

12. J. V. Metzger, *Thiazole and Its Derivatives*, Vol. 1, Interscience Publ., New York (1970).
13. W. Walter and J. Voss, *The Chemistry of Amides*, Interscience Publ., New York (1970), p. 386.
14. F. Fischer and S. Besthorn, *Ann.*, 212, 329 (1879).

CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

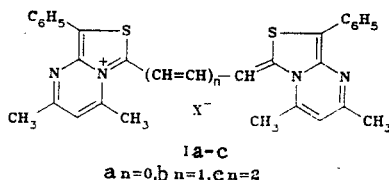
14\* NATURE OF THE ELECTRONIC SPECTRA OF SYMMETRICAL  
POLYMETHINE DYES OF THE THIAZOLO[3,4-b][1,2,4]TRIAZINE SERIES.

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Symmetrical mono-, tri-, and pentamethinecyanine dyes with a thiazolo[3,4-b][1,2,4]triazine ring were synthesized. The electron-density distributions in the dye molecules in the ground and first and second excited states were obtained by quantum-chemical calculations. It was established that the first two electron transitions are localized on the same atoms and that charge transfer to the triazine fragment of the molecule is realized in the case of excitation. The degree of participation of the heterocyclic ring in the first electron transition, which is responsible for the color of the dye, decreases with lengthening of the polymethine chain.

Narrow high-intensity bands due to the first  $\pi\text{-}\pi^*$  electron transition are observed in the visible part of the absorption spectra of most polymethine dyes [2]. This transition is localized primarily on the atoms of the polymethine chain, where the maximum change in the electron density occurs during primary excitation. A second shorter-wave band is most often due to  $\pi\text{-}\pi^*$  transitions in the terminal heterocyclic residues and is observed in the UV part of the spectrum. A bathochromic shift ( $\sim 100$  nm) of the long-wave absorption band is observed with lengthening of the polymethine chain of symmetrical cyanines by one vinylene group [3], while the position of the short-wave band is virtually unchanged. However, in an investigation of the spectral characteristics of polymethine dyes - thiazolo[3,4-a]pyrimidine derivatives Ia-c - it was established [4] that both absorption bands of solutions of such compounds are observed in the visible part of the spectrum; with an increase in the length of the chain both bands are shifted to the red part of the spectrum: the long-wave band to a greater extent, and the short-wave band to a smaller extent (Table 1). In this connection it seemed of interest to study the interrelationship between the chemical structure and spectral characteristics of similar dyes with other terminal heteroresidues.



The previously synthesized 6-methylthio-substituted thiazolotriazines of the II type [6] can be used in the synthesis of merocyanines or unsymmetrical monomethinecyanines. The corresponding 6-methylthiazolotriazines are necessary for the synthesis of symmetrical dyes; the former can be obtained by conversion of the active alkylthio group of quaternary salts

\*See [1] for communication 13.

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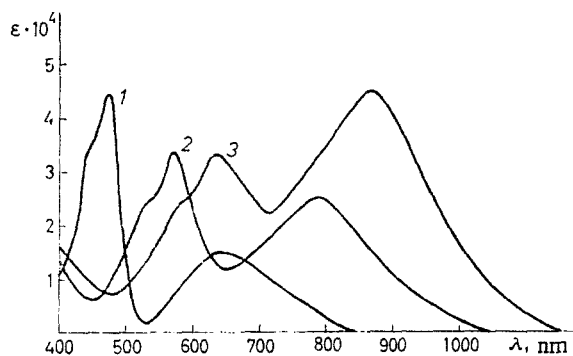


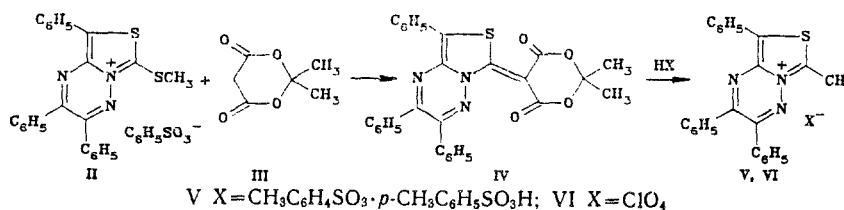
Fig. 1. UV absorption spectra of VIIa (1), VIIb (2), and VIIc (3).

TABLE 1. Absorption Spectra of Ia-c and VIIa-c

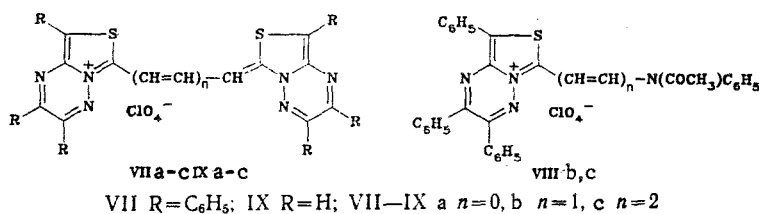
Compound	$\lambda_{\max}$ , nm (lg $\epsilon$ )	$\Delta\lambda^1$ , nm*	$\Delta\lambda^2$ , nm*	$\epsilon_1/\epsilon_2$
Ia	430 (3.69), 625 (4.37)	—	—	4.78
Ib	470 (3.99), 805 (4.76)	180	40	5.68
Ic	498 (4.10), 895 (4.92)	90	28	6.59
VIIa	470 (4.65), 640 (4.19)	—	—	0.35
VIIb	568 (4.10), 790 (4.92)	150	98	0.74
VIIc	630 (4.52), 870 (4.65)	80	62	1.35

\*The symbols  $\Delta\lambda^1$  and  $\Delta\lambda^2$  are the vinylene shifts of the first and second absorption bands.

to a methyl group [7] by means of Meldrum's acid [8]. In fact, benzenesulfonate II reacts readily with Meldrum's acid (III), and the resulting derivative IV is cleaved by heating with *p*-toluenesulfonic acid monohydrate. However, the toluenesulfonate of the product is isolated from the reaction mixture in the form of, probably, a complex salt with *p*-toluenesulfonic acid. This composition of salt V is retained in unchanged form even after its crystallization. However, perchlorate VI is formed by the action of sodium perchlorate or perchlorate acid on salt V.



Salts V and VI react readily with the electrophilic agents that are used for the synthesis of polymethine dyes. Thus, for example, the reaction of perchlorate VI with benzenesulfonate II gives symmetrical monomethinecyanine VIIa, while the reaction with diphenylformamide or malonaldehyde dianil hydrochloride in acetic anhydride gives the corresponding intermediates VIIIb,c, which in turn, react with salts V and VI to give carbo- and dicarbocyanines VIIb,c. Dicarbocyanine VIIc was also obtained in good yield in one step by reaction of salt VI with 1,1,3,3-tetraethoxypropane in acetic anhydride in the presence of triethylamine.



It followed from quantum-chemical calculations made for the model thiazolotriazininium cation [5] that the color of compounds of this type is due to transfer of electron density from

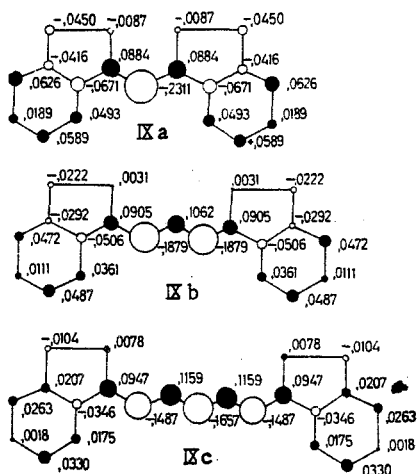


Fig. 2

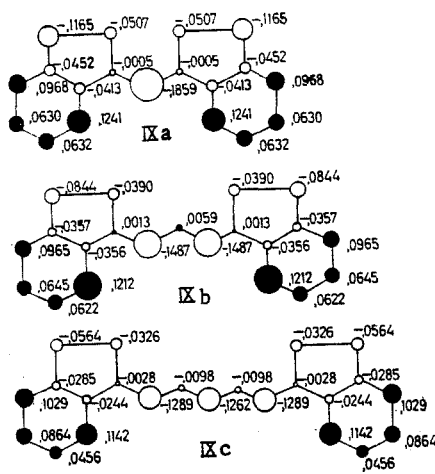
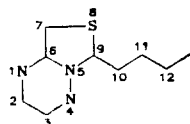


Fig. 3

Fig. 2. Change in the electron density in the case of transition of the molecule from the ground to the first excited state for model compounds IXa-c.

Fig. 3. Change in the electron density in the case of transition of the molecule from the ground to the second excited state for model compounds IXa-c.

TABLE 2. Electron Density Distribution in Cations IXa-c in the Ground State



Atom	Compound			Atom	Compound		
	IXa	IXb	IXc		IXa	IXb	IXc
N <sub>(1)</sub>	1,1305	1,1323	1,1333	C <sub>(7)</sub>	1,0584	1,0588	1,0611
C <sub>(2)</sub>	0,8677	0,8694	0,8705	S <sub>(8)</sub>	1,7500	1,7437	1,7438
C <sub>(3)</sub>	0,8575	0,8620	0,8651	C <sub>(9)</sub>	0,9829	0,9783	0,9794
N <sub>(4)</sub>	1,1996	1,1944	1,1920	C <sub>(10)</sub>	1,2069	1,1563	1,1435
N <sub>(5)</sub>	1,5135	1,5095	1,5094	C <sub>(11)</sub>	—	0,9231	0,9162
C <sub>(6)</sub>	1,0364	1,0364	1,0366	C <sub>(12)</sub>	—	—	1,0981

the thiazole ring and the exocyclic sulfur atom to the triazine ring. This explains the hypsochromic shift (47 nm) in the electronic spectrum when the 6-methylthio group in salt II is replaced by a methyl group (salt VI). A similar effect was previously observed in a number of thiazolopyrimidinium salts [9, 10].

Two bands - short-wave bands that are narrower with the inflection that is characteristic for the long-wave bands of ordinary cyanine dyes and broad long-wave bands - are observed in the visible part of the absorption spectra of dyes VIIa-c (Fig. 1). The intensity ratio ( $\epsilon_1/\epsilon_2$ ) of the bands changes with lengthening of the polymethine chain of the dyes. Whereas the short-wave absorption in the spectrum of monomethinecyanine IXa is considerably more intense than the long-wave absorption, just the opposite is true in the case of dicarbocyanine VIIc. The vinylene shifts for the long-wave bands correspond approximately to the values observed in a number of dyes of the thiazolo[3,4-a]pyrimidine series (Table 1), whereas they are substantially greater for the short-wave bands.

According to a quantum-chemical evaluation [4], the presence of two absorption bands in the spectra of thiazolo[3,4-a]pyrimidine derivatives is explained by the existence of two  $\pi-\pi^*$  electron transitions; the long-wave transition is localized primarily on the polymethine

TABLE 3. Characteristics of the Synthesized Compounds

Compound	mp, °C*	Found, %		Empirical formula	Calc., %		Yield, %
		Cl (N)	S		Cl (N)	S	
IV	224—225	(8,0)	6,2	C <sub>29</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> S	(8,3)	6,3	97
V	126—127	(5,9)	13,2	C <sub>35</sub> H <sub>33</sub> N <sub>3</sub> O <sub>6</sub> S <sub>3</sub>	(5,8)	13,3	90
VI	243—244	5,5	6,7	C <sub>24</sub> H <sub>18</sub> ClN <sub>3</sub> O <sub>4</sub> S	5,4	6,7	95
VIIa	315—316	4,1	7,6	C <sub>47</sub> H <sub>31</sub> ClN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	4,2	7,6	73
VIIb	241—242	3,9	7,6	C <sub>49</sub> H <sub>33</sub> ClN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	4,1	7,4	63
VIIc	211—212	3,8	7,2	C <sub>51</sub> H <sub>35</sub> ClN <sub>6</sub> O <sub>4</sub> S <sub>2</sub>	4,0	7,2	22
VIIIb	251—252	5,5	5,2	C <sub>33</sub> H <sub>25</sub> ClN <sub>4</sub> O <sub>4</sub> S	5,6	5,1	80
VIIIc	234—235	5,4	5,0	C <sub>35</sub> H <sub>27</sub> ClN <sub>4</sub> O <sub>4</sub> S	5,4	4,9	62

\*The compounds were crystallized: V from benzene, VI from alcohol, VIIa from DMF-acetic acid (1:3), and VIIb from acetic acid-acetonitrile (5:1). Compound VIIc was reprecipitated from solution in DMF with ether. Compounds VIIIb,c were washed with alcohol.

chain, while the short-wave transition is due not only to transfer of electron density in the ring (from the triazole fragment to the electron-acceptor pyrimidine fragment) but also to charge transfer during excitation from the polymethine chain to the atoms of the pyrimidine part of the ring. Considering the informative character of this approach for revealing the nature and localization of the electron transitions that are responsible for the color of dyes of this type we performed similar calculations [within the Pariser-Parr-Pople (PPP) approximation] [11, 12] of the electron-density distribution on the atoms of model compounds IXa-c in the ground (Table 2) and first and second excited states (Figs. 2 and 3).

It is apparent from the diagrams of the redistribution of electron density in the first and second excitations (Figs. 2 and 3) that the first electron transition is due primarily to transfer of electron density from the carbon atoms in the even-numbered positions of the polymethine chain not only to the carbon atoms in the odd-numbered positions (the Kuhn chain), as in the case of dyes of the thiazolopyrimidine series [4], but also to an even greater extent to the atoms of the triazine fragment of the molecule. The degree of participation of the latter in the electron transition decreases with lengthening of the polymethine chain. However, just as in dyes of the thiazolopyrimidine series, in the second electron transition transfer of electron density is realized from the same atoms of the polymethine chain and also from the atoms of the thiazole ring to the atoms of the triazine fragment of the molecule.

Thus the data obtained indicate significant participation of the atoms of the heterocyclic ring in both the first electron transition, which is responsible for the long-wave absorption band of the dyes, and in the second electron transition, which is responsible for the short-wave absorption band. Since both transitions are localized primarily on the same atoms, the symbatic character of the behavior of the two bands when the length of the polymethine chain of the dyes is changed becomes understandable.

In analyzing the dependence of the color of dyes Ia-c and VIIa-c as a function of the structure of the heteroring one may state that replacement of the carbon atom in the 4 position of the thiazolopyrimidine by a nitrogen atom should lead to an increase in the electron-acceptor character of the ring. The contribution of mesomeric structures with localization of the negative charge on the heteroresidue should increase as a result of this; this affects the color of the compounds and the distribution of the electron densities in their molecules.

In fact, the electron densities on the nitrogen atom in the 1 position of the molecule of triazinium dye VIIa in the ground and first excited states are 1.1305 (Table 2) and 1.1931 (Fig. 2), while these values are 1.1885 and 1.2000, respectively, for the analogous model pyrimidine derivative [4].

In correlating the above-noted spectral peculiarities of the synthesized cyanines VIIa-c it should be stated that, on the whole, the described principles are similar to those observed in dyes whose molecules contain two chromophore systems [13]. In the molecules of VIIa-c there are also two electron transitions with comparable energies that evidently have an effect on one another, and both are determined by the length of the polymethine chain of the dye.

In comparing the maxima of the absorption bands of the dyes of the thiazolotriazine and thiazolopyrimidine series Ia-c it is apparent that the short-wave bands of all cyanines VIIa-c are situated in the longer-wave part of the spectra, whereas for the long-wave bands a bathochromic shift is observed only for monomethinecyanine VIIa (Table 1). However, in the case of carbo- and dicarbocyanines VIIb,c the long-wave bands are shifted hypsochromically. These data fit into the framework of the explanation of the interaction of the chromophores in series of biscyanine dyes. According to this concept, the interaction of the chromophores in the spectra of biscyanines is manifested in drawing apart of the bands of the corresponding monochromophore systems ("matrix dyes") and in a change in the ratio of their intensities; the redistribution of the intensities is determined by the angle between the chromophores, while the degree of interaction is determined by the energies of the electron transitions [13].

Thus the deep color of monomethinecyanine VIIa is evidently due to a bathochromic shift of the long-wave absorption band as a result of a strong interaction of electron transitions with close energies in its molecule. The interaction decreases with lengthening of the polymethine chain, and the absorption bands in the spectrum of dicarbocyanine VIIc can be regarded as basically independent.

#### EXPERIMENTAL

The electronic spectra of solutions of the compounds in acetonitrile were obtained with an SF-8 spectrophotometer. The PMR spectra of solutions in  $\text{CF}_3\text{COOH}$  were obtained with a BS-467 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The characteristics of the compounds are presented in Table 3.

2,3,8-Triphenyl-6-[2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene]-6H-thiazolo[3,4-b][1,2,4]triazine (IV). A 5.7-g (10 mmole) sample of benzenesulfonate II was dissolved in 50 ml of alcohol, and 2.7 g (20 mmole) of Meldrum's acid [8] and 1 g (10 mmole) of triethylamine were added. The precipitated reaction product was removed by filtration and washed with alcohol. The yield was 4.9 g.

6-Methyl-2,3,8-triphenylthiazolo[3,4-b][1,2,4]triazinium Salts V and VI. A mixture of 5.1 g (10 mmole) of merocyanine IV and 5 g (25 mmole) of p-toluenesulfonic acid monohydrate was heated for 1 h at 130°C. The cooled melt was dissolved in 50 ml of isopropyl alcohol, 150 ml of ether was added, and the precipitated p-toluenesulfonate V was removed by filtration and crystallized. Perchlorate VI was formed by the action of sodium perchlorate on an alcohol solution of salt V. PMR spectrum,  $\delta$ : V 1.93 (6H, s,  $2\text{CH}_3$  of p-toluenesulfonic acid); 2.83 (3H, s,  $6\text{-CH}_3$ ); 6.40-7.30 ppm (23H, m, arom.); VI 2.71 (3H, s,  $6\text{-CH}_3$ ); 6.70-7.70 ppm (15H, m, arom.). UV spectrum  $\lambda_{\text{max}}$  ( $\log \epsilon$ ): V 290 (4.26), 425 nm (3.70); VI 303 (4.23), 423 nm (3.78).

2,3,8-Triphenyl-6-[(2,3,8-triphenyl-6(6H)-thiazolo[3,4-b][1,2,4]triazinylidene)methyl]-thiazolo[3,4-b][1,2,4]triazinium Perchlorate (VIIa). A mixture of 0.24 g (0.5 mmole) of perchlorate VI and 0.26 g (0.5 mmole) of benzenesulfonate II in 25 ml of alcohol was heated to boiling point, and 0.05 g (0.5 mmole) of triethylamine was added. The mixture was cooled, and the precipitate was removed and crystallized. The yield was 0.31 g.

6-(2-Acetanilidovinyl)-2,3,8-triphenylthiazolo[3,4-b][1,2,4]triazinium Perchlorate (VIIIb). A mixture of 0.48 g (1 mmole) of perchlorate VI, 0.40 g (2 mmole) of diphenylformamide, 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 10 ml of hot alcohol. The yield was 0.49 g.

6-(4-Acetanilido-1,3-butadienyl)-2,3,8-triphenylthiazolo[3,4-b][1,2,4]triazinium Perchlorate (VIIIc). This compound was similarly obtained from salt VI and malonaldehyde dianil hydrochloride.

2,3,8-Triphenyl-6-[3-(2,3,8-triphenyl-6(6H)-thiazolo[3,4-b][1,2,4]triazinylidene)propenyl]thiazolo[3,4-b][1,2,4]triazinium Perchlorate (VIIb). A mixture of 0.35 g (0.5 mmole) of VIIIb, 0.24 g (0.5 mmole) of perchlorate VI, 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 20°C and treated with 10 ml of isopropyl alcohol. The precipitate was removed by filtration and washed with alcohol. The yield was 0.27 g.

2,3,8-Triphenyl-6-[5-(2,3,8-triphenyl-6(6H)-thiazolo[3,4-b][1,2,4]triazinylidene)-1,3-pentadienyl]thiazolo[3,4-b][1,2,4]triazinium Perchlorate (VIIC). This compound was similarly obtained from salts VI and VIIIc.

#### LITERATURE CITED

1. Yu. A. Nesterenko and N. N. Romanov, *Khim. Geterotsikl. Soedin.*, No. 4, 551 (1987).
2. S. Dähne, *Z. Chem.*, 10, 168 (1970).
3. S. Dähne and R. Radeğlia, *Tetrahedron*, 27, 3673 (1971).
4. G. Dyadyusha, A. Tolmachev, N. Romanov, E. Mikitenko, and A. Kachkovskii (Kachkovskiy), *Dyes and Pigments*, 4, 179 (1983).
5. A. D. Kachkovskii, Yu. P. Kovtun, and N. N. Romanov, *Khim. Geterotsikl. Soedin.*, No. 12, 1693 (1986).
6. Yu. P. Kovtun and N. N. Romanov, *Khim. Geterotsikl. Soedin.*, No. 4, 498 (1985).
7. L. Fieser and M. Fieser, in: *Reagents for Organic Synthesis*, Vol. 2, Wiley, New York (1981).
8. Yu. L. Slominskii, A. I. Tolmachev, and L. M. Shulezhko, *Ukr. Khim. Zh.*, 41, 284 (1975).
9. E. K. Mikitenko and N. N. Romanov, *Khim. Geterotsikl. Soedin.*, No. 1, 42 (1983).
10. E. K. Mikitenko, N. N. Romanov, and A. D. Kachkovskii, *Khim. Geterotsikl. Soedin.*, No. 5, 634 (1982).
11. G. G. Dyadyusha, A. D. Kachkovskii, N. N. Romanov, and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, No. 12, 1618 (1980).
12. T. Tani, *J. Phot. Sci.*, 19, 161 (1971).
13. A. I. Kiprianov, *Usp. Khim.*, 40, 1283 (1971).