

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 THIAZOLE[3,4-a]PYRIMIDINE SERIES

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543.42:668.819.4

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.

\*See [1] for communication 1.

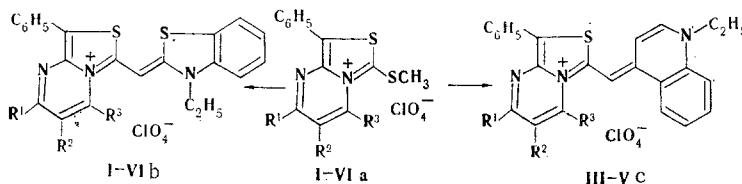
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TABLE 1. Absorption Spectra of the Synthesized Dyes

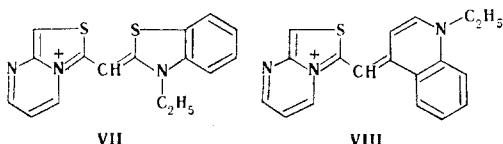
Compound	$\lambda_{\text{max}}$ , nm (lg $\epsilon$ )	$\Delta\lambda^*$ , nm
Ib	420 (4.27), 440 (4.27), 534 (4.39)	—
IIb	424 (4.28), 444 (4.30), 532 (4.41)	-2
IIIb	428 (4.31), 448 (4.33), 552 (4.35)	18
IVb	420 (4.03), 440 (4.04), 540 (4.46)	6
Vb	478 (4.47), 545 (4.34)	11
VIb	478 (4.47), 546 (4.36)	12
IIIc	485 (4.01), 520 (4.01), 630 (4.56)	
IVc	636 (4.59)	
Vc	636 (4.51)	

\*The shift of the absorption maximum of the long-wave band as compared with dye Ib.



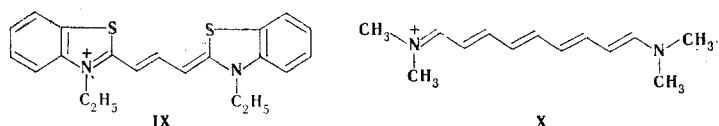
I  $R^1=R^2=R^3=H$ ; II  $R^1=R^3=H$ ,  $R^2=CH_3$ ; III  $R^1=R^3=H$ ,  $R^2=C_6H_5$ ; IV  $R^1=R^3=CH_3$ ,  $R^2=H$ ; V  $R^1=C_6H_5$ ,  $R^2=H$ ,  $R^3=CH_3$ ; VI  $R^1=p-CH_3OC_6H_4$ ,  $R^2=H$ ,  $R^3=CH_3$

Two bands are also observed in the visible region in the absorption spectra of solutions of these dyes (Table 1). In order to interpret the first absorption bands and determine the localization of the electron transitions in the dyes we calculated the energies of the transitions and the electron distributions in the ground, first, and second excited states for model compounds VII and VIII and dyes Ib, c (Table 2) in the self-consistent-field (SCF) approximation with allowance for the singly excited states [the Pariser-Parr-Pople (PPP) method]. The calculated absorption maxima of the first and second transitions are close to the experimental values.



It is apparent from the data presented in Table 2 that, as in the case of thiazolopyrimidinium salts of the Ia type [1], a phenyl group in the 8 position has a significant effect on the position of the absorption maximum.

Diagrams of the electron redistribution, which make it possible to form a judgment as to which atoms of the conjugated system participate in electron transfer during excitation, are extremely convenient for the analysis of the localization of the electron transitions. Such diagrams for the transition of dye VII to the first and second singlet states are presented in Fig. 1. It is apparent that primarily the atoms of the polymethine chain of the dye (the Kuhn chain) participate in the first  $\pi-\pi^*$  transition (Fig. 1a). The changes in the electron density are numerically of the same order of magnitude as in ordinary dyes, viz., thiacyanine IX or streptopolymethine X (Fig. 2).



Consequently, the first band of dyes that are thiazolopyrimidine derivatives has the same nature as the long-wave bands of typical polymethines. The collectiveness of this transition for monomethinylcyanine VII  $\chi = 1.086$  [2], i.e., the first excited state, consists of electron configuration  $\Phi_1$  with two of the lowest singly filled molecular orbitals:

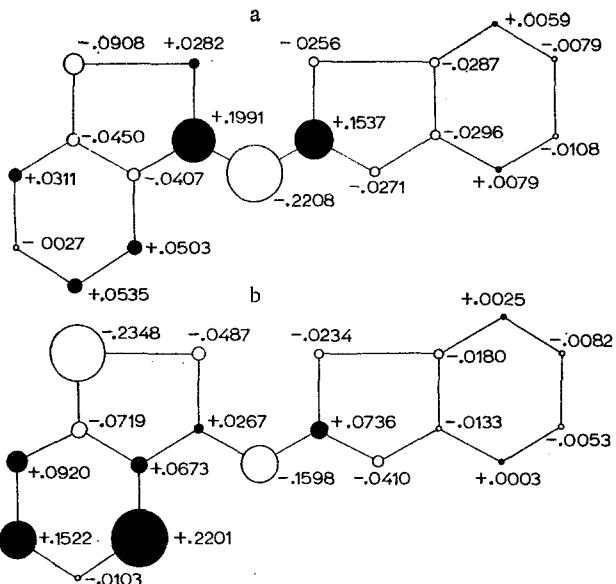


Fig. 1. Diagrams of the change in the  $\pi$ -electron density on the atoms of dye VII ( $q^*_i - q_i^0$ ) during transition to the first  $[S_0 \rightarrow S_1]$  (a) and second  $[S_0 \rightarrow S_2]$  (b) excited states.

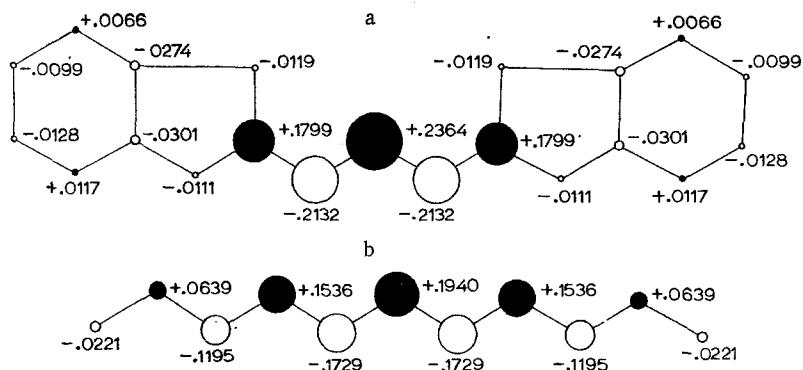


Fig. 2. Diagrams of the change in the  $\pi$ -electron density on the atoms of the IX (a) and X (b) molecules during transition to the first excited state.

TABLE 2. Calculated Absorption Maxima of the Model Compounds

Compound	$\lambda_{\max}$ , nm
VII	389, 499
Ib	417, 560
VIII	407, 548
Ic	441, 604

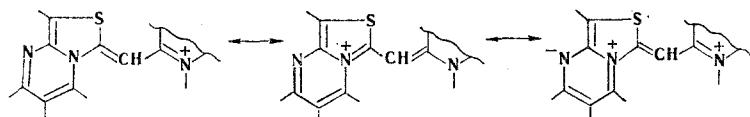
$|S_1\rangle = 0.9873|\Phi_1\rangle + \sum_{i \geq 2} T_i|\Phi_i\rangle$ , where  $T_i < 0.1$ . The second electron transition in the dyes

that are thiazolopyrimidine derivatives is localized primarily in the thiazolo[3,4-a]pyrimidine ring and on the carbon atom of the polymethine chain (Fig. 1b) and is accompanied by transfer of electron density from the thiazole ring and the carbon atom in the meso position of the polymethine chain to the pyrimidine ring. The change in the electron density in this case corresponds qualitatively to the electron redistribution during the first  $\pi-\pi^*$  transition in 6-methylthiothiazolo[3,4-a]pyrimidinium cation Ia [1], except that in the dye mole-

culcule the carbon atom corresponds to the exocyclic divalent sulfur atom of Ia. The collectiveness of this transition  $\chi = 1.068$ , i.e., the second excited state is determined primarily by the  $\Phi_2$  configuration:  $\Phi_2: |S_2\rangle = 0.9835|\Phi_2\rangle + \sum_{i \neq 2} T_i \Phi_i$  ( $T_i < 0.1$ ). The fact that both

electron transitions include several common atoms, while the sign of the change in the charges on them coincides in both cases, is important.

The fact that the first band of the dyes that are thiazolopyrimidine derivatives lies in the longer-wave region as compared with the absorption of many different monomethinylcyanines is explained by the greater effective length [3] of the thiazolo[3,4-a]pyrimidine ring in the dyes:  $L_{\text{theor}} = 6.89$ . In the language of the theory of valence schemes the information stated above constitutes evidence for the significant contribution of a structure with a localized negative charge on the carbon atom in the 1 position.



This conclusion of the theory of valence schemes is also confirmed by calculations that give the charge on this atom in the ground (-0.1773) and first (-0.2084) excited states. The existence of such structures (Sachs graphs with nonzero weight [4]) leads to an increase in the overall length of the chromophore of the dye molecules.

It is apparent from the experimental data (Table 1) that the ratio of the intensities between the first and second bands in the absorption spectra of solutions of the dyes turns out to be dependent on the type of dye. On passing from the dyes with a benzothiazole ring to lepidine derivatives with a greater effective length (symmetrical 4-quinocyanines absorb in a longer-wave part of the spectrum than the corresponding benzothiazole analogs with the same number of vinylene groups in the polymethine chain) the distance between the absorption bands of the ring and the chromophore increases, and the intensity of the second band due to transfer of  $\pi$  electrons to the thiazolopyrimidine ring decreases. An increase in the intensity of the second transition (resonance) evidently occurs when the bands are close to one another, whereas in the case of a great difference in the lengths of the waves the bands become independent, and the intensity of the short-wave band is lower than the intensity of the long-wave band, as is usually observed.

The substituents in the thiazolopyrimidine ring also have a pronounced effect on the position and form of the bands in the absorption spectra of solutions of the dyes. In the case of Ib-IIIb, for which two bands with close intensities are observed, the substituent in the 3 position ( $R^2$ ) has a greater effect on the position of the bands than on their form. Transition from dye IIb to its phenyl-substituted analog IIIb is accompanied by a bathochromic shift of the long-wave absorption band, while a similar change in the  $R^1$  substituent (transition from IVb to Vb) is accompanied by a large bathochromic shift of the short-wave band and an increase in its intensity. In the case of monomethinylcyanines IIIc-Vc (with a lepidine ring), in the absorption spectra of which an intense long-wave band is observed, while the short-wave band is either not seen at all or appears in the form of an inflection on the short-wave slope of the absorption curve, the effect of substituents on the form of the bands is insignificant.

This effect of substituents in the thiazolopyrimidine ring on the absorption spectra of dyes is in agreement with the assumption of the possibility of inclusion of the atoms of the pyrimidine ring in the overall chromophore and also with the results of quantum-chemical calculations regarding the change in the distribution of the electron density in dye molecules during excitation.

It is possible that the effect of lengthening of the chromophore of dyes due to the inclusion of part of a heterocyclic ring in it can be used to obtain other deeply colored dyes with a short polymethine chain.

## EXPERIMENTAL

The electronic spectra of solutions of the compounds in dimethylformamide (DMF) were obtained with an SF-10 spectrophotometer. Quantum-chemical calculations were made within the Pariser-Parr-Pople (PPP) approximation by the method in [1]. For the calculation of the

TABLE 3. Monomethinylcyanines

Com- pound	mp,* °C	Found, %		Empirical formula	Calc., %		Yield, %
		Cl	S		Cl	S	
Ib	>310	7,1	13,1	C <sub>22</sub> H <sub>18</sub> CIN <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	7,3	13,1	42
IIb	>310	7,2	12,9	C <sub>23</sub> H <sub>20</sub> CIN <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	7,1	12,8	78
IIIb	291—293	6,2	11,2	C <sub>28</sub> H <sub>22</sub> CIN <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	6,3	11,4	51
IVb	273—275	6,9	12,2	C <sub>24</sub> H <sub>22</sub> CIN <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	6,9	12,4	54
Vb	281—283	6,2	11,0	C <sub>29</sub> H <sub>24</sub> CIN <sub>3</sub> O <sub>4</sub> S <sub>2</sub>	6,1	11,1	67
VIb	277—278	5,8	10,3	C <sub>30</sub> H <sub>26</sub> CIN <sub>3</sub> O <sub>5</sub> S <sub>2</sub>	5,8	10,5	48
IIIc	231—233	6,3	6,0	C <sub>30</sub> H <sub>24</sub> CIN <sub>3</sub> O <sub>4</sub> S	6,4	5,7	54
IVc	182—183	7,0	6,5	C <sub>26</sub> H <sub>24</sub> CIN <sub>3</sub> O <sub>4</sub> S	7,2	6,5	81
Vc	202—203	6,3	5,6	C <sub>31</sub> H <sub>26</sub> CIN <sub>3</sub> O <sub>4</sub> S	6,2	5,6	56

\*Compound IVb was crystallized from alcohol, while the remaining compounds were crystallized from alcohol-DMF mixtures: 1:1 for Ib and IIIc, 3:1 for IIb and IIIb, 1:3 for Vb and VIb, and 4:1 for IVc and Vc.

effective length of the thiazolopyrimidine ring the Hückel parameters were estimated from the corresponding elements of the effective self-consistent field (SCF) Hamiltonian:

$$\alpha_{-N} = \alpha + 0.5\beta, \alpha_{-N^+} = \alpha + 1.5\beta, \alpha_{-S} = \alpha + 1.5\beta, \beta_{CN} = \beta_{CC} = \beta, \beta_{CS} = 0.6\beta.$$

2,4-Dimethyl-8-phenyl-6-[(3-ethyl-2(3H)-benzothiazolinylidene)methyl]thiazolo[3,4-a]-pyrimidinium Perchlorate (IVb). A mixture of 0.38 g (1 mmole) of perchlorate IVa, 0.35 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate, and 5 ml of absolute alcohol was heated until the components dissolved, and 0.1 g (1 mmole) of triethylamine was added. The precipitated dye was removed by filtration and crystallized (Table 3).

Monoethylidenecyanines Ib-IIIb, Vb, and VIb. These compounds were similarly obtained from the corresponding salts.

2,4-Dimethyl-8-phenyl-6-[(1,4-dihydro-1-ethyl-4-quinolinylidene)methyl]thiazolo[3,4-a]-pyrimidinium Perchlorate (IVc). A 0.38-g (1 mmole) sample of perchlorate IVa and 0.27 g of 4-methyl-1-ethylquinolinium perchlorate were dissolved by heating in a mixture of 12 ml of absolute alcohol and 1 ml of DMF, and 0.1 g (1 mmole) of triethylamine was added. The precipitated dye was removed by filtration and crystallized.

Monomethylidynecyanines IIIc and Vc. These compounds were similarly obtained from the corresponding salts.

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