CONDENSED HETEROCYCLES WITH A THIAZOLE RING.
16.* CYANINE DYES BASED ON THIAZOLO[3,4-*a*]PYRIDINIUM SALTS

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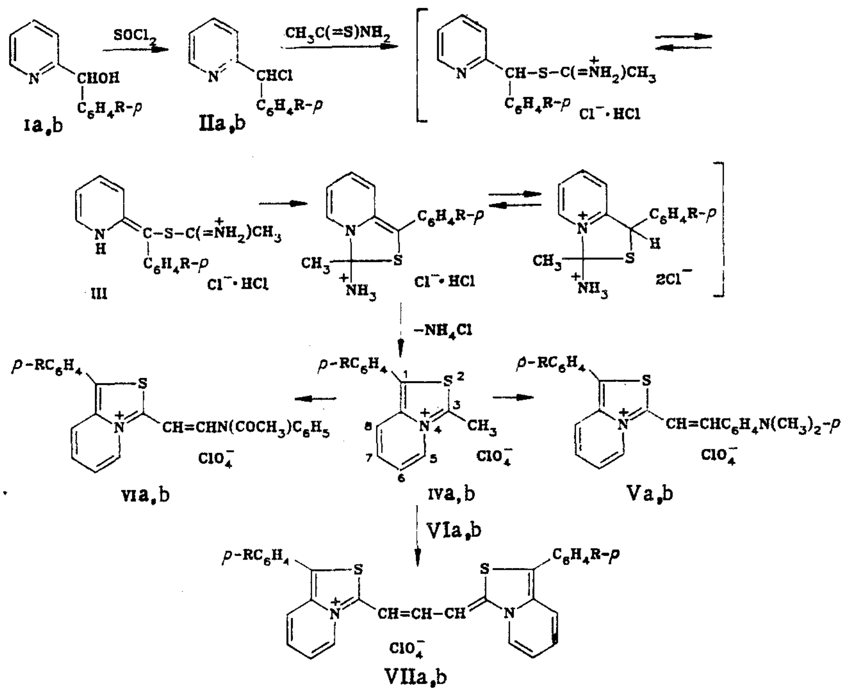
The reaction of 2-(α-chlorobenzyl)pyridines with thioacetamide gave 3-methyl-1-arylthiazolo[3,4-*a*]pyridinium salts, which form cyanines. It was established that the thiazolopyridinium ring in the dyes has high electron-donor character and a great effective length.

Quaternary salts of 2-methylthiazoles are widely used in the synthesis of polymethine dyes [2]. Condensed heterocyclic systems with a nodal nitrogen atom that contain a thiazole ring have also recently attracted the attention of researchers [3]. Thiazolo[3,4-*a*]-pyridine derivatives undoubtedly occupy a special place among the simplest compounds of this type; however, only individual representatives of this class have been described [4, 5].



I–VII a R=H; b R=OCH₃

In order to synthesize new methylthiazolo[3,4-*a*]pyridinium salts that are suitable for obtaining polymethine dyes we studied the reaction of 2-(α-chlorobenzyl)pyridines IIa,b which are formed from 2-(α-hydroxybenzyl)pyridines Ia,b [6], with thioacetamide. Salts, which were isolated in the form of the perchlorates IVa,b, are formed when these reagents are fused. It was found that IVa,b can also be obtained directly from hydroxypyridines Ia,b by successive treatment of them with thionyl chloride and thioacetamide. The formation of IVa,b evidently proceeds through the formation of thioimino esters III, for which, in analogy with the data in [7], one may assume the existence of two tautomeric forms and

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*See [1] for Communication 15.

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp,* °C	λ_{max}, nm (log ε)	Found, %		Empirical formula	Calc., %		Yield, %
			Cl	S		Cl	S	
IVa	164...166	307 (3,70), 361 (3,78)	11,0	10,1	$C_{14}H_{12}ClNO_4S$	10,9	9,9	28
IVb	195...197	376 (3,94)	10,2	9,3	$C_{15}H_{14}ClNO_5S$	10,1	9,1	23
Va	267...268	383 (3,99), 547 (4,47)	7,8	7,3	$C_{23}H_{21}ClN_2O_4S$	7,8	7,0	38
Vb	273...274	404 (3,99), 513 (4,56)	7,4	6,7	$C_{24}H_{23}ClN_2O_5S$	7,5	6,8	82
VIa	145...148		7,2	6,9	$C_{23}H_{19}ClN_2O_5S$	7,5	6,8	92
VIb	179...180		7,4	6,2	$C_{24}H_{21}ClN_2O_6S$	7,1	6,4	87
VIIa	199...200	438 (3,96), 728 (4,83)	6,0	10,9	$C_{29}H_{21}ClN_2O_4S_2$	6,3	11,4	55
VIIb	224...225	440 (3,80), 732 (4,81)	5,7	9,9	$C_{31}H_{23}ClN_2O_6S_2$	5,7	10,3	40

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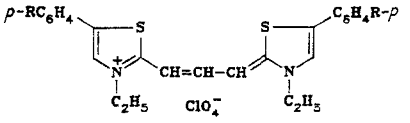
*The compounds were crystallized: IVa from water, IVb from nitromethane—ethyl acetate (1:2), VIIa from acetic anhydride, Vb and VIIb from alcohol—nitromethane (1:1), and Va from acetic acid—acetic anhydride (3:1).

their subsequent intramolecular cyclization with the participation of the nucleophilic nitrogen atom of the pyridine ring and the electrophilic carbon atom of the thioimino ester with subsequent splitting out of an ammonium cation.

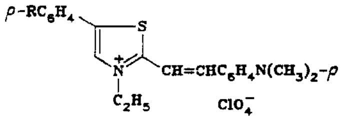
The compositions and structures of the products obtained were confirmed by the results of elementary analysis and the PMR spectral data. Thus in the PMR spectra of IVa,b in trifluoroacetic acid one observes singlets of protons of methyl groups and multiplets of aromatic protons (2.80 and 6.60-8.10 ppm, respectively), and for salt IVb one also observes a singlet of protons of a methoxy group at 3.53 ppm. The chemical shifts of the signals of the protons of the C—CH_3 groups of the compounds described and their aza-substituted structural analog — 6-methyl-8-phenylthiazolo[3,4-b]pyrimidinium perchlorate [8] — virtually coincide. As in the case of ordinary quaternary pyridinium salts [9], a signal of the 5-H atom in the α position relative to the electron-acceptor nitrogen atom is observed at weakest field (8.66-8.69 ppm) in the PMR spectra of perchlorates IVa,b in DMSO. The signals of the γ-pyridinium proton in the 7 position (8.00-8.05 ppm) and two β protons (6-H and 8-H) (7.5 ppm) are located at stronger field. Bathochromic shifts of the absorption maximum (by 15 and 21 nm, respectively) as compared with their aza analog [8] are observed in the electronic spectra of salts IVa,b (Table 1).

As in [10], 3-methylthiazolo[3,4-*a*]pyridinium salts IVa,b react readily with electrophilic intermediate compounds that are used in the synthesis of polymethine dyes. Thus the reaction of salts IVa,b with p-dimethylaminobenzaldehyde in acetic anhydride leads to styryl dyes Va,b, while the reaction with diphenylformamidine leads to acetanilidovinyl derivatives VIa,b, which readily give symmetrical carbocyanines VIIa,b on reaction with salts IVa,b in the presence of triethylamine. According to the data on the maxima of the long-wave bands of carbocyanines VIIa,b (see Table 1), the thiazolopyridinium ring in the dyes has a great effective length (L = 6.28-6.30) [11].

One of the most important characteristics of the terminal heteroresidue in the dyes is its electron-donor character (Φ_0) [11], which determines the electronic asymmetry and disposition of the boundary energy levels in the molecules [12], as well as the possibility of the practical application of cyanines. This evaluation can be realized extremely simply by the method of deviations [13]. On the basis of the deviation for styryl Va (117 nm) it may be assumed that the electron-donor character of the 1-phenylthiazolo[3,4-*a*]pyrimidinium ring approaches that of naphthimidazoles (118.5 nm) [14]. However, the introduction of a methoxy group into the phenyl ring of the styryl molecule leads, in the case of Vb, to a significant hypsochromic shift of the long-wave band (34 nm) and a somewhat smaller bathochromic shift of the short-wave band (21 nm); the deviations increase significantly (162 nm) and even surpass in value the analogous parameters of most of the known heterocycles that are used in the synthesis of polymethine dyes. In other words, the methoxy group has virtually no effect on the effective length of the 1-phenylthiazolo[3,4-*a*]pyridinium ring in the dyes but substantially increases its electron-donor character.



VIIIa,b



IXa,b

VIII, IX a R=H; b R=OCH$_3$

A comparison of the data from the electronic spectra of Va,b and 2-methyl-3-ethyl-5-phenyl(4-methoxyphenyl)thiazolium derivatives VIIIa,b and IXa,b [15] (592, 616, and 510, 505 nm, respectively) shows that annelation of the pyridine fragment with a thiazole fragment leads to a significant increase in both the effective length and the electron-donor character of the heterocycle. The calculated deviations for styryls IXa,b are 88 and 103 nm, respectively, while the L values for dyes VIIIa,b are 4.92 and 5.12.

Thus the synthesized thiazolo[3,4-*a*]pyridinium derivatives can be used to create new deeply dolored dyes with predesignated properties.

EXPERIMENTAL

The electronic spectra of solutions fo the compounds in acetonitrile were obtained with an SF-8 spectrophotometer. The PMR spectra of solutions in trifluoroacetic acid were recorded with a Tesla BS-467 spectrometer (60 MHz, hexamethyldisiloxane as the internal standard), while the PMR spectra of solutions in d$_6$-DMSO were recorded with a WP-100SY spectrometer (100 MHz, tetramethylsilane as the internal standard).

The characteristics of the synthesized compounds are presented in Table 1.

3-Methyl-1-phenylthiazolo[3,4-*a*]pyridinium Perchlorate (IVa). A 4-g (3 mmole) sample of thionyl chloride was added to a solution of 3.7 g (2 mmole) of 2-(α-hydroxybenzyl)pyridine (Ia) in 20 ml of benzene, and the mixture was refluxed for 10 min. The benzene was then evaporated at reduced pressure, the oily residue was washed with ether and treated with 1.5 g (1 mmole) of thioacetamide, and the mixture was heated for 20 min at 125°C. It was then cooled and dissolved in 20 ml of isopropyl alcohol, the ammonium chloride was separated, and 2 ml of 57% perchloric acid was added to the solution. The precipitate was removed by filtration and crystallized to give 0.18 g of product. PMR spectrum (CF$_3$COOH): 2.80 (s, 3H, CH$_3$), 6.60-8.10 ppm (m, 9H, aromatic); (d$_6$-DMSO): 3.40 (s, 3H, CH$_3$), 7.50-7.80 (m, 7H, aromatic), 8.05 (m, 1H, 7-H), 8.69 ppm (dd, 1H, 5-H, $J_{5,6}$ = 6 Hz, $J_{5,7}$ = 2 Hz).

3-Methyl-1-(4-methoxyphenyl)thiazolo[3,4-*a*]pyridinium Perchlorate (IVb). This compound was similarly obtained from pyridine Ib. PMR spectrum (CF$_3$COOH): 2.80 (s, 3H, CH$_3$), 3.57 (s, 3H, OCH$_3$), 6.60-8.10 ppm (m, 8H, aromatic); (d$_6$-DMSO): 3.22 (s, 3H, CH$_3$), 3.88 (s, 3H, OCH$_3$), 7.22 (d, 2H, aromatic, J_{ortho} = 9 Hz), 7.40-7.60 (m, 2H, 6-H and 8-H), 7.71 (d, 2H, aromatic, J_{ortho} = 9 Hz), 8.00 (m, 1H, 7-H), 8.66 ppm (dd, 1H, 5-H, $J_{5,6}$ = 6 Hz, $J_{5,7}$ = 2 Hz).

3-(2-Acetanilidovinyl)-1-phenylthiazolo[3,4-*a*]pyridinium Perchlorate (VIa). A mixture of 0.32 g (1 mmole) of perchlorate Ia, 0.40 g (2 mmole) of diphenylformamidine, and 5 ml of acetic anhydride was refluxed for 5 min, after which it was cooled and treated with 15 ml of ether, and the precipitate was removed by filtration and washed with alcohol to give 0.43 g of product.

3-(2-Acetanilidovinyl)-1-(4-methoxyphenyl)thiazolo[3,4-*a*]pyridinium Perchlorate (VIb). This compound was similarly obtained from perchlorate IVb.

3-(p-Dimethylaminostyryl)-1-phenylthiazolo[3,4-*a*]pyridinium Perchlorate (Va). A mixture of 0.32 g (1 mmole) of perchlorate Ia, 0.15 g (1 mmole) of p-dimethylaminobenzaldehyde, and 5 ml of acetic anhydride was refluxed for 3 min, after which it was cooled and treated with 15 ml of isopropyl alcohol, and the precipitate was removed by filtration and crystallized to give 0.17 g of product.

Styryl Vb. This compound was similarly obtained from salt IVb.

1-Phenyl-3-[3-(1-phenyl-3(3H)-thiazolo[3,4-*a*]pyridinylidene)-1-propenyl]thiazolo[3,4-*a*]pyridinium Perchlorate (VIIa). A mixture of 0.23 g (0.5 mmole) of salt VIa, 0.16 g (0.5 mmole) of perchlorate IVa, and 3 ml of acetic anhydride was heated to the boiling point, after which 0.05 g (0.5 mmole) of triethylamine was added, and the mixture was cooled rapidly to room temperature and treated with 10 ml of isopropyl alcohol. The precipitated dye was removed by filtration and crystallized to give 0.15 g of product.

Carbocyanine VIIb. This compound was similarly obtained from salts IVb and VIb.

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SYNTHESIS AND ABSORPTION SPECTRA OF POLYMETHINE DYES — DERIVATIVES OF SUBSTITUTED THIENO- AND INDOLOTHIAZOLES

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Cyanine, merocyanine, and styryl dyes that are derivatives of halo-, alkyl-, alkylene-, and arylthieno[2,3-d]thiazoles and halo- and alkylindolo[3,2-d]-thiazoles were synthesized. It is shown that both electron-donor and electron-acceptor substituents in the 5 and 5' positions of the heteroresidues of thienothiazolocarbocyanines lead to a more uniform distribution of the electron density in their chromophore than in the unsubstituted dye and to a bathochromic shift of the absorption maximum. Methyl groups in the heteroresidues of indolothiazolocarbocyanines give rise to a small bathochromic effect.

Polymethine dyes that are derivatives of thieno- and indolothiazoles absorb in a longer-wave region than the corresponding thia- and naphthothiazolocyanines [1-4]. It is also known that some cyanines that are derivatives of benzo- and naphthothiazoles are effective spectral sensitizers of silver halide emulsions, in connection with which it seemed

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