POLYMETHINE DYES WITH A THIAZOLOTRIAZINOINDOLE RING

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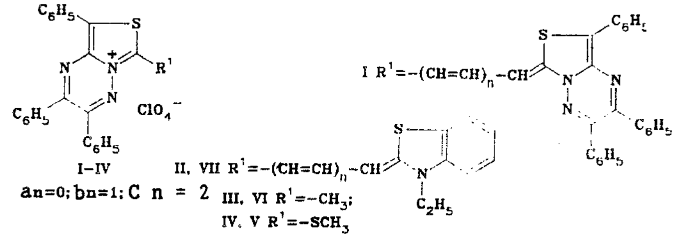
UDC 547.789.6:668.819.45:543.422:541.651

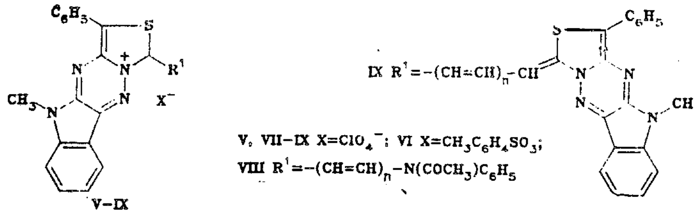
The nature of the color of synthesized polymethine dyes is examined from the point of view of the theory of chromophore interaction.

We have previously shown that two bands of comparable intensity are observed in the visible part of the absorption spectra of solutions of polymethine dyes Ia-c and IIa-c based on thiazolotriazines III and IV [1, 2]. A change in the chemical structures of polymethines I and II (lengthening of the polymethine chain) affects the positions of the maxima and the relative intensities of both bands; this indicates substantial interaction (particularly for dyes with a short polymethine chain) of the corresponding electron transitions.



According to the results of quantum-chemical analysis of the cations of model dyes, the long-wave absorption band is due to a $\pi-\pi^*$ electron transition localized not only on the atoms of the polymethine chain but also (to a significant extent) on the atoms of the terminal heteroring, while the short-wave band is associated with transfer of π-electron density from the polymethine chain and the thiazole fragment of the terminal residue to the electron-acceptor triazine fragment of the molecule. In this connection the corresponding electron transitions can be arbitrarily designated as polymethine and heterocyclic transitions, and the dyes can be regarded as two-chromophore dyes. Since with respect to its nature (the change in the electron density on the atoms upon excitation), one of the absorption bands of the dye is quite close to the long-wave band of the starting 6-substituted thiazolotriazine, it is possible to thoroughly analyze the interrelationship of the spectral characteristics of thiazolotriazines and dyes based on them.

It is known [3] that in the biscyanine series, other things being equal, the interaction of the chromophores is more markedly expressed in separation of the bands, the closer the absorption maxima of the "mother" polymethines. In this connection one might have assumed that in series of dyes with a thiazolotriazine ring that have a close effective length [4] the effect of interaction of the electron transitions would also be manifested more appreciably in the case of more deeply colored heterocyclic terminal groups. It therefore seemed of interest to synthesize new cyanine dyes of this type on the basis of thiazolo-[3',4']:2,3]-1,2,4-triazino[5,6-b]indole derivatives, since the latter have characteristic absorption in the visible part of the spectrum. For example, the absorption maximum of a solution of methylthio-substituted V is shifted bathochromically 84 nm as compared with the corresponding thiazolotriazine III and is observed at 554 nm; this approaches the absorption maximum of a solution of a thiacarbocyanine [5].



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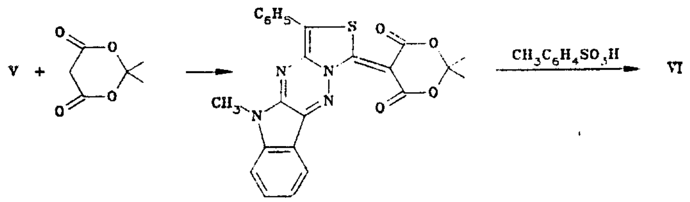
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1547-1551, November, 1988. Original article submitted April 15, 1987; revision submitted February 8, 1988.

0009-3122/88/2411-1285$12.50

We obtained the 1,5-dimethyl-3-phenylthiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium toluenesulfonate (VI) necessary for the synthesis of carbo- and dicarbocyanines by cleavage of the product of condensation of methylthio derivative V with Meldrum's acid [6]:



The composition and structure of the synthesized VI correspond to the results of elementary analysis and the PMR data (see the experimental section) and are also confirmed by its chemical properties. Thus, thiamonomethinecyanine VIIa, which was obtained from toluenesulfonate VI by reaction with 3-ethyl-2-ethylthiobenzothiazolium perchlorate, is identical to the compound previously synthesized from perchlorate V and a 2-methyl-3-ethylbenzothiazolium salt [7].

As in the thiazolotriazine III and IV series [1, 2], in the case of thiazolotriazinoindoles VI and V replacement of the methylthio group by a methyl group leads to a hypsochromic shift of the absorption maximum (34 and 47 n, respectively), and consequently, the difference in the spectral characteristics of monotypic derivatives even increases somewhat (97 nm).

The methyl group of salt VI was found to be rather active in reactions involving condensation with nucleophilic intermediates used for the synthesis of polymethine dyes. For example, acetanilidovinyl derivative VIIIb is formed in the reaction with diphenylformamidine, while acetanilidobutadienyl derivative VIIIc is formed in the reaction with malonaldehyde dianil hydrochloride. Symmetrical carbo- and dicarbocyanines IXb, c, were obtained by the reaction of hemicyanines VIIIb, c with toluenesulfonate VI, while unsymmetrical carbo- and dicarbocyanines VIIb, c were obtained with 2-methyl-3-ethylbenzothiazolium toluene sulfonate. A symmetrical monomethinecyanine was obtained from the corresponding methyl- and methylthio-substituted thiazolotriazinoindolium salts V and VI.

The spectral characteristics of the synthesized polymethines are presented in Table 1. In the spectra of solutions of dyes with a thiazolotriazinoindole ring, as for their analogs based on thiazolotriazine, one observes two bands, the positions and intensities of which are determined by the length of the polymethine chain. In fact, an approximately equal bathochromic shift of the maxima of both the long-wave and short-wave bands is observed with lengthening of the polymethine chain by one vinylene group; the intensity of the short-wave band decreases regularly, while that of the long-wave band increases. Proceeding from the positions of the long-wave absorption maxima of monomethinecyanines Ia and IXa (640 and 740 nm, respectively) it may be concluded that the thiazolotriazinoindolium ring has a significantly greater effective length and, with respect to this parameter, approaches one of the record rings, viz., the selenoflavylium ring ($\ell = 7.44$ [8]). However, with an increase in the length of the polymethine chain of dyes I and IX one observes a distinct tendency for drawing together of the maxima of the long-wave absorption bands of their solutions ($\Delta\lambda_1$ decreases). This evidently indicates that the thiazolotriazine and thiazolotriazinoindole rings still have close effective lengths, whereas in the spectra of solutions of dyes with a short polymethine chain from the last heteroring one observes an additional shift of the absorption maximum as a result of the great degree of interaction of the electron transitions. Let us note that, in contrast to the long-wave bands, the maxima of the short-wave bands of solutions of dyes based on thiazolotriazine and thiazolotriazinoindole are rather close. Similar spectral effects are also observed in the symmetrical thiacyanine II and VII series.

As we have already pointed out above, the interaction of chromophores is usually manifested in separation of the bands. In our case also the distance between the maxima of the long-wave and short-wave bands ($\lambda_1 - \lambda_2$) in series of dyes based on thiazolotriazinoindole is greater than for their thiazolotriazine analogs (Table 1); difference $\Delta(\lambda_1 - \lambda_2)$ decreases with an increase in the length of the polymethine chain, i.e., the properties of the dyes approach one another with an increase in the length of the chromophore. Proceeding from this one can determine the specific characteristics of the special properties introduced into the

TABLE 1. Spectral Characteristics of Dyes VIIa-c, IXa-c, Ia-c, and IIa-c

Compound	λ_{max}, nm (lg ε)	Vinyl shift, nm		$\lambda_1-\lambda_2$, nm	$\varepsilon_1/\varepsilon_2$	$\lambda_{TTI}-\lambda_{TT}$,* nm		
		λ_1	λ_2			$\Delta\lambda_1'$	$\Delta\lambda_2'$	$\Delta(\lambda_1-\lambda_2)$
IXa	740 (4,13), 481 (4,47)	—	—	259	0,46	100	11	89
IXb	848 (4,34), 570 (4,44)	108	89	278	0,80	58	2	56
IXc	907 (4,36), 625 (4,37)	59	55	282	0,97	37	−5	42
VIIa	625 (3,86), 465 (4,61)	—	—	160	0,18	70	11	59
VIIb	720 (4,26), 565 (4,54)	95	100	155	0,52	70	−1	71
VIIc	790 (4,16), 643 (4,18)	70	78	147	0,95	40	−2	42
Ia	640 (4,19), 470 (4,65)	—	—	170	0,35	—	—	—
Ib	790 (4,41), 568 (4,54)	150	98	222	0,74	—	—	—
Ic	870 (4,65), 630 (4,52)	80	62	240	1,35	—	—	—
IIa	555 (3,84), 454 (4,68)	—	—	101	0,14	—	—	—
IIb	650 (4,37), 566 (4,76)	95	112	84	0,42	—	—	—
IIc	750 (4,33), 645 (4,69)	100	79	105	0,43	—	—	—

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*The difference in the maxima of the dyes of the thiazolotriazinoindole (TTI) and thiazolotriazine (TT) series.

TABLE 2. Calculated Spectral Characteristics of Dyes IIIa-c and IXa-c (nm)

Compound	λ_1*	$\lambda_1-\lambda_1$*	λ_2*	$\lambda_2-\lambda_2$*	λ_1**	$\lambda_1-\lambda_1$**	λ_2**	$\lambda_2-\lambda_2$**
VIIa	595	30	452	13	652	−27	551	−86
VIIb	690	30	564	1	747	−27	663	−98
VIIc	790	0	643	0	847	−57	742	−99
IXa	677	63	465	16	737	3	567	−86
IXb	827	21	563	7	887	−39	665	−95
IXc	907	0	625	0	967	−60	727	−102

dyes by an additional condensed indole ring. In fact, if the degree of interaction of the transitions were the same for cyanines based on thiazolotriazine and thiazolotriazinoindole, the vinylene shifts of the maxima would also evidently be close. If it is assumed that interaction is absent ($\Delta\lambda^* = 0$) for dicarbocyanines, a maximum (λ^*) that is equal to the difference in the maxima for the dicarbocyanine from thiazolotriazinoindole and the second vinylene shift of the corresponding dyes of the thiazolotriazine series should have been observed for carbocyanines. The calculated maximum of the carbocyanine minus the first vinylene shift is similarly expected for monomethinecyanines. The data obtained are presented in Table 2. It is apparent from the results presented that the observed absorption maxima of dyes of the thiazolotriazinoindole series, particularly in the case of monomethinecyanines, are shifted bathochromically as compared with the calculated values, whereas the shift of the long-wave bands is substantially greater than that of the short-wave bands.

Since, according to the results of quantum-chemical calculations, the atoms of the thiazolotriazine heteroresidue participate appreciably in both transitions [2], it seemed of interest to also compare the maxima of the long-wave absorption bands of solutions of the starting heterocycles III and VI and dyes based on them. We started from the assumption that the shifts of the absorption maxima on passing from the heterocycle to the dye (other things being equal) should be identical both in the thiazolotriazine series and in series of corresponding thiazolotriazinoindoles. Consequently, a certain maximum λ_2** could occur in the case (Table 2). The difference between the observed absorption maximum of the dye and the calculated value evidently can serve as a measure of the participation of the atoms of the thiazolotriazinoindole residue in the electron transition responsible for the long-wave bands of the dyes as compared with the analogous contribution of the thiazolotriazine atoms. It was found that the calculated value of the maximum of the long-wave absorption band of a solution of the dye virtually coincides with the experimental value only in the case of symmetrical monomethinecyanine IXa. In all of the remaining cases the maxima are shifted hypsochromically. The shift increases with lengthening of the polymethine chain; this indicates a decrease in the participation of the atoms of the heteroresidue in the

TABLE 3. Characteristics of the Synthesized Compounds

Compound	mp,* °C	Found, %		Empirical formula	Calc., %		Yield, %
		Cl (N)	S		Cl (N)	S	
VI	158...160	(11,1)	13,0	$C_{26}H_{22}N_4O_3S_2$	(11,1)	12,8	80
VIIb	215...216	5,6	10,5	$C_{30}H_{24}ClN_5O_4S_2$	5,7	10,4	64
VIIc	199...200	5,3	10,1	$C_{32}H_{26}ClN_5O_4S_2$	5,5	9,9	22
VIIIb	177...178	6,3	5,4	$C_{28}H_{22}ClN_5O_5S$	6,2	5,7	95
VIIIc	145...147	5,5	5,1	$C_{30}H_{24}ClN_5O_5S$	5,9	5,3	79
IXa	289...290	4,6	8,4	$C_{37}H_{25}ClN_8O_4S_2$	4,8	8,6	87
IXb	226...228	5,0	8,4	$C_{39}H_{27}ClN_8O_4S_2$	4,6	8,3	75
IXc	239...240	4,2	7,8	$C_{41}H_{29}ClN_8O_4S_2$	4,4	8,0	40

*The compounds were crystallized: VI from acetic acid–ethyl acetate (5:1), VIIb and VIIIc from acetic acid, IXb from acetic acid–nitromethane (1:1), and VIIc from pyridine–isopropyl alcohol (1:5). Compounds VIIIb and IXa, c were washed with hot acetic acid.

first electron transition. One may evidently assert that the long-wave bands of monoethinecyanine dyes and the starting condensed heterocycles are similar in nature. At the same time, the fact that the maxima of the short-wave bands of the dyes based on thiazolotriazine and thiazolotriazinoindole are rather close and depend to a small extent on the structure of the heteroresidue constitutes evidence that in both cases the corresponding electron transitions are similar in nature to those observed for ordinary cyanine dyes.

EXPERIMENTAL

The electronic spectra of solutions of the compounds in acetonitrile were obtained with an SF-8 spectrophotometer. The PMR spectrum of a solution in CF_3COOH was recorded with a BS-467 radiospectrometer (60 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The charactristics of the synthesized compounds are presented in Table 3.

1-5-Dimethyl-3-phenyl-5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium p-Toluenesulfonate (VI). A 2.6-g (20 mmoles) sample of Medrum's acid and 1 g (10 mmoles) of triethylamine were added to a solution of 4.6 g (10 mmoles) of perchlorate V in 15 ml of DMF and 5 ml of alcohol, after which 50 ml of water was added, and the precipitate was removed by filtration, washed with hot isopropyl alcohol, and heated for 20 min at 140°C with 4 g (20 mmoles) of p-toluenesulfonic acid monohydrate. The melt was triturated with water, and the solid material was removed by filtration and crystallized to give 4.0 g of product. UV spectrum, λ_{max}, nm (log ε): 520 (3.50). PMR spectrum, δ: 1.83 (3H, s, CH_3 residue of toluenesulfonic acid), 2.73 (3H, s, $C_{(1)}-CH_3$), 3.23 (3H, s, $N_{(5)}-CH_3$), 6.3-7.7 ppm (13H, m, Ar-H.

5-Methyl-1-[(3-ethyl-2(3H)-benzothiazolylidene)methyl]-3-phenyl-5H-thiazolo[3',4']:2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (VIIa). A mixture of 0.25 g (0.5 mmole) of p-toluene sulfonate VI and 0.31 g (0.5 mmole) of 2-ethylthio-3-ethylbenzothiazolium perchlorate in 25 ml of alcohol was heated to the boiling point, and 0.05 g (0.5 mmole) of triethylamine was added. The dye was removed by filtration and crystallized from a mixture of acetic acid and nitromethane to give 0.42 g (70%) of a product with mp 305-306°C. The product was identical to the product previously obtained by the method in [7].

1-(2-Acetanilidovinyl)-5-methyl-3-phenyl-5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]-indolium Perchlorate (VIIIb). A solution of 0.5 g (1 mmole) of p-toluenesulfonate VI and 0.2 g (1 mmole) of diphenylformamidine in 3 ml of acetic anhydride was refluxed for 3 min, after which it was cooled, and a solution of 0.12 g (1 mmole) of sodium perchlorate in 0.5 ml of water and 15 ml of isopropyl alcohol were added. The precipitate was removed by filtration and washed with alcohol. The yield was 0.55 g.

1-(4-Acetanilido-1,3-butadienyl)-5-methyl-3-phenyl-5H-thiazolo[3',4':2,3'-1,2,4-triazino[5,6-b]indolium Perchlorate (VIIIc). This compound was obtained from salt VI and malonaldehyde dianil hydrochloride via a method similar to that in the preceding experiment.

5-Methyl-3-phenyl-1-[(5-methyl-3-phenyl-1(1H)-5H-thiazolo[3',4':2,3]-1,2,4-triazino-[5,6-b] indolylidene)methyl]-5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (IXa). A mixture of 0.46 g (1 mmole) of perchlorate V, 0.5 g (1 mmole) of p-toluenesulfonate VI, and 50 ml of alcohol was heated to the boiling point, and 0.1 g (1 mmole) of triethylamine was added. The dye was removed by filtration and washed with hot acetic acid. The yield was 0.65 g.

5-Methyl-3-phenyl-1-[3-(5-methyl-3-phenyl-1(1H)-5H-thiazolo[3',4':2,3]-1,2,4-triazino-5,6-b]indolylidene)-1-propenyl]-5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (IXb). A mixture of 0.58 g (1 mmole) of acetanilidovinyl derivative VIIIb, 0.5 g (1 mmole) of salt VI, and 3 ml of acetic anhydride was heated to the boiling point, 0.1 g (1 mmole) of triethylamine was added, the mixture was cooled rapidly to room temperature, and 15 ml of acetic acid was added. The dye was removed by filtration and crystallized.

5-Methyl-3-phenyl-1-[5-(5-methyl-3-phenyl-1(1H)-5H-thiazolo[3',4':2,3]-1,2,4-triazino-5,6-b]indolylidene)-1,3-pentadienyl]5H-thiazolo[3',4':2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (IXc). This compound was similarly obtained from hemicyanine VIIIc and salt VI.

5-Methyl-3-phenyl-1-[3-(3-ethyl-2(3H)-benzothiazolylidene)-1-propenyl]-5H-thiazolo-[3',4':2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (VIIb). A solution of 0.58 g (1 mmole) of acetanilidovinyl derivative VIIIb and 0.35 g (1 mmole) of 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate in 3 ml of pyridine was refluxed for 3 min, and 0.1 g (1 mmole) of triethylamine was added. The solution was then cooled to room temperature, 25 ml of water was added and the dye was removed by filtration and crystallized. The yield was 0.39 g.

5-Methyl-3-phenyl-1-[5-(3-ethyl-2(3H)-benzothiazolylidene)-1,3-pentadienyl]-5H-thiazolo-[3',4':2,3]-1,2,4-triazino[5,6-b]indolium Perchlorate (VIIc). This compound was similarly obtained from acetanilidobutadienyl derivative VIIIc and 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate.

LITERATURE CITED

1. Yu. P. Kovtun, N. N. Romanov, and A. D. Kachkovskii, Khim. Geterotsikl. Soedin., No. 7, 985 (1988).
2. Yu. P. Kovtun, A. D. Kachkovskii, and N. N. Romanov, Khim. Geterotsikl. Soedin., No. 3, 418 (1988).
3. A. I. Kiprianov, Usp. Khim., 40, 1283 (1971).
4. G. G. Dyadyusha and A. D. Kachkovskii, Ukr. Khim. Zh., 44, 948 (1978).
5. T. H. James, Theory of the Photographic Process [Russian translation], Khimiya, Leningrad (1980).
6. Yu. L. Slominskii, A. A. Tolmachev, and L. M. Shulezhko, Ukr. Khim. Zh., 41, 284 (1975).
7. Yu. P. Kovtun and N. N. Romanov, Khim. Geterotsikl. Soedin., No. 2, 211 (1985).
8. A. I. Tolmachev and M. A. Kudinova, Khim. Geterotsikl. Soedin., No. 7, 924 (1971).