(1 mmole) of triethylamine was added. The precipitated dye was removed by filtration and crystallized from alcohol with DMF (4:1) to give 0.23 g of a product with λ_{max} 455 nm (log ε 4.59).

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CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

7.* THIAZOLO[3,4-a]THIAZOLO[5,4-e]PYRIMIDINES

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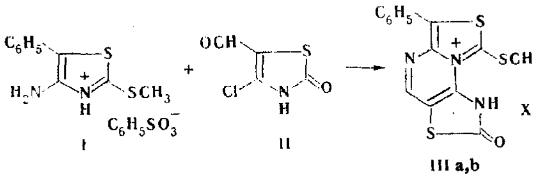
The condensation of 4-amino-2-methylthio-5-phenylthiazolium benzenesulfonate with 2-oxo-5-formyl-4-chloro-4-thiazoline gave a salt of a previously unknown three-ring heterosystem, which was used for the synthesis of thia- and 4-quinomonomethylidyne-cyanine dyes. The absorption spectra of these dyes are similar to the spectra of the analogous dyes obtained from thiazolo[3,4-a]pyrimidine.

It has been previously shown that, in contrast to their analogs, which are ordinarily used in the chemistry of polymethine dyes (benzothiazole, benzimidazole, quinoline, and other dyes), several absorption bands are observed in the visible part of the absorption spectra of solutions of polymethine dyes obtained from thiazolo[3,4-a]pyrimidine derivatives [2]. This phenomenon is due to the specific characteristics of the thiazolopyrimidine ring. It therefore seemed of interest to continue the synthesis and study of dyes based on heterocyclic compounds of this type. In order to obtain derivatives of a new heterocyclic system that contains a thiazolo[3,4-a]pyrimidine fragment we studied the reaction of benzenesulfonate I with 2-oxo-5-formyl-4-chlorothiazoline (II).



III a X=$C_6H_5SO_3$; b X=ClO_4

Considering the data in [3] on the formation of a condensed system in the reaction of chloro aldehyde II with 2-aminopyridine, one might have hoped that in our case also cyclization would lead to compounds of the III type. In fact, according to the results of elemental analysis (Table 1), the reaction gives salts III, the structure of which was proved by data from the IR and PMR spectra. Thus only bands of stretching vibrations of C=N and C=O bonds (1645 and 1740 cm^{-1}) are observed in the IR spectrum of perchlorate IIIb, and absorption bands of the N-H bonds of starting salt I and of the C=O and C-H bonds of the aldehyde group of II (1690, 1720, and 2710 cm^{-1} [4]) do not appear. A singlet of protons of the methylthio group, a multiplet of protons of two phenyl groups, and a singlet of a proton in the 4

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*See [1] for communication 6.

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TABLE 1. Thiazolo[3,4-a]thiazolo[5,4-e]pyrimidinium Salts (IIIa,b) and Dyes (IV-VI)

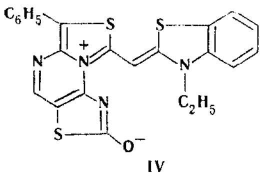
Compound	mp, deg C	Found, %		Empirical formula	Calculated, %		Yield, %
		N (Cl)	S		N (Cl)	S	
III a	223—225	8,7	25,9	$C_{20}H_{15}N_3O_4S_4$	8,6	26,2	56
III b	242—243	(8,2)	22,3	$C_{14}H_{10}ClN_3O_5S_3$	(8,2)	22,3	62
IV	300—301	11,9	20,7	$C_{23}H_{16}N_4OS_3$	12,2	20,9	71
V	287—288	12,1	14,0	$C_{25}H_{18}N_4OS_2$	12,3	14,1	55
VI	306—308	(6,3)	16,8	$C_{23}H_{17}ClN_4O_5S_3$	(6,3)	17,1	80

TABLE 2. Absorption Spectra of III-VI

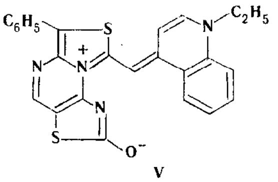
Compound	Solvent	λ_{max}, nm (log ε)
IIIb	DMF	300 (4,47), 313 (4,48), 450 (3,92)
IV	DMF	421 (4,03), 438 (3,97), 544 (4,45)
V	DMF	630 (4,55), 650 (4,54)
VI	HCOOH	426 (4,02), 442 (4,17), 546 (4,24)

position of the heteroring with chemical shifts (δ) 2.60, 6.8-7.6, and 8.23 ppm, respectively, are observed in the PMR spectrum of benzenesulfonate IIIa.

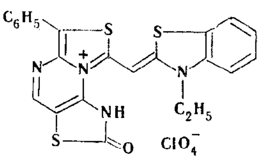
The derivative of a new heterocyclic cation that we obtained reacts under ordinary conditions with the nucleophilic agents that are used for the synthesis of polymethine dyes. Condensation at the 8 position of the heteroring with displacement of the methylthio group in the presence of triethylamine is accompanied by splitting out of a proton from the 1 position to give mesoionic compounds. Thus mesoionic monomethylidynecyanines IV and V, respectively, were obtained in the reaction with 2-methyl-3-ethylbenzothiazolium toluenesulfonate or 4-methyl-1-ethylquinolinium perchlorate.



IV



V



VI

The structures of the dyes are confirmed by the IR spectra, in which a shift of the band of the stretching vibrations of the C=O bond (1680 cm^{-1}) is observed. The isolated oxides react readily with acids to give saltlike dyes. Thus perchlorate VI (νC=O 1730 cm^{-1}) was obtained from monomethylidynecyanine IV.

The characteristics of the absorption bands of the synthesized monomethylidynecyanines (Table 2) are close to the analogous characteristics of the corresponding compounds of the thiazolopyrimidine series [2]. It is apparent from a comparison of the absorption spectra of oxide IV and perchlorate VI that protonation leads primarily to equalization of the intensities of the short-wave and long-wave absorption bands, which, in turn, evidently indicates a higher degree of participation of the π electrons of the heteroring in the electron transition that is responsible for the color of the dye. Thus we have established that the addition to thiazolopyrimidine of yet another thiazole ring, in contrast to annelation of a quinoline ring in the same positions [5], does not substantially change the spectral characteristics of the corresponding monomethylidynecyanines.

EXPERIMENTAL

The electronic spectra were obtained with SF-4 and SF-8 spectrophotometers. The IR spectra of KBr pellets were obtained with an IR-10 spectrometer. The PMR spectra of solutions in CF_3COOH were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

2-Oxo-8-methylthio-6-phenyl-1,2-dihydrothiazolo[3,4-a]thiazolo[5,4-e]pyrimidinium Benzenesulfonate and Perchlorate (IIIa,b, Table 1). A mixture of 0.76 g (2 mmole) of benzenesulfonate I, 0.32 g (2 mmole) of aldehyde II, and 2 ml of acetic acid was heated at 100°C for 1 h, after which the precipitated benzenesulfonate (IIIa) was removed by filtration and crystallized from DMF to give 0.5 g of product. The perchlorate (IIIb) was obtained by adding 0.5 ml of 72% perchloric acid to the reaction mixture prior to cooling. It was crystallized from alcohol—DMF (1:1).

6-Phenyl-8-[(3-ethyl-2-benzothiazolinylidene)methyl]thiazolo[3,4-a]thiazolo[5,4-e]pyrimidinium 2-Oxide (IV). A mixture of 0.43 g (1 mmole) of salt IIIa and 0.35 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium toluenesulfonate in 5 ml of absolute alcohol and 3 ml of DMF was heated to the boiling point, and 0.2 g (2 mmole) of triethylamine was added. Dye IV was removed by filtration and crystallized from alcohol—DMF (1:1). The yield was 0.3 g.

6-Phenyl-8-[(1-ethyl-1,4-dihydroquinolin-4-ylidene)methyl]thiazolo[3,4-a]thiazolo[5,4-e]-pyrimidinium 2-Oxide (V). A mixture of 0.43 g (1 mmole) of salt IIIa and 0.27 g (1 mmole) of 4-methyl-1-ethylquinolinium perchlorate was dissolved by heating in 5 ml of absolute alcohol and 2 ml of DMF, after which 0.2 g (2 mmole) of triethylamine was added. Dye V was removed by filtration and crystallized from alcohol—DMF (1:1). The yield was 0.25 g.

2-Oxo-6-phenyl-8-[(3-ethyl-2-benzothiazolinylidene)methyl]1,2-dihydrothiazolo[3,4-a]thiazolo[5,4-e]pyrimidinium Perchlorate (IV). This compound was obtained by adding excess 72% perchloric acid to a solution of dye IV in alcohol—DMF (1:1).

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SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES OF THIAZOLINO[3,2-a]BENZIMIDAZOLES

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The reaction of 1-β-hydroxyalkyl(aralkyl)-2-chlorobenzimidazoles with thiourea or the reduction of 1-acylmethylbenzimidazoline-2-thiones with sodium borohydride gave 1-β-hydroxyalkyl(aralkyl, hetaryl)benzimidazoline-2-thiones, which were converted to 2-alkyl(aryl, hetaryl)-substituted thiazolino[3,2-a]benzimidazoles by the action of $POCl_3$.

The antispasmodic activity of 2,3-dihydrothiazolo[3,2-a]benzimidazole derivatives is known [1, 2]. In a continuation of our search for preparations of this series of compounds with the indicated activity [3, 4] we isolated 1-β-hydroxyalkyl(aralkyl)benzimidazoline-2-thiones (IIIa,c,d,f, Table 3), which were obtained by the reaction of the corresponding 1-β-hydroxyalkyl(aralkyl)-2-chlorobenzimidazoles (Ia,c,d,f) [5] with thiourea in methanol (ethanol). Substances IIIb,e,g were synthesized by the reduction of 1-acylmethylbenzimidazoline-2-thiones (IIb,e,g) [6] with sodium borohydride in an aqueous alcohol medium. 2-Alkyl(aryl,

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