mp 233-234°. IR spectrum: 1483 (NHC=S) and 1290 cm^{-1} (Ar–NH). Found %: C 48.6; H 2.2; N 6.0. $C_9H_5NS_3$. Calculated %: C 48.5; H 2.3; N 6.25.

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THIAZOLOCYANINES

XVIII.* N-HETARYLTHIAZOLIUM SALTS AND CYANINE DYES BASED ON THEM

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and A. Ya. Il'chenko

UDC 668.819.45:547.789.1.5.7

Some results of an investigation of thiazolocyanines containing α-hetaryl residues attached to the nitrogen atoms of the thiazole ring are summed up. The effect of the nature of these residues, their basicities, and mainly the steric hindrance generated by them on the absorption of the dyes was investigated. The angles of rotation of the hetaryl residues about their bond with the nitrogen atom of the thiazole ring in the dyes both in the presence and absence of substituents in the thiazole ring were calculated, and the associated disruption of the planarity of the thiazolotrimethylidynecyanine molecules is examined.

One of our earlier papers [2] was the first publication dealing with systematic investigations of N-hetarylthiazolocyanines and intermediates for their synthesis – quaternary thiazolium salts in which residues of heterocyclic nitrogen bases were substituents attached to the nitrogen atom of the thiazole rings. In the present paper some of the preliminary results, with the inclusion of additional data, are summed up.

A peculiarity of the structure of the investigated N-α-hetarylthiazolium salts is the fact that the hetaryl residues are bonded to the nitrogen atom of the thiazole ring in the α position and thus are to a certain degree analogs of the electronegative CN group. It has long been known that attachment of electronegative groups (for example, CN, dinitrophenyl, etc.) to the pyridinium nitrogen atoms promotes facile cleavage of the pyridine ring. Cleavage of a pyridinium salt in which a 2-benzoxazolyl residue is attached to the nitrogen atom is also known [3]. It is very possible that this is the reason that quaternary salts of the thiazole series and dyes with electronegative residues, particularly those with N-α-hetaryl rings, were not obtained prior to our studies, although individual communications regarding dyes of the pyridine [4] and benzimidazole [5] series of this type have appeared in the literature.

We have developed several variants of the synthesis of N-α-hetarylthiazolium salts with active methyl (IA) [2] and methylthio (IB) [6] groups and have synthesized dyes from them – nullimethylidynemerocyanines

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*See [1] for communication XVII.

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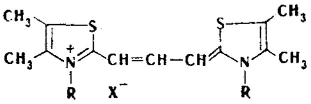
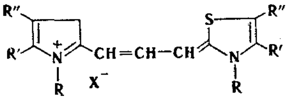
TABLE 1



Compound	R	«A»	pK_a	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$
V	Ethyl	$2{,}4 \cdot 10^{-3}$	3,03	566	8,3
VI	Phenyl	$1{,}08 \cdot 10^{-1}$	1,32	571	6,7
VII	2-Pyridyl	$2{,}2 \cdot 10^{-1}$	1,02	576	6,7
VIII	2-Thiazolyl	$9{,}5 \cdot 10^{-1}$	0,19	584	9,8
IX	2-Benzothiazolyl	$2{,}75 \cdot 10$	−0,58	591	

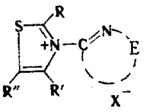
TABLE 2



Dye	R	R′	R″	λ_{max}, nm
X	2-Thiazolyl	CH_3	H	575
XI	2-Thiazolyl	H	CH_3	604
XII	2-Thiazolyl	CH_3	CH_3	585
XIII	Ethyl	CH_3	H	556
XIV	Ethyl	H	CH_3	553
V	Ethyl	CH_3	CH_3	566

and some dimethylidynemerocyanines from IB, and symmetrical and unsymmetrical trimethylidynecyanines from IA [2]. One approach to a method for the preparation of N-hetarylthiazolium salts consisted in the reaction of 2-mercapto derivatives of azoles (benzothiazole, N-methylimidazole, and 4,5-dimethylthiazole) with 2-chlorobenzothiazole or 2-chlorobenzoxazole with subsequent rearrangement of the resulting sulfide (II) to thione III and quaternization of the latter to quaternary salt IV.

In an investigation of this reaction [1] it was found that, depending on the reagent, the reaction may proceed in different directions. Thus in the case of 1-methyl-2-mercaptoimidazole and 2-mercaptobenzothiazole it goes to completion and gives merocyanines. Unexpected results were obtained in the reactions of other azoles. For example, in the reaction of 2-mercapto-4,5-dimethylthiazole with 2-chlorobenzothiazole, bis(2-benzothiazolyl) sulfide was isolated along with sulfide IIa, whereas bis(4,5-dimethyl-2-thiazolyl) sulfide was isolated in the reaction with 2-chlorobenzoxazole.



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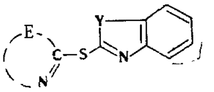

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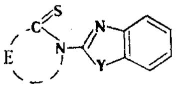

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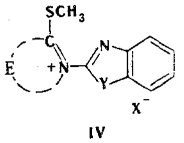
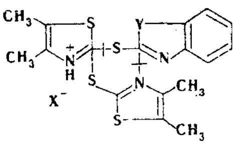


IV



V

A R=CH_3; B R=SCH_3; R′, R″=H, CH_3; E is a group of atoms that closes the heteroring (a — 4,5-dimethylthiazole, b—benzothiazole, c—pyridine, d—tetrohydrobenzothiazole).

These anomalies are satisfactorily explained by the formation and subsequent cleavage of complex V* with liberation in the first case (Y = S) of 2-mercaptobenzothiazole, which then reacts with the unchanged 2-chlorobenzothiazole to give bis(2-benzothiazolyl) sulfide. The second cleavage product may be bis(4,5-dimethyl-2-thiazolyl) sulfide, which was also isolated in the reaction with 2-chlorobenzoxazole.

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*An error in the depiction of the complex was made in [1].

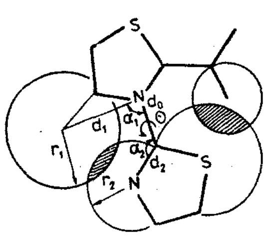

Fig. 1

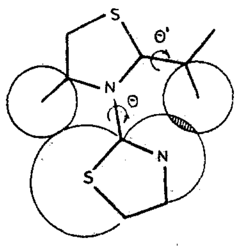

Fig. 2

Fig. 1. Thiazolocarbocyanine fragment with a methyl group in the 4 position of the thiazole ring and radii (r): CH_3 1.80, S 1.67, N 1.35, and H 1.08 Å.

Fig. 2. Thiazolocarbocyanine fragment without substituents in the 4 and 5 positions of the thiazole ring. The symbols are the same as in Fig. 1.

Individual products were not isolated in the reactions of the remaining azoles with 2-chlorobenzothiazole.

The effect of various hetaryl residues attached to the nitrogen atom of the thiazole rings on the color of the dyes was traced in series of symmetrical and unsymmetrical carbocyanines and styryls from salts IA (a-d). It was found that when an alkyl residue is replaced by a residue of electronegative character, one observes a bathochromic shift of the absorption maximum that is more pronounced, the lower the basicity of the residue, i.e., in the order ethyl < phenyl < pyridyl < thiazolyl < tetrahydrobenzothiazolyl < benzothiazolyl (the λ_{max} values of dyes with these rings are, respectively, 566, 572, 585, 586, and 591 nm*). The order of the relative basicities of the hetaryl groups was derived on the basis of the deviations of the unsymmetrical dyes and the styryls and coincides with the order presented by Kiprianov [7] and Brooker [8]. The relative basicities (the A values [9]) and the pK_a values, which are also in agreement with the data presented above (Table 1), were also determined for carbocyanine dyes with α-hetaryl residues attached to the nitrogen atoms of the thiazole ring.

There is no doubt that the bathochromic effect of the α-hetaryl residues is weakened by steric hindrance on the part of the 4-methyl groups of the thiazole rings. This is seen distinctly from the data in Table 2, in which the absorption maxima of thiazolocarbocyanines with 4-methyl-, 5-methyl-, and 4,5-dimethylthiazole rings are presented.

The data in Table 2 confirm the stronger effect of α-hetaryl residues as compared with alkyl residues and make it possible to draw the qualitative conclusion that the bathochromic effect of the α-hetaryl residues is intensified when steric hindrance is removed. In addition, these data are too inadequate to enable one to form a judgment regarding the degree of participation of steric hindrance in the development of the color, inasmuch as both the effect of the basicities of the hetaryl residues and the possibility of lengthening the conjugation chain as a consequence of the inclusion of N-α-hetaryl residues in it should be taken into account. In the latter case, the stronger bathochromic effect of the benzothiazole ring as compared with the thiazole ring may be due to this factor to a greater degree than the difference in their basicities. However, removal of the hetaryl residues from the plane by their rotation about the bond with the nitrogen atom may reduce this factor to a minimum. The angle of rotation (θ) of these residues can be estimated from the geometry of the molecule by means of a formula found by one of us:

$$\mathrm{Cos}\ \theta = \frac{d_0^2 + d_1^2 + d_2^2 - (r_1 + r_2)^2 - 2d_0(d_1 \cos \alpha_1 + d_2 \cos \alpha_2) + 2d_1 d_2 \cos \alpha_1 \cos \alpha_2}{2d_1 d_2 \sin \alpha_1 \sin \alpha_2}.$$

Geometrical parameters d_0, d_1, d_2, r_1, r_2, α_1, and α_2 are presented in Fig. 1.

The geometry of the thiazole ring was taken from [10]. When there is a 2-thiazolyl residue attached to the nitrogen atom these parameters are as follows: $d_0 = 1.5$ Å, $d_1 = 2.5$ Å, $\alpha_1 = 92°$, $d_2 = 1.34$ Å, $\alpha_2 = 123°$, $r_1 = 1.80$ Å, and $r_2 = 1.35$ Å.

It was found from the formula indicated above that the angle of rotation (θ) is 58°. When phenyl or 2-pyridyl groups are attached to the nitrogen atom, θ is 59°. As seen from the projection formula of the dye (Fig. 1), steric hindrance also arises between the sulfur atom and the hydrogen atom in the α position of the polymethine chain, but this hindrance vanishes when θ = 58°, and the principal chromophore in dye XII is

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*See also [6].

therefore planar. The situation is somewhat different in the case of dye XI, which does not contain a bulky methyl group in the 4 position of the thiazole ring (Fig. 2). In this case the steric hindrance between the nitrogen atom of the thiazole ring and the hydrogen atom of the polymethine chain proves to be substantial. This hindrance can be eliminated both by rotation of the thiazole ring (angle θ) and by partial rotation of the bond of the first link of the polymethine chain (angle θ').

If it is assumed that $\theta' = 0$, θ_{XI} will be 44°. The difference in the θ_{XII} and θ_{XI} values (58 and 44°) is not large enough to explain the large difference $\Delta\lambda$ in the case of dyes XI and XIV (51 nm) as compared with the $\Delta\lambda$ values of dyes XII and V (19 nm). In the case of dye XI the planarity of the principal chromophore is probably also disrupted, i.e., rotation θ' is realized, and this should also lead to a certain deepening of the color accompanied by a decrease in the absorption extinction: The $\varepsilon \cdot 10^{-4}$ values for dyes XI, XII, and V are, respectively, 6.3, 9.8, and 8.3.

EXPERIMENTAL

2-Thioacetamido-4,5,6,7-tetrahydrobenzothiazole (XVI). A 0.98-g (5 mmole) sample of 2-acetamido-4,5,6,7-tetrahydrobenzothiazole (XV) [11] and 1 g of phosphorus pentasulfide were refluxed in 13 ml of dry dioxane for 1.5 h, after which the resulting solution was decanted, and the solid residue was extracted repeatedly with boiling dioxane. The solution was evaporated, and the residue was dissolved in 8% sodium hydroxide solution. The solution was filtered, the filtrate was diluted to three times its original volume, and a stream of CO_2 was bubbled through it to give 0.65 g of a precipitate, which was recrystallized three times from alcohol to give 0.4 g (40%) of a product with mp 179-180°. Found %: N 13.3; S 29.8. $C_9H_{12}N_2S_2$. Calculated %: N 13.2; S 30.2.

2,4,5-Trimethyl-3-(4,5,6,7-tetrahydro-2-benzothiazolyl)thiazolium Bromide (XVII). A 1.06-g (5 mmole) sample of XVI was heated with 0.75 g (5 mmole) of 3-bromo-2-butanone at 100° for 1.5 h, after which the melt was stirred with hot benzene, and the benzene was decanted. The residue was triturated with acetic anhydride, and the solid material was removed by filtration. Ether was added to the filtrate, and the resulting oil was separated and dissolved in water. The aqueous solution was boiled with activated charcoal and filtered, and the filtrate was evaporated to dryness to give 0.5 g (30%) of a quaternary salt of viscous consistency, which was used without further purification.

2-{3-[3-(4,5,6,7-Tetrahydro-2-benzothiazolyl)-4,5-dimethyl-2-thiazolinylidene]propenyl}-3-(4,5,6,7-tetrahydro-2-benzothiazolyl)-4,5-dimethylthiazolium Perchlorate (XVIII). A mixture of 0.48 g (1.4 mmole) of XVII, 1.5 g (0.01 mole) of ethyl orthoformate, and 1 ml of acetic anhydride was heated until coloration developed, after which it was heated at 120° for 45 min. The dye was precipitated by the addition of ether, dissolved in isopropyl alcohol, and precipitated in the form of the perchlorate by the addition of 20% sodium perchlorate solution. Workup gave a product with mp 221-222° (from ethanol–isopropyl alcohol). Found %: C 50.4; H 5.0; S 19.6. $C_{27}H_{31}ClN_4S_4$. Calculated %: C 50.7; H 4.9; S 20.0.

2-{3-[3-(2-Thiazolyl)-4-methyl-2-thiazolinylidene]propenyl}-3-(2-thiazolyl)-4-methylthiazolium Perchlorate (XIX). A 0.6-g sample of 2-thioacetamidothiazole [2] was fused with 0.6 g of chloroacetone at 84° until a homogeneous mass was obtained. The melt was dissolved in water, and the aqueous solution was extracted with ether and chloroform. The aqueous layer was evaporated to dryness, the residue was triturated with acetic anhydride, and the solid material was removed by filtration. A semisolid mass of 2,4-dimethyl-3-(2-thiazolyl)-thiazolium bromide was isolated from the filtrate with ether. This salt was refluxed for a few minutes with a large excess of ethyl orthoformate in acetic anhydride, after which the reaction mixtures were combined, and the dye was precipitated by the addition of ether. A 0.8-g sample of the crude salts yielded 0.065 g of the dye. The dye was chromatographed twice on deactivated aluminum oxide in chloroform solution containing 1-2% alcohol. It was isolated in the form of the perchlorate with mp 213-214° (from isopropyl alcohol). Found %: S 23.7. $C_{17}H_{15}ClN_4O_4S_4 \cdot 2H_2O$. Calculated %: S 23.8.

2-{3-[3-(2-Thiazolyl)-5-methyl-2-thiazolinylidene]propenyl}-3-(2-thiazolyl)-5-methylthiazolium Perchlorate (XX). A 1.58-g (0.01 mole) sample of 2-thioacetamidothiazole was fused with 1.37 g (0.01 mole) of α-bromopropionaldehyde at 105° for 2 h, after which the melt was extracted twice with hot benzene. The benzene was decanted, and the residue was triturated with acetic anhydride. The solid material was removed by filtration, and 2,5-dimethyl-3-(2-thiazolyl)thiazolium bromide was precipitated from the filtrate by the addition of ether. The salt was dissolved in water, and the solution was refluxed with charcoal and evaporated to dryness to give 1.1 g of purified salt. A 0.5-g (1.8 mmole) sample of this salt was refluxed with 4 ml of acetic anhydride and 1.2 g of ethyl orthoformate. The dye was isolated in the form of the perchlorate and was chromatographed twice and precipitated from alcohol solution by the addition of ether to give 0.018 g of a product with mp 191°. Found %: N 11.4. $C_{17}H_{15}ClN_4O_4S_4$. Calculated %: N 11.1.

The authors thank É. B. Lifshits under whose supervision the A values were determined (see Table 1).

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STRUCTURE AND TAUTOMERISM OF SUBSTITUTED 2-AMINO-4H-1,3-THIAZINES

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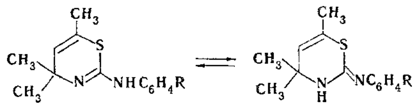
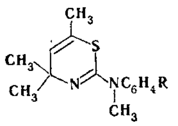
It is shown by means of the IR, UV, and PMR spectra of substituted 2-amino-4H-1,3-thiazines that they exist primarily in the amino form in the crystalline state and in solution.

In a previous communication [1] it was shown that an amino structure is characteristic for 4,4,6-trimethyl-2-alkylamino-4H-1,3-thiazine. It might have been assumed that the presence of an electronegative substituent attached to the exocyclic nitrogen atom would promote a shift in the tautomeric equilibrium to favor the imino form [2]. In this connection, in the present research we studied the structure and tautomerism of 4,4,6-trimethyl-2-arylamino-4H-1,3-thiazines (I) [3].



I A IB



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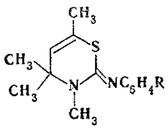

III

There are two distinct bands of approximately equal intensity associated with the stretching vibrations of the NH bond in the high-frequency region of the IR spectra of all of the investigated compounds (I) in the crystalline state (3105-3200 cm^{-1}) and in solution (3370-3430 cm^{-1}). The intensity of the low-frequency band at ~3380 cm^{-1} in the spectra of very dilute solutions (0.02% in CCl_4) is considerably reduced as compared

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