CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

1. THIAZOLO[3,4-a]PYRIMIDINE DERIVATIVES

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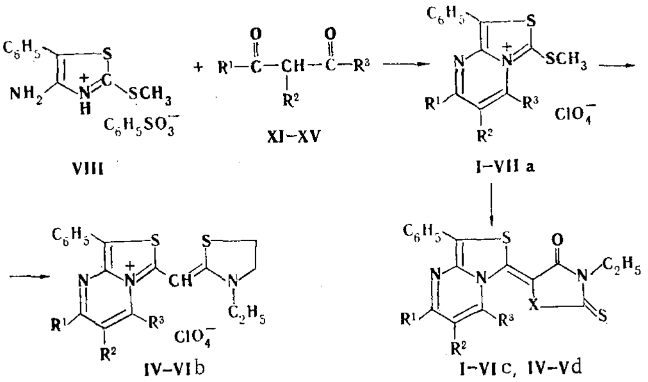
It is shown that the reaction of 1,3-dicarbonyl compounds or their acetals with 2-methylthio-4-amino-5-phenylthiazolium benzenesulfonate gives 6-methylthiothiazolo[3,4-a]pyrimidinium salts, which react with the appropriate intermediates to give polymethine dyes.

It seemed of interest to us to obtain previously unknown polymethine dyes of the thiazolo[3,4-a]pyrimidine series. In analogy with the data in [1], the 6-methylthiothiazolo[3,4-a]pyrimidinium salts (Ia-VIIa) necessary for this purpose were obtained by the reaction of 5-phenyl-4-amino-2-methylthiothiazolium benzenesulfonate (VIII) with diketones XI-XV and with tetraethoxypropanes IX and X. The formation of a condensed system is in agreement with the results of elementary analysis (Table 1) and the IR spectra, which do not contain absorption bands of the N-H bond of starting salt VIII at 3220-3410 cm^{-1}.



In the case of the reaction with benzoylacetone XIII and its substituted analog XIV one might have expected the formation of a mixture of two possible isomers; however, the position of the signals of the methyl and methylthio groups in the PMR spectra of the compound (see Table 2) indicates unambiguously that only one product, viz., 4-methyl-2,8-diphenyl-6-methylthiothiazolo[3,4-a]pyrimidinium salt (Va), is formed in the condensation of salt VIII with benzoylacetone: In contrast to the spectrum of IVa, the signal of only one methyl group in the weak-field region is observed, which indicates its closeness to the quaternary nitrogen atom. In addition, the signal of the protons of the methylthio group, as in the spectra of Ia-IVa, in which R^1 and R^3 = H or CH_3, is shifted to the weak-field region (∿0.3 ppm) as compared with the analogous signal in the spectrum of VIIa, in which additional shielding of this group occurs under the influences of the ring currents of the phenyl substituent in the 4 position.

Several bands, of which the longest-wave band is located at 390-450 nm and is due to a $\pi-\pi^*$ transition in the conjugation system of the thiazolopyrimidinium molecule, are observed in the electronic absorption spectra of solutions of Ia-VIIa (Table 1). A quantum-chemical estimate of the absorption maximum of a model compound, viz., the unsubstituted 6-methylthiothiazolo[3,4-a]pyrimidinium ion (XVI), leads to a value of 377 nm, as compared with 453 nm for cation Ia. In the calculation it was assumed that the phenyl group lies in the plane of the heterocyclic ring. Since the calculated wavelength of the first transition is some-

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TABLE 1. 6-Methylthiothiazolo[3,4-a]pyrimidinium Perchlorates Ia-VIIa

Compound	R^1	R^2	R^3	mp,[a] °C	λ_{max}, nm (log ε)	Δλ,[b] nm	Found, %		Empirical formula	Calc. %		Yield, %
							Cl	S		Cl	S	
Ia	H	H	H	211—212	295 (3,89), 340 (3,74), 422 (3,77)	—	9,9	17,8	$C_{13}H_{11}ClN_2O_4S_2$	9,9	17,9	66
IIa	H	CH_3	H	220—221	335 (3,70), 410 (3,80)	−12	9,6	17,2	$C_{14}H_{13}ClN_2O_4S_2$	9,5	17,2	81
IIIa	H	C_6H_5	H	237—238	292 (4,23), 390 (3,81)	−22	8,2	14,6	$C_{19}H_{15}ClN_2O_4S_2$	8,2	14,7	80
IVa	CH_3	H	CH_3	221—222	345 (3,76), 417 (3,90)	−5	9,3	16,8	$C_{15}H_{15}ClN_2O_4S_2$	9,2	16,6	60
Va	C_6H_5	H	CH_3	218—219	300 (4,38), 370 (3,90), 440 (3,74)	18	7,8	14,2	$C_{20}H_{17}ClN_2O_4S_2$	7,9	14,3	50
VIa	p-$CH_3OC_6H_5$	H	CH_3	211—212	305 (4,10), 349 (4,20), 440 (2,95)	18	7,1	13,2	$C_{21}H_{19}ClN_2O_5S_2$	7,4	13,3	62
VIIa	C_6H_5	H	C_6H_5	232—233	310 (4,36), 370 (3,77), 450 (3,74)	28	7,0	12,7	$C_{25}H_{19}ClN_2O_4S_2$	7,0	12,5	51

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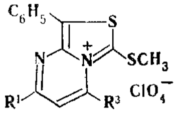
[a] Compounds Ia and IVa were crystallized from alcohol, while the remaining compounds were crystallized from alcohol–dimethylformamide: 3:1 for IIa and IIIa, 4:1 for Va and VIa, and 1:1 for VIIa. [b] A shift of the long-wave band as compared with Ia.

TABLE 2. Chemical Shifts in the PMR Spectra of Thiazolopyrimidinium Salts



Compound	S—CH_3	C—CH_3	Ar—H	—CR^1=CH—CR^3—
Ia	2,68	—	7,0—7,6	7,00 dd
IVa	2,69	2,89, 2,29	7,25	6,60
Va	2,65	2,85	7,10—7,75	7,00
VIIa	2,38	—	7,10—7,75	—

what shifted to the long-wave part of the spectrum as compared with the experimental value of the absorption maximum for Ia, it may be assumed that the phenyl group, as a consequence of steric hindrance, deviates somewhat from the plane of the thiazolopyrimidinium ring.

Diagrams of the redistribution of the electron density on the atoms of the condensed system in the case of transition of the molecule to the first excited state for XVI and Ia are presented in Fig. 1. It is apparent that the first transition is due to electron transfer from the thiazole ring (in which the electron density is decreased) to the pyrimidine ring. In the case of model compound XVI the exocyclic sulfur atom and the carbon atom in the 8 position make a particularly large contribution to the overall transfer. When a phenyl group is introduced in this position, electron transfer occurs from the carbon atoms of this group, which naturally lengthens the chromophore. Since the charge on the carbon atom in the 8 position of model compound XVI in the excited state is greater in absolute value ($z^0 = -0.0056$, $z^* = +0.1602$), the introduction of a phenyl group also stabilizes this state to a greater extent, which leads to bathochromic shifts of the absorption maximum. It is also apparent from the diagrams that substituents with electronic natures of the same type in the pyrimidine ring of the condensed system (all other things being equal) should have a qualitatively similar effect on the color, and this is observed experimentally in the case of methyl-substituted salts IIa and IVa.

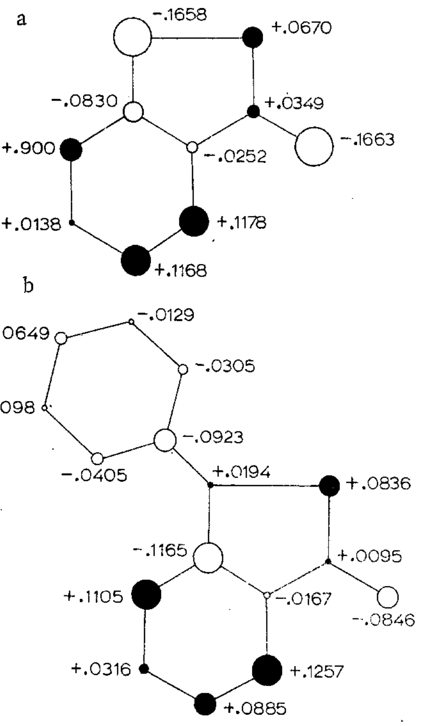


Fig. 1. Change in the electron density ($\Delta q_r = q^*_r - q_r^\circ$) in the transition of the molecule to the first excited state for model compound XVI (a) and cation Ia (b).

TABLE 3. Thiazolomonomethylidynecyanines IVb-VIb

Compound	mp, °C[a]	λ_{max}, nm (log ε)	Δλ, nm[b]	Found, %		Empirical formula	Calc., %		Yield, %
				Cl	S		Cl	S	
IVb	246—247	410 (3,97), 514 (4,27)	—	7,7	13,6	$C_{20}H_{22}ClN_3O_4S_2$	7,6	13,7	78
Vb	263—265	450 (4,35), 526 (4,11)	12	6,8	12,1	$C_{25}H_{24}ClN_3O_4S_2$	6,7	12,1	51
VIb	252—253	450 (4,36), 526 (4,12)	12	6,2	11,3	$C_{26}H_{26}ClN_3O_5S_2$	6,3	11,4	49

[a] Compounds Vb and VIb were crystallized from alcohol—dimethylformamide, while IVb was crystallized from alcohol.
[b] A shift of the long-wave absorption band as compared with IVb.

All of the synthesized methylthio derivatives Ia-VIa react with the intermediates used for the synthesis of polymethine dyes to give the corresponding monomethylidynecyanine and nullomethylidynemerocyanine dyes IVb-VIb, Ic-VIc, IVd, and Vd. Compound VIIa constitutes an exception. This difference in the reactivities is apparently due to steric hindrance produced by the phenyl group in the peri position relative to the methylthio group of VIIa.

It is interesting to note that, in contrast to the corresponding dyes of the 3-ethyl-5-phenyl-4-aminothiazolium [2], thiazolotriazolium [3], and thiazolothiadiazolium [4] series, two bands, one of which either coincides or is shifted somewhat to the short-wave part of the spectrum, the other of which is located in the longer-wave part of the spectrum (50-100 nm) as compared with the spectra of the indicated analogs, are observed in the visible part of the absorption spectra of solutions of the synthesized dyes.

We found that the substituents in the pyrimidine ring of the dyes have a substantial effect on the intensities and positions of the absorption bands just as if they were located directly in the polymethine chain. Of course, a substituent in the 4 position (R^3) of the thiazolopyrimidine ring may have a certain effect on the planarity of the dye molecules, and it is therefore more accurate to investigate the effect of only the substituents in the 2 and 3 positions (R^1 and R^2) on the color.

TABLE 4. Nullomethylidynemerocyanines

Compound	X	mp,[a] °C	λ_{max}, nm (log ε)	$\Delta\lambda^b$, nm	Found, %		Empirical formula	Calc., %		Yield, %
					N	S		N	S	
Ic	S	287—288	435 (4,17), 454 (4,19), 550 (4,20)	—	11,7	25,6	$C_{17}H_{13}N_3OS_3$	11,3	25,9	60
IIc	S	270—272	436 (4,23), 457 (4,26), 540 (4,23)	−10	11,2	24,8	$C_{18}H_{15}N_3OS_3$	10,9	24,9	84
IIIc	S	297—299	440 (4,30), 461 (4,31), 566 (4,22)	16	8,9	21,3	$C_{23}H_{17}N_3OS_3$	9,4	21,5	72
IVc	S	198—200	470 (4,00), 556 (4,34)	6	10,4	23,9	$C_{19}H_{17}N_3OS_3$	10,5	24,1	60
Vc	S	210—211	491 (4,17), 570 (3,92)	20	9,2	20,8	$C_{24}H_{19}N_3OS_3$	9,1	20,8	56
VIc	S	225—226	492 (4,36), 567 (4,18)	17	8,5	19,0	$C_{25}H_{21}N_3O_2S_3$	8,6	19,6	49
IVd	O	207—208	430 (4,01), 446 (4,02), 536 (4,23)		10,9	16,8	$C_{19}H_{17}N_3O_2S_2$	11,0	16,7	69
Vd	O	221—222	470 (4,34), 560 (3,99)		9,3	13,9	$C_{24}H_{19}N_3O_2S_2$	9,4	14,4	54

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[a] Compound Ic was crystallized from alcohol, while the remaining compounds were crystallized from alcohol—DMF: 1:2 for IIc and IIIc, 3:1 for IVd, and 2:1 for Vc and VIc. [b] A shift of the long-wave absorption band as compared with Ic.

It is apparent from the data in Tables 3 and 4 that the position of the absorption bands of solutions of the dyes do not depend on their type but rather are determined only by the substituents in the molecules of starting salts I-VI.

It is known [5] that the appearance of two bands in the visible part of the absorption spectra of dyes is often due to the presence of two chromophore systems in the molecule; the position of these bands and their intensities depend on the position of the absorption bands of the isolated chromophore systems and the angle between them in the molecule under consideration. The peculiarities of the absorption spectra of the dyes that are thiazolo[3,4-a]pyrimidine derivatives are also probably due to the presence of two chromophores, viz., a polymethine chromophore and a thiazolopyrimidine ring, in our case also.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were obtained with a UR-10 spectrometer. The electronic spectra of solutions of the compounds in dimethylformamide (DMF) were obtained with SF-8 and SF-10 spectrophotometers. The PMR spectra of solutions of the compounds in CF_3COOH were obtained with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The quantum-chemical calculations were performed by the method in [6].

2-Methylthio-4-amino-5-phenylthiazole Benzenesulfonate (VIII). A mixture of 2.73 g (10 mmole) of cyanobenzyl benzenesulfonate and 1.1 g (10 mmole) of S-methyldithiocarbamate was heated until a vigorous reaction commenced, after which the mixture was triturated with acetone, and the product was removed by filtration. The yield was 2.5 g (66%). Found: N 7.4; S 25.5%. $C_{10}H_{10}N_2S_2 \cdot C_6H_6O_3S$. Calculated: N 7.4; S 25.3%.

6-Methylthio-8-phenylthiazolo[3,4-a]pyrimidinium Perchlorate (Ia). A mixture of 0.76 g (2 mmole) of benzenesulfonate VIII, 0.3 g (2.5 mmole) of 1,1,3,3-tetraethoxypropane, and 5 ml of absolute alcohol was heated at 90°C for 1 h, after which 1 ml of 72% perchloric acid was added, and the product was removed by filtration and crystallized (Table 1).

Perchlorates IIa and IIIa. These compounds were similarly obtained.

2,4-Dimethyl-6-methylthio-8-phenylthiazolo[3,4-a]pyrimidinium Perchlorate (IVa). A mixture of 0.76 g (2 mmole) of benzenesulfonate VIII and 0.3 g (3 mmole) of acetylacetone was fused at 85-90°C for 1 h, after which an alcohol solution of sodium perchlorate was added, and the mixture was triturated with acetone. The reaction product was removed by filtration and crystallized.

Perchlorates Va-VIIa. These compounds were obtained in the same way as the preceding compound (at 110°C for 5 h in the case of Va, at 100°C for 1 h in the case of VIa, and at 150°C for 3 h in the case of VIIa).

2,4-Dimethyl-8-phenyl-6-[(3-ethylthiazolidin-2-ylidene)methyl]thiazolo[3,4-a]pyrimidinium Perchlorate (IVb). A mixture of 0.38 g (1 mmole) of perchlorate IVa, 0.26 g (1 mmole) of 2-methyl-3-ethyl-4,5-dihydrothiazolium iodide, and 8 ml of absolute alcohol was heated until the components dissolved, 0.1 g (1 mmole) of triethylamine was added, and the precipitated dye was removed by filtration and crystallized (Table 3).

Monomethylidynecyanines Vb and VIb. These compounds were similarly obtained from the corresponding quaternary salts.

3-Ethyl-5-(2,4-dimethyl-8-phenylthiazolo[3,4-a]pyrimidin-6-ylidene)thiazolidine-2-thion-4-one (IVc). A mixture of 0.38 g (1 mmole) of perchlorate IVa, 0.16 g (1 mmole) of 3-ethylthiazolidine-2-thion-4-one, and 5 ml of absolute alcohol was heated until the components dissolved, 0.1 g (1 mmole) of triethylamine was added, and the dye was removed by filtration and crystallized (Table 4).

Nullomethinylmerocyanines Ic-IIIc, Vc, and VIc. These compounds were similarly obtained from the corresponding salts, while nullomethinylmerocyanines IVd and Vd were obtained from salts IVa and Va and 3-ethyloxazolidine-2-thion-4-one.

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CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

2.* MONOMETHYLIDYNECYANINE DYES OF THE THIAZOLO[3,4-a]PYRIMIDINE SERIES

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Unsymmetrical monomethylidynecyanine dyes that contain benzothiazole or quinoline residues were obtained on the basis of thiazolopyrimidine. The energies of the transitions and the electron distributions in the ground, first, and second excited states were calculated for several of the dyes obtained and for model compounds by the self-consistent-field configuration-interaction (SCF CI) method in order to interpret the first absorption bands and determine the localization of the electron transitions.

In a previous communication [1] we described nullomethinylmerocyanines obtained on the basis of thiazolopyrimidines Ia-VIa and unsymmetrical monomethinylcyanines that contain a thiazoline residue. Two absorption bands of comparable intensity are generally observed in the absorption spectra of such dyes in the visible region; this is not at all usual for simple polymethine dyes that are derivatives of nitrogen heterocycles. In order to study the nature of this sort of phenomenon, in the present research we obtained monomethinylcyanines Ib-VIb and IIIc-Vc, which contain benzothiazole and quinoline residues, by the reaction of methylthio derivatives Ia-VIa with the corresponding quaternary salts of 2-methylbenzothiazole and 4-methylquinoline.

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*See [1] for communication 1.

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