yield,[b] %
						found	calc.	
IIIb	NO_2	H	C_2H_5	H	217—218	19,6	19,3	70
IIIc	NO_2	H	$CH_2CH{=}CH_2$	H	120—122	19,5	19,2	82,5
IIId	NO_2	H	C_3H_7	H	126—128	19,1	19,0	75
IIIe	NO_2	H	C_4H_9	H	118—119	18,2	17,9	70
IIIf	NO_2	H	C_6H_{11}	H	150—152	15,9	16,1	79
IIIg	NO_2	H	CH_2Ph	H	148—149	15,4	15,6	79
	H	NO_2	CH_3	H	116—117	21,7	21,8	87
	H	NO_2	C_2H_5	H	121—122	20,3	20,3	83
	H	NO_2	$CH_2CH{=}CH_2$	H	102—104	19,4	19,2	92
IIIh	H	NO_2	C_3H_7	H	129—130	19,2	19,0	85,5
IIIi	H	NO_2	C_4H_9	H	123—125	17,7	17,9	86
IIIj	H	NO_2	C_6H_{11}	H	145—146	16,1	16,1	93
	H	NO_2	CH_2Ph	H	122—124	15,7	15,6	87
IIIk	Cl	H	CH_3	H	156—158	15,5	15,3	77
IIIl	Cl	H	C_2H_5	H	108—110	14,6	14,2	76
IIIm	Cl	H	C_3H_7	H	104—105	13,5	13,3	81
IIIn	Cl	H	C_4H_9	H	103—104	12,6	12,5	92
IIIo	Cl	H	C_6H_{11}	H	140—142	11,4	11,2	91
IIIp	Cl	H	CH_2Ph	H	155—157	10,8	10,8	79
IIIq	H	Br	C_2H_5	H	117—118	11,9	11,6	68,5
IIIr	H	Br	C_3H_7	H	108—109	10,9	11,0	79
IIIs	H	Br	C_4H_9	H	88—89	10,6	10,4	85
IIIt	H	Br	C_6H_{11}	H	132—133	9,4	9,5	89
IIIu	H	Br	CH_2Ph	H	128—130	8,9	9,2	83
IIIy	NO_2	H	C_2H_5	C_2H_5	96—97	18,0	17,9	77
IIIz	NO_2	H	C_4H_9	C_4H_9	85—86	14,4	14,4	80
IIIa	NO_2	H	$(CH_2)_5$		123—124	17,2	17,0	70
	H	NO_2	C_2H_5	C_2H_5	112—114	18,1	17,9	90
	H	NO_2	C_4H_9	C_4H_9	109—111	14,5	14,4	78
	H	NO_2	$(CH_2)_5$		124—125	17,2	17,0	75
	NO_2	H	C_6H_5	H	236	16,5	16,3	92[c]
III'a	NO_2	H	$(CH_2)_2O(CH_2)_2$		142	17,1	16,9	90
	H	NO_2	C_6H_5	H	155—156	16,6	16,3	78[c]
	H	NO_2	$(CH_2)_2O(CH_2)_2$		131—132	17,1	16,9	88
IIIw	H	Br	$(CH_2)_2O(CH_2)_2$		137—139	10,2	9,9	73
IIIx	H	Br	$(CH_2)_5$		88—89	9,8	10,0	66
IIIv	Cl	H	$(CH_2)_5$		107—109	11,8	11,9	63[c]
	H	H	p-CH_3Ph	H	169—171	12,2	12,6	88

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[a] Only the compounds mentioned in Table 2 are designated by numbers. [b] We always subjected 1 g of the starting thiourea or benzoxazole-2-thione to the reaction. [c] The reaction heating time was 12 h, with the exception of IIId, for which the heating time was 9 h.

TABLE 2. Stretching Vibrations of the Azomethine Group of 2-Aminobenzoxazoles, cm^{-1}

Compound	$CHCl_3$[a]	Mineral oil	Compound	$CHCl_3$[a]	Mineral oil
IIIb	—	1676	IIIp	1650	1680
IIIc	—	1678	IIIq	1652	1690
IIId	—	1675	IIIr	1650	1687
IIIe	1657	1680	IIIs	1650	1650, 1680
IIIf	—	1680	IIIt	1650	1692
IIIg	—	1680	IIIu	1640	1688
IIIh	1650	1650, 1690	IIIv	1645	1645
IIIi	1650	1650, 1695	IIIw	1645	1645
IIIj	1650	1645, 1692	IIIx	1645	1645
IIIk	—	1690	IIIy	—	1645
IIIl	1655	1690	IIIz	—	1645
IIIm	1655	1690	IIIa	—	1647
IIIn	1655	1710	III'a	—	1620
IIIo	1648	1690			

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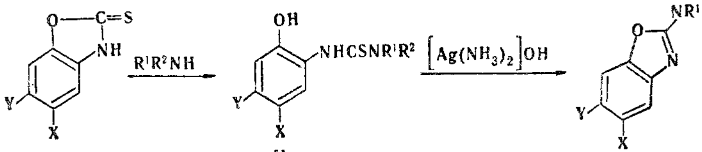
[a] The spectra were recorded from 1% solutions in $CHCl_3$.

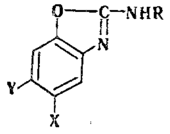
amino-6-bromobenzoxazole from the corresponding benzoxazoline-2-thiones by reaction with amines via the scheme (see Table 1):



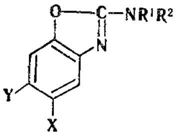
I II III

In the reaction of aromatic amines with 5- or 6-nitrobenzoxazoline-2-thiones we immediately isolated 2-aminobenzoxazole derivatives.

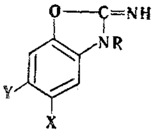
From a comparison of IIIb, IIIy, and IV it may be assumed that tautomerism is possible only in IIIb:



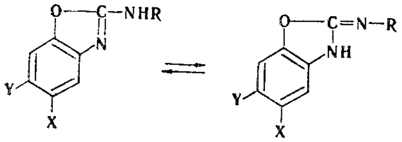
IIIb



IIIy



IV



A B

According to the data in [8], the stretching vibrations of the endocyclic azomethine group are found at 1640-1660 cm^{-1}, while those of the exocyclic azomethine group are found at 1635-1690 cm^{-1}. We have established that the frequency of the stretching vibrations of the endocyclic azomethine group in such systems is found at 1640-1657 cm^{-1}, while the frequency of the exocyclic azomethine group is found at 1710-1738 cm^{-1} [5, 6]. The results of measurements of the IR spectra of III are presented in Table 2. The frequency of the stretching vibrations of the azomethine group of these compounds in chloroform is found at 1640-1655 cm^{-1}. This shows that in chloroform solution derivatives III have an endocyclic azomethine group and consequently probably exist in the A form, i.e., they are 2-aminobenzoxazole derivatives. The spectra of the 5-chloro and 6-bromo derivatives recorded in mineral oil show that the frequencies of the stretching vibrations of the azomethine group are found at 1680-1710 cm^{-1}. Such frequencies of the stretching vibrations are characteristic for an exocyclic azomethine group, and consequently in the solid state these compounds exist exclusively in the B form and are 2-iminobenzoxazoline derivatives.

5-Nitro derivatives III are insoluble in chloroform, except for 5-nitro-2-butylaminobenzoxazole (IIIe). A band at 1658 cm^{-1}, which corresponds to the stretching vibrations of an endocyclic azomethine group, is observed in the IR spectrum of the latter, while the IR spectra of these compounds recorded in mineral oil contain bands of an exocyclic azomethine group at 1675-1680 cm^{-1}.

The IR spectra of the 6-nitro derivatives proved to be interesting: A band of an azomethine group at 1650 cm^{-1} is observed in the spectra of chloroform solutions, while in the spectra in mineral oil we observed two bands of an azomethine group at 1645-1650 cm^{-1}, which corresponds to an endocyclic azomethine group, and at 1690-1695 cm^{-1} we observed the band of an exocyclic azomethine group. These data show that the 6-nitro derivatives in the solid state probably exist simultaneously in two forms. The IR spectra of 6-bromo-2-butylaminobenzoxazole recorded in mineral oil are similar: Bands of stretching vibrations of an azomethine group are found at 1680 and 1650 cm^{-1}. Thus electron-acceptor substituents in the 6 position of the benzoxazole ring stabilize to a certain degree the existence of these compounds in the A form. Tautomerism is impossible in IIIy and IV, and the frequency of the stretching vibrations of the azomethine group do not undergo a substantial change in solution or in the solid state.

EXPERIMENTAL

2-Butylamino-5-nitrobenzoxazole (IIIe). A solution of 1.36 g (0.008 mole) of $AgNO_3$ in 5 ml of concentrated ammonium hydroxide was added to a solution of 1 g (0.0037 mole) of N-2-hydroxy-5-nitrophenyl-N^1-butylthiourea in 40 ml of alcohol, as a result of which Ag_2S precipitated. Stirring was continued for 1 h, after which another 5 ml of ammonium hydroxide was added, and the temperature was raised to 40-50°C. After 1 h, 30 ml of ethanol was added to the mixture, and the precipitate was removed by filtration. The filtrate was acidified to pH 3-4 with 6% hydrochloric acid, during which AgCl precipitated. After 30 min, the precipitate was removed by filtration, and the filtrate was made alkaline with 5% NaOH. Work-up gave 0.61 g (69%) of yellow crystals with mp 113°C. After recrystallization from dilute alcohol, the pure product had mp 118°C.

2-Morpholino-5-nitrobenzoxazole (III'a). A 2.08-g (0.024 mole) sample of morpholine was added to 1 g (0.005 mole) of 5-nitrobenzoxazoline-2-thione, and the mixture was heated for 4 h on a water bath. It was then cooled and treated with 50-60 ml of water, during which the excess amine remained in solution, while the benzoxazole precipitated. The precipitate was removed by filtration and washed with water to give 1.45 g (93%) of a product with mp 140°C. Recrystallization from dilute alcohol gave a product with mp 143°C.

The remaining substances III (Table 1) were similarly obtained. All of the substances were crystalline and soluble in alcohol, ether, ethyl acetate, acetone, and acid but insoluble in water, alkalis, etc.

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