cooled rapidly to room temperature and treated with 10 ml of isopropyl alcohol. The precipitated dye was removed by filtration and crystallized to give 0.15 g of product.

Carbocyanine VIIb. This compound was similarly obtained from salts IVb and VIb.

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SYNTHESIS AND ABSORPTION SPECTRA OF POLYMETHINE DYES — DERIVATIVES OF SUBSTITUTED THIENO- AND INDOLOTHIAZOLES

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and P. I. Abramenko

UDC 547.759.3'789.3'735:668.8:543.422.6

Cyanine, merocyanine, and styryl dyes that are derivatives of halo-, alkyl-, alkylene-, and arylthieno[2,3-d]thiazoles and halo- and alkylindolo[3,2-d]thiazoles were synthesized. It is shown that both electron-donor and electron-acceptor substituents in the 5 and 5' positions of the heteroresidues of thienothiazolocarbocyanines lead to a more uniform distribution of the electron density in their chromophore than in the unsubstituted dye and to a bathochromic shift of the absorption maximum. Methyl groups in the heteroresidues of indolothiazolocarbocyanines give rise to a small bathochromic effect.

Polymethine dyes that are derivatives of thieno- and indolothiazoles absorb in a longer-wave region than the corresponding thia- and naphthothiazolocyanines [1-4]. It is also known that some cyanines that are derivatives of benzo- and naphthothiazoles are effective spectral sensitizers of silver halide emulsions, in connection with which it seemed

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TABLE 1. Absorption Maxima of Cyanines with Structure III ($R = R^1 = C_2H_5$, $R^2 = H$)

Compound	Z-thiazole	Z'	λ_{max}^{abs} (in C_2H_5OH), nm	$\Delta\lambda$,* nm (pK_a)
	Benzo-†		558	(—0,62)
	6-Bromobenzo-†		560	(—1,00)
	5,6-Dimethylbenzo-†		568	(—0,42)
	4,5-Tetramethylenebenzo-†		574	—
	6-Phenylbenzo-†		574	(—0,70)
	Thieno[2,3-d]-†		594	(0,74)
	4,5-Benzobenzo-†		597	(—0,04)
	Indolo[3,2-d]-† [3]		634	
IIIa	5-Bromothieno[2,3-d]-†		607	(0,05)
IIIb	5,6-Dimethylthieno[2,3-d]-†		610	(0,83)
IIIc	5,6-Tetramethylenethieno[2,3-d]-†		612	(1,17)
IIId	5-Phenylthieno[2,3-d]-†		634	(0,30)
IIIe	5-Methylindolo[3,2-d]-†		640	—
IIIf	7-Methylindolo[3,2-d]-†		628	—
IIIg	5-Bromoindolo[3,2-d]-†		632	—
IIIh	5,7-Dichloroindolo[3,2-d]-†		624	—
IIIi	Thieno[2,3-d]-	Benzothiazole	573	3,0
IIIj	5-Bromothieno[2,3-d]-	Benzothiazole	581	1,5
IIIk	5,6-Dimethylthieno[2,3-d]-	Benzothiazole	579	5,0
IIIl	5,6-Tetramethylenethieno[2,3-d]-	Benzothiazole	581	4,0
IIIm	5-Phenylthieno]2,3-d]-	Benzothiazole	594	2,0
IIIn	Indolo[3,2-d]-	Benzothiazole	590	6,0
IIIo	5-Methylindolo[3,2-d]-	Benzothiazole	592	7,0
IIIp	5-Bromoindolo[3,2-d]-	Benzothiazole	592	3,0
IIIq	7-Methylindolo[3,2-d]-	Benzothiazole	596	—3,0
	Benzo-	2-Quinoline	580	2,5
	Thieno[2,3-d]-	2-Quinoline	602	1,5
IIIr	5,6-Dimethylthieno]2,3-d]-	2-Quinoline	608	0,5
IIIs	5,6-Tetramethylenethieno[2,3-d]-	2-Quinoline	611	1,5
	Benzo-	3,3-Dimethylindolenine	542	11,0
IIIt	Thieno]2,3-d]-	3,3-Dimethylindolenine	556	15,0
IIIu	5-Bromothieno[2,3-d]-	3,3-Dimethylindolenine	565	12,5
IIIx	5,6-Dimethylthieno[2,3-d]-	3,3-Dimethylindolenine	560	19,0
IIIy	5,6-Tetramethylenethieno[2,3-d]-	3,3-Dimethylindolenine	562	18,0
IIIz	5-Phenylthieno [2,3-d]-	3,3-Dimethylindolenine	577	14,0

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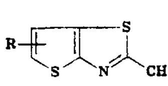
*The deviations of the absorption maxima of the unsymmetrical dyes from the arithmetic means calculated with respect to the λ_{max} values of the corresponding symmetrical trimethinecyanines.

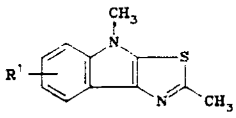
†Z = Z^1.

expedient to investigate the effect of substituents that differ in character in the heteroresidues of thieno- and indolothiazolocyanines on their properties.

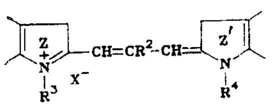
In this paper we describe the synthesis and discuss the spectral properties of dyes of different classes of derivatives of alkyl-, alkylene-, aryl-, and halothieno[2,3-d]thiazoles (I) and halo- and methylindolo[3,2-d]thiazoles (II). From the polymethine dyes with residues of bases (I and II) we obtained symmetrical and unsymmetrical carbocyanines III, dimethinemerocyanines IV, and p-dimethylaminostyryl dyes V, as well as a number of unsymmetrical meso-alkyl-substituted trimethinecyanines with a benzothiazole residue.



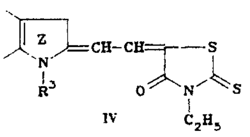
I



II



III



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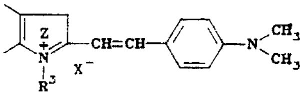

V

I R = CH_3, C_6H_5, Br, $(CH_2)_4$; II R^1 = CH_3, Cl, or Br; Z is a thieno[2,3-d]- or 8-methyl-indolo[3,2-d]thiazole residue, Z^1 is a thieno[2,3-d]- or 8-methylindolo[3,2-d]thiazole, unsubstituted or substituted benzothiazole, 3,3-dimethylindolenine, or quinoline residue, R^2 is H or alkyl, R^3 and R^4 are alkyl groups, and X^- is an anion.

TABLE 2. Absorption Maxima of Dimethinemerocyanines IV and Styryls V

Compound	Z-thiazole	λ_{max}^{abs} (in C_2H_5OH), nm	$\Delta\lambda$,* nm
	In structure IV		
	Benzo-	524	26
IVa	Thieno[2,3-d]-	549	19
IVb	5-Bromothieno[2,3-d]-	550	24,5
IVc	5,6-Dimethylthieno[2,3-d]-	558	18
IVd	5,6-Tetramethylenethieno[2,3-d]-	558	19
	5-Phenylthieno[2,3-d]-	564	24
	Indolo[3,2-d]-	576	12
IVe	5-Methylindolo[3,2-d]-	580	11
IVf	7-Methylindolo[3,2-d]-	573	12
IVg	5-Bromoindolo[3,2-d]-	574	13
IVh	5,7-Dichloroindolo[3,2-d]-	568	15
	In structure V		
	Indolo[3,2-d]-	512	111,5
Va	5-Methylindolo[3,2-d]-	508	118,5
Vb	7-Methylindolo[3,2-d]-	506	114,5
Vc	5-Bromoindolo[3,2-d]-	512	110,5
Vd	5,7-Dichloroindolo[3,2-d]-	520	98,5

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*The deviations of the absorption maxima from the arithmetic means calculated with respect to the λ_{max} values of symmetrical trimethinecyanines and the monomethineoxanine (λ 542 nm) of the 3-ethylrhodanine derivative (for IV) or the hydrol of Michler's blue (λ 613 nm) (for V).

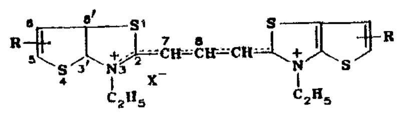
Symmetrical carbocyanines III ($Z = Z^1$, $R^2 = H$) were obtained by condensation of quaternary saltsof base I with ethyl orthoformate in acetic anhydride or by the reaction of quaternary salts of II with their 2-β-acetanilidovinyl derivatives in acetic anhydride in the presence of triethylamine with heating (see [5]). Dimethinemerocyanines IV were synthesized from quaternary salts of 2-acetanilidovinyl derivatives of I and II and 3-ethylrhodanine (or 3-ethyl-5-acetanilidomethylenerhodanine and ethiodides of I and II) in ethanol by heating in the presence of triethylamine. For the preparation of styryl dyes V alkiodides of II were condensed with p-dimethylaminobenzaldehyde in ethanol in the presence of piperidine.

For the synthesis of unsymmetrical III ($Z \neq Z^1$) the alkiodies of 2-β-acetanilidovinyl derivatives of I and II were condensed by heating with quaternary salts of 2-methylbenzothiazole, 3,3-dimethylindolenine, or quinoline in aceticanhydride, ethanol, or chloroform in the presence of triethylamine.

The incorporation of substituents into the 5 and 5' positions of thienothiazolocarbocyanine residues leads to an appreciably greater shift of the absorption maximum in the long-wave region of the spectrum than in the series of corresponding benzothiazole derivatives (see Table 1). The greatest bathochromic shift is characteristic for phenyl-substituted dyes. Halo-, alkyl-, and alkylenethienothiazolocarbocyanines absorb in virtually the same region of the spectrum.

The results of quantum-chemical calculations of the electronic structures of polymethine dyes that are derivatives of substituted thieno[2,3-d]thiazoles in the ground ($^1S_0$) and excited ($^1S_1$) singlet states (Table 3, carried out by the Pariser—Parr—Pople (PPP) method with the parameters proposed in [6] and used by us previously for calculations of thienothiazoles and polymethine dyes [7, 8] show that both electron-donor and electron-acceptor substituents in the 5 and 5' positions of the heteroresidues of thienothiazolocarbocyanines lead to a more uniform distribution of the electron density in the chromophore than in the unsubstituted dye. Significant changes in the charges of the carbon atoms and small changes in the charges of the sulfur atoms of the annelated thiophene rings are observed in this case; this indicates transmission of the electronic effects of the substituents to the chromophore of the dye via the system of mobile π electrons of the thiophene rings. The greater effects of the substituents on the electronic structure of the

TABLE 3. Charges on the Atoms (q_r) and Bond Orders (P_{rs}) in the Chromophore of the Dyes



R	State	q_r on the atoms										P_{rs}		
		1	2	3	4	5	6	7	8	3′	6′	2—3	2—7	7—8
H	$^1S_0$	0,089	0,102	0,393	0,087	0,018	−0,022	−0,122	0,140	−0,073	−0,041	0,574	0,645	0,630
H	$^1S_1$	0,101	−0,093	0,405	0,084	0,059	−0,006	0,018	−0,086	−0,009	−0,015	0,475	0,622	0,599
C_6H_5	$^1S_0$	0,087	0,096	0,395	0,082	0,021	−0,036	−0,121	0,134	−0,082	−0,030	0,564	0,643	0,630
C_6H_5	$^1S_1$	0,083	−0,088	0,397	0,079	0,050	0,001	0,018	−0,082	−0,017	−0,035	0,476	0,646	0,600
p-$CH_3OC_6H_4$	$^1S_0$	0,088	0,097	0,390	0,081	0,022	−0,037	−0,122	0,130	−0,086	−0,028	0,566	0,642	0,632
Br	$^1S_0$	0,087	0,100	0,394	0,083	0,020	−0,024	−0,120	0,138	−0,084	−0,036	0,568	0,644	0,629
NO_2	$^1S_0$	0,084	0,109	0,406	0,080	−0,092	0,056	−0,111	0,150	−0,031	−0,050	0,564	0,630	0,627
NO_2	$^1S_1$	0,107	−0,067	0,436	0,078	−0,070	0,055	0,050	−0,071	0,005	−0,023	0,498	0,626	0,601

TABLE 4. Characteristics of the Dyes

Compound	mp,* °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C (Br)	H (I)	N (S)		C (Br)	H (I)	N (S)	
IIIa	247...248	44,9	4,6	4,8)	$C_{17}H_{15}Br_2IN_2S_4$	45,0	4,5	5,0	13
IIIc	238...239	47,4	5,3	(20,3)	$C_{25}H_{29}IN_2S_4\cdot H_2O$	47,6	5,0	(20,3)	46
IIIe	262...263	—	(20,3)	(10,0)	$C_{29}H_{31}IN_4S_2$	—	(20,3)	(10,2)	25
IIIf	235...236	—	(20,1)	(10,0)	$C_{29}H_{31}IN_4S_2$	—	(20,3)	(10,2)	30
IIIg	263...264	(21,2)	16,7	—	$C_{27}H_{25}Br_2IN_4S_2$	21,2	16,8	—	27
IIIj	244...245	(13,7)	(22,2)	—	$C_{19}H_{18}BrIN_2S_3$	(13,8)	(22,0)	—	70
IIIk	257...258	48,1	4,9	5,1	$C_{21}H_{23}IN_2S_3$	47,9	4,4	5,3	68
IIIl	213...215	50,3	4,8	4,9	$C_{23}H_{25}IN_2S_3\cdot C_2H_5OH$	50,2	5,2	4,7	75
IIIo	258...259	—	(22,6)	(11,3)	$C_{25}H_{26}IN_3S_2$	—	(22,7)	(11,45)	70
IIIp	208...209	(12,6)	(20,2)	—	$C_{24}H_{23}BrIN_3S_2$	(12,1)	(20,3)	—	40
IIIq	245...246	—	(22,5)	(11,3)	$C_{25}H_{26}IN_2S_3$	—	(22,7)	(11,45)	74
IIIr	249...250	52,8	4,9	5,2	$C_{23}H_{25}IN_2S_2$	53,1	4,8	5,4	29
IIIs	255...256	—	(23,4)	(11,9)	$C_{25}H_{27}IN_2S_2$	—	(23,2)	(11,7)	70
IIIu	212...213	44,5	4,5	4,6	$C_{22}H_{24}BrIN_2S_2\cdot 0{,}5H_2O$	44,3	4,7	4,7	83
IIIx	223...224	53,5	5,8	4,8	$C_{24}H_{29}IN_2S_2\cdot 0{,}5C_2H_5OH$	53,7	5,8	5,0	90
IIIy	234...235	—	(22,3)	(11,2)	$C_{26}H_{31}IN_2S_2$	—	(22,5)	(11,4)	54
IVa	190...191	(18,7)	—	(29,7)	$C_{14}H_{13}BrN_2OS_4$	(18,4)	—	(22,6)	80
IVb	247...248	50,3	5,0	(33,6)	$C_{16}H_{18}N_2OS_4$	50,2	4,7	(33,5)	75
IVc	267...268	—	—	(31,4)	$C_{18}H_{20}N_2OS_4$	—	—	(31,4)	36
IVe	247...248	57,6	5,3	—	$C_{20}H_{21}N_3OS_3$	57,8	5,1	—	11
IVf	285...287	53,4	6,7	—	$C_{20}H_{21}N_3OS_3\cdot C_2H_5OH\cdot 2H_2O$	53,1	6,4	—	21
IVg	272...273	47,3	4,0	—	$C_{19}H_{18}BrN_3OS_3$	47,5	3,75	—	11
IVh	>300	48,3	3,8	8,7	$C_{19}H_{17}Cl_2N_3OS_3$	48,5	3,6	8,9	29
Va	246...247	—	(24,8)	(6,2)	$C_{23}H_{26}IN_3S\cdot 0{,}5H_2O$	—	(24,8)	(6,25)	25
Vb	238...239	—	(25,2)	(6,1)	$C_{23}H_{26}IN_3S$	—	(25,3)	(6,3)	37
Vc	207...208	(13,9)	(22,2)	—	$C_{22}H_{23}BrIN_3S$	(14,1)	(22,4)	—	20
Vd	292...293	—		13,5†	$C_{23}H_{23}Cl_2N_3O_3S_2$	—	—	13,5†	43

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*Compounds IIIa, j-l, o-q, u-y and IVb, e-g were dark-violet prisms, IIIc, e-g, r, s were dark-blue prisms, IVa, c were brown prisms, and V -d were dark-red plates.

†The percentage of chlorine.

chromophore in cyanines with thieno[2,3-d]thiazole residues as compared with benzothiazole derivatives and, correspondingly, on their absorption spectra can probably also be explained in the same way. The most uniform distribution of the electron density in the chromophore is characteristic for 5,5'-di(p-methoxyphenyl)- and 5,5'-diphenylthienothiazolocarbocyanines.

The introduction of methyl groups into indolothiazole residues leads to a small shift of the absorption maximum of symmetrical carbocyanines to the short- and long-wave regions of the spectrum; the 5,5'- and 7,7'-dimethylindolo[3,2-d]thiazolocarbocyanines differ in color. However, the incorporation of halogen atoms into the 5 and 5,7 positions of the indolothiazole heteroresidue gives rise only to a hypsochromic shift of the absorption maximum of the symmetrical dyes (by 2-10 nm). The 5-halo- and 5,7-dihalo derivatives also differ appreciably in color. With respect to their basicities the thienothiazolo- and indolothiazolotrimethinecyanines (Table 1, see the pK_a values) significantly surpass the benzo- and naphthothiazole derivatives, respectively. It follows from Tables 1 and 2 (see the $\Delta\lambda$ values of unsymmetrical carbocyanines, dimethinemerocyanines, and styryl dyes) that the presence of electron-donor groups in thieno- and indolothiazolocyanine heteroresidues increases their basicities somewhat, whereas the presence of halogen atoms produces the opposite effect.

EXPERIMENTAL

The amounts of solvents in the dyes were determined by means of GLC. The characteristics of the dyes are presented in Table 4.

Symmetrical Unsubstituted (in the polymethine chain) Carbocyanines III. A mixture of 1 mmole of the ethiodide of 5-bromo- or 5,6-tetramethylene-2-methylthieno[2,3-d]thiazole, 0.375 g (2.5 mmole) of ethyl orthoformate, and 3.5 ml of acetic anhydride was heated for 30 min at 140°C, after which it was cooled and diluted with ether. The precipitate was removed by filtration, washed with water, air dried, and recrystallized from ethanol. This method gave IIIa and IIIc. A mixture of 1 mmole of 2,5,8-trimethylindolo[3,2-d]thiazole ethiodide, 1 mmole of 2-β-acetanilidovinyl-5,8-dimethylindolo[3,2-d]thiazole, 15 ml of anhydrous ethanol, and 1 mmole of triethylamine was refluxed for 2 h, after which it was cooled, and the precipitate was removed by filtration, washed with ether, and purified as in the case of IIIa to give IIIe. Compounds IIIf and IIIg were similarly synthesized by condensation of the ethiodides of 2,7,8-trimethyl- and 2,8-dimethyl-5-bromoindolo[3,2-d]-thiazole with their 2-β-acetanilidovinyl derivatives in 20 ml of acetic anhydride for 10 min at 60°C.

Unsymmetrical Unsubstituted (in the polymethine chain) Carbocyanines III. A mixture of 1 mmole of 2-methylbenzothiazole ethiodide, 1 mmole of 2-β-anilidovinyl-5-bromothieno[2,-3-d]thiazole ethiodide, 15 ml of acetic anhydride, and 1 mmole of triethylamine was maintained at room temperature for 12 h, after which the precipitate was removed by filtration, washed successively with water, aqueous ethanol, and ether, and purified as in the case of IIIa. Compounds IIIk and IIIl were similarly synthesized from 5,6-dimethyl- and 5,6-tetramethylene-2-β-acetanilidovinylthieno[2,3-d]thiazole ethiodides in the course of 5 min in 250 ml of chloroform at 20°C, and IIIo, IIIp, and IIIq were obtained from 5,8-dimethyl-, 5-bromo-8-methyl-, and 7,8-dimethyl-2-β-acetanilidovinylindolo[3,2-d]thiazole ethiodides, respectively, in 25 ml of anhydrous ethanol (30 min, 20°C), 25 ml of acetic anhydride, 25 ml of acetic anhydride (10 min, 50°C), and 20 ml of anhydrous ethanol (30-40 min, 20-25°C). Compounds IIIr (30 ml of ethanol, refluxing for 5 min) and IIIs (200 ml of chloroform, with 30 min cooling and subsequent dilution of the reaction mixture with 200 ml of ether) were obtained from quinaldine ethiodide by a method similar to that used to prepare carbocyanines IIIj. Carbocyanines IIIu, IIIx, and IIIy were synthesized by condensation of 2,3,3-trimethylindolenine ethiodide with the ethiodides of 2-β-acetanilidovinyl derivatives of 5-bromo-, 5,6-dimethyl-, and 5,6-tetramethylenethieno[2,3-d]thiazole in 20 ml of acetic anhydride for 10 min at 120°C.

Dimethinemerocyanines IV. A mixture of 1 mmole of 2-β-acetanilidovinyl-5-bromothieno-[2,3-d]thiazole ethiodide, 1 mmole of 3-ethylrhodanine, 10 ml of ethanol, and 1 mmole of triethylamine was refluxed for 15 min, after which it was cooled, and the precipitate was removed by filtration, washed with water and ethanol, dried and recrystallized to give IVa. Compounds IVb,d-h were similarly synthesized. Dye IVc was obtained by condensation of 1.4 mmole of 2-methyl-5,6-tetramethylenethieno[2,3-d]thiazole ethiodide with 1.4 mmole of

3-ethyl-5-acetanilidomethylenerhodanine in 10 ml of ethanol in the presence of 0.35 ml of triethylamine by refluxing for 30 min.

Styryl Dyes Va-d. A 1-mmole sample of the quaternary salt of indolothiazole II was refluxed with 1 mmole of p-dimethylaminobenzaldehyde in 4 ml of ethanol in the presence of a drop of piperidine.

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