POLYMETHINE DYES – INDOLO[3,2-d]THIAZOLE DERIVATIVES

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New polymethine dyes with an indolo[3,2-d]thiazole residue are described, and their spectral properties are discussed. Replacement of the vinylene group in the naphtho[1,2-d]thiazole residue by an NH group leads to a considerably greater bathochromic shift of the absorption maximum of carbo- and merocyanines as compared with replacement by a sulfur atom. The basicity of the indolo[3,2-d]thiazole residue is higher than the basicity of the naphtho[1,2-d]thiazole and thionaphtheno[3,2-d]thiazole residues.

Naphthothiazole and thionaphthenothiazole derivatives that are carbocyanine dyes are effective spectral sensitizers of silver halide materials [1-3].

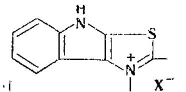
We have synthesized various classes of polymethine dyes (II-IV) with a new heterocyclic base residue – indolo[3,2-d]thiazole – in order to study their color and investigate their photographic properties.

The positions of the absorption maxima of the synthesized carbo- and merocyanines and, for comparison, the corresponding benzothiazole, naphtho[1,2-d]thiazole, and thionaphtheno[3,2-d]thiazole derivatives, as well as the hypsochromic shifts for unsymmetrical carbocyanines and the basicities (A), measured for the ethylates of symmetrical carbocyanines, are presented in Table 1.

The positions of the absorption maxima of p-dimethylaminostyryl dyes that are derivatives of the synthesized base, benzothiazole, and naphtho[1,2-d]thiazole are presented in Table 2 along with the calculated hypsochromic shifts.

The data in Table 1 demonstrate that all of the carbocyanines and merocyanines derived from indolo[3,2-d]thiazole are more deeply colored than the corresponding naphtho[1,2-d]thiazole and thionaphtheno[3,2-d]thiazole derivatives (by 35 and 30 nm, respectively, in the case of symmetrical carbocyanines).

Thus replacement of the vinylene group by NH leads to a considerably greater bathochromic shift of the absorption maxima of carbo- and merocyanines as compared with replacement by a sulfur atom; this can probably be explained by the difference in the degree of conjugation with the primary chromophore of the π electrons of the indole ring as compared with the benzene and thiophene rings (in the case of dyes with a thionaphtheno[3,2-d]thiazole residue).



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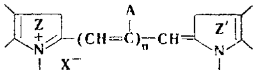

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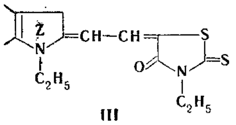

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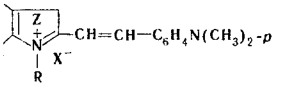

IV

Z is an indolo[3,2-d]thiazole residue, Z' is an indolo[3,2-d]thiazole, benzoxazole, benzothiazole, benzoselenazole, napththothiazole, or a derivative residue, R and R' are alkyl or sulfoalkyl groups, A = H or alkyl, n = 0 or 1, and X is an acid residue.

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TABLE 1. Characteristics of Carbo- and Merocyanines

Compound	Z in formula II (R=R′=C_2H_5, n=1 and A=H)	Z′ in formula II	λ_{max}, nm (in methanol	Hypsochromic shift*, nm	A†	pK_a
	Benzothiazole	Benzothiazole	558		2,8[4]	−0,66
IV	Indolo[3,2-d]thiazole	Indolo[3,2-d]thiazole	632		$4{,}1\cdot10^{-2}$	1,79
	Naphtho[1,2-d]thiazole	Naphtho[1,2-d]thiazole	597[5]		1,15[4]	−0.04
	Thionaphtheno[3,2-d]thiazole	Thionaphtheno[3,2-d]thiazole	602[6]		$3{,}5\cdot10^{-1}$	
VI	Indolo[3,2-d]thiazole	Benzothiazole	587	8,0		
	Thionaphteno[3,2-d]thiazole	Benzothiazole	580[6]	0		
VII	Indolo[3,2-d]thiazole	Naphtho[1,2-d]thiazole	607	7,5		
	Thionaphtheno[3,2 2-d]thiazole	Naphtho[1,2-d]thiazole	602[6]	2,5		
VIII	Indolo[3,2-d]thiazole	Benzoxazole	550	8,5		
	Naphtho[1,2-d]thiazole	Benzoxazole	542	1,0		
IX	Indolo[3,2-d]thiazole	Benzoselenazole	583	19,0		
	Z in formula III					
X	Indolo[3,2-d]thiazole		576	11,0		
	Naphtho[1,2-d]thiazole		542[7]	26,5		
	Thionaphtheno[3,2-d]thiazole		553[3]	19		

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*The hypsochromic shifts are the deviations of the absorption maxima from the arithmetic mean values calculated (in the case of unsymmetrical carbocyanines) from the absorption maxima of the corresponding symmetrical dyes with indolo[3,2-d]thiazole and benzoselenazole (λ_{max} 572 nm) [9], benzothiazole, naphtho[1,2-d]thiazole or benzoxazole (λ_{max} 485 nm) [10] residues, or, in the case of dimethylidynemerocyanines, from the absorption maxima of the corresponding symmetrical carbocyanines and monomethylidyneoxanine – a derivative of 3-ethylrhodanine (λ_{max} 542 nm).

† The A value is the molar concentration of hydrochloric acid that induces conversion of the carbocyanines ($1\cdot10^5$ M solution in 57% ethanol) to the diacid salt [4,8].

TABLE 2. Characteristics of the Styryl Dyes

Compound	Z in formula IV (R = C_2H_5)	λ_{max}, nm (in ethanol)	Hypsochromic shift, nm*
	Benzothiazole	528	56
	Naphtho[1,2-d]thiazole	542	61,5
XI	Indolo[3,2-d]thiazole	506	115

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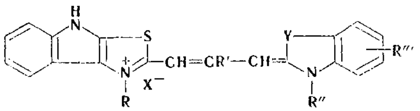
*The hypsochromic shifts are the deviations of the absorption maxima of the styryl dyes from the arithmetic mean values calculated from the absorption maxima of the corresponding symmetrical carbocyanines and Michler's blue hydrol in nitromethane (λ_{max} 610 nm).

It is seen from a comparison of the hypsochromic shifts of unsymmetrical carbocyanines, dimethylidynemerocyanines (Table 1), and p-dimethylaminostyryl dyes (Table 2) that the basicity of the indolo[3,2-d]thiazole residue is higher than the basicity of both the naphtho[1,2-d]thiazole and thionaphtheno[3,2-d]thiazole residues (see also the experimental A values in Table 1).

TABLE 3



Comp.	R	R′	R″	R‴	Y	X	Mp, °C	λ_{max}, nm (from ethanol)	Empirical formula	Found, %				Calc., %				Yield, %
										C	H	I	S	C	H	I	S	
VI	C_2H_5	H	C_2H_5	H	S	I	243—244[a]	586	$C_{23}H_{22}IN_3S_2$	51,8	4,1	23,7	12,0	52,0	4,1	23,9	12,1	38
VIII	C_2H_5	H	C_2H_5	H	O	I	221—222[b]	551	$C_{22}H_{22}IN_3OS$	52,4	4,3	25,1	6,2	52,5	4,5	25,2	6,4	29
IX	C_2H_5	H	C_2H_5	H	Se	I	229—230[a]	582	$C_{23}H_{22}IN_3SSe$	47,7	3,7	21,8	5,4	47,8	3,8	21,9	5,5	43
VII	C_2H_5	H	C_2H_5	4,5-Benzo	S	I	225—226[a]	606	$C_{27}H_{24}IN_3S_2$	55,7	4,0	21,9	11,1	55,8	4,1	21,8	11,0	36
XIII	C_2H_5	C_2H_5	C_2H_5	5-OCH_3	S	Br	>300[a]	582	$C_{26}H_{28}BrN_3OS_2$	57,8	5,0	14,6[c]	11,7	57,7	5,2	14,7[c]	11,8	37
XIV	$(CH_2)_3SO_3^-$	C_2H_5	C_2H_5	5-OCH_3	S	—	281—282[b]	586	$C_{27}H_{29}N_3O_4S_3$	58,0	5,1	7,5[d]	17,4	58,0	5,2	7,5[d]	17,3	44
XV	C_2H_5	C_2H_5	$(CH_2)_3SO_3^-$	5-OCH_3	S	—	>300[e]	580	$C_{27}H_{29}N_3O_4S_3$	58,0	5,1	6,6[d]	17,3	58,0	5,2	6,7[d]	17,3	43
XVI	C_2H_5	C_2H_5	C_2H_5	4,5-Benzo	S	Br	>300[a]	588	$C_{29}H_{28}BrN_3S_2$	61,8	4,9	14,3[c]	11,3	61,9	5,0	14,2[c]	11,4	50
XVII	$(CH_2)_3SO_3^-$	C_2H_5	C_2H_5	4,5-Benzo	S	—	285—286[b]	592	$C_{30}H_{29}N_3O_3S_3$	62,5	5,0	7,2[d]	16,6	62,6	5,0	7,8[d]	16,7	43
XVIII	C_2H_5	C_2H_5	C_2H_5	5,6-Dimethyl	S	Br	214—215[e]	571	$C_{27}H_{30}BrN_3S_2$	59,9	5,4	14,7[c]	11,8	60,0	5,5	14,8[c]	11,8	52
XIX	$(CH_2)_3SO_3^-$	C_2H_5	C_2H_5	5,6-Dimethyl	S	—	267—268[f]	587	$C_{28}H_{31}N_3O_3S_3$	60,6	5,5	7,5[d]	17,3	60,7	5,6	7,6[d]	17,4	37
XX	$(CH_2)_3SO_3^-$	C_2H_5	C_2H_5	H	Se	—	238—239[a]	580	$C_{26}H_{27}N_3O_3S_2Se$	54,6	4,6	7,3[d]	11,1	54,5	4,7	7,3[d]	11,3	65
XXII	$(CH_2)_3SO_3^-$	C_2H_5	$(CH_2)_3SO_3^- \cdot \overset{+}{N}H(C_2H_5)_3$	5-OCH_3	S	—	272—274[b,g]	579	$C_{34}H_{46}N_4O_7S_4$	54,4	6,0	—	17,2	54,4	6,1	—	17,1	29
XXIII	$(CH_2)_3SO_3^-$	C_2H_5	$(CH_2)_3SO_3^- \cdot \overset{+}{N}H(C_2H_5)_3$	4,5-Benzo	S	—	236—238[a,g]	588	$C_{37}H_{46}N_4O_6S_4$	57,6	5,9	—	16,5	57,6	6,0	—	16,6	34

[a] Dark violet prisms. [b] Violet prisms. [c] Analysis for bromine. [d] Analysis for nitrogen. [e] Dark green prisms. [f] Violet plates. [g] With decomposition.

EXPERIMENTAL

2-Methylindolo[3,2-d]thiazole. This compound was obtained as colorless needles (from ethanol) with mp 242-243° by heating 2-hydroxy-3-acetamidoindole with phosphorus pentasulfide in xylene [11]. UV spectrum (in ethanol): λ_{max}, nm ($\varepsilon \cdot 10^{-4}$): 229 (6.75), 278 (2.43).

2-Methyl-3-(γ-sulfopropyl)indolo[3,2-d]thiazolium Betaine. This compound was obtained in 75% yield by refluxing 2-methylindolo[3,2-d]thiazole with an equimolar amount of propane sultone in xylene for 20 h. The light yellow prisms (from anhydrous ethanol) melted above 300°. Found,%: C 50.2; H 4.4; N 9.1; S 20.5. $C_{13}H_{14}N_2O_3S_2$. Calculated,%: C 50.3; H 4.5; N 9.0; S 20.7.

3-(γ-Sulfopropyl)-1'-ethyl-6'-methylindolo[3,2-d]thiazoloquino-2'-monomethylidynecyanine Betaine (XII). This compound was obtained in 78% yield by heating 0.3 g (0.001 mole) of 2-methyl-3-(γ-sulfopropyl)-indolo[3,2-d]thiazolium betaine with 0.25 g (0.001 mole) of 1-ethyl-6-methylquinoline-2-sulfo betaine in 15 ml of anhydrous ethanol for 60 min on a boiling-water bath in the presence of triethylamine. The dark-red prisms (from ethanol) melted above 300° and had λ_{max} 522 nm (in ethanol). Found,%: C 62.6; H 5.2; N 8.7; S 13.4. $C_{25}H_{25}N_3O_3S_2$. Calculated,%: C 62.6; H 5.2; N 8.7; S 13.4.

3,3'-Diethylindolo[3,2-d]thiazolocarbocyanine Iodide (V). This compound was obtained in 16% yield by heating 0.68 g (0.002 mole) of 2-methylindolo[3,2-d]thiazole ethiodide with 24 g of ethyl orthoformate in 100 ml of acetic anhydride at 130-135° for 10 min. The dark blue prisms (from ethanol) had mp 243-244°. Found,%: C 52.5; H 3.9; S 11.2; I 22.2. $C_{25}H_{23}IN_4S_2$. Calculated,%: C 52.6; H 4.0; S 11.2; I 22.3.

Unsymmetrical Chain-Unsubstituted Carbocyanines (VI, VII, VIII, and IX). These dyes were synthesized by heating 0.34 g (0.001 mole) of 2-methylindolo[3,2-d]thiazole ethiodide with an equimolar amount of 2-(β-acetanilidovinyl)-substituted benzothiazole, naphtho[1,2-d]thiazole, benzoxazole, or benzoselenazole ethiodides, respectively, at 100-105° for 15 min in 10 ml of pyridine in the presence of triethylamine. To isolate the dyes, ether was added to the cooled reaction mass, and the resulting precipitate or resinous mass was dissolved by heating in ethanol. The solution was treated with 10% aqueous potassium iodide solution. The dyes were purified by recrystallization from ethanol (Table 3).

Mesoalkyl-Substituted Unsymmetrical Carbocyanines (XIII-XX, XXII, and XXIII). These dyes were synthesized by heating 0.001 mole of 2-methylindolo[3,2-d]thiazole ethiodide or γ-sulfopropylbetaine with 0.001 mole of the ethylmethosulfates of 2-(β-methylmercaptobutenyl) derivatives of naphtho[1,2-d]thiazole, 5-methoxybenzothiazole, or benzoselenazole in 10 ml of anhydrous ethanol for 2 h on a boiling-water bath in the presence of triethylamine. To isolate the bromides of the 3,3'-diethylcarbocyanines (XIII, XVI, and XVIII), ether was added to the cooled reaction mass, and the precipitate was dissolved in hot ethanol. The solution was treated with 10% potassium bromide solution, and the dye was recrystallized from alcohol (Table 3). To isolate sulfobetaines XIV, XV, XVII, and XIX-XXIII, the reaction mixture was cooled, and the dye was removed by filtration, washed with anhydrous ethanol, and purified by recrystallization from anhydrous ethanol (Table 3).

3-Ethyl-5-[3'-ethylindolo[3,2-d]thiazolinylidene-2'-ethylidene[thiazolidine-2-thion-4-one (X). This compound was obtained in 31% yield by heating a mixture of 0.34 g (0.001 mole) of 2-methylindolo[3,2-d]-thiazole ethiodide, 0.30 g (0.001 mole) of 3-ethyl-5-(acetanilidomethylene)thiazolidine-2-thion-4-one, 10 ml of anhydrous ethanol, and 0.2 g (0.002 mole) of triethylamine on a boiling-water bath for 1 h. The dark violet plates melted above 300° (from anhydrous ethanol). Found,%: C 55.6; H 4.25; N 10.8; S 24.8. $C_{18}H_{17}NOS_3$. Calculated,%: C 55.8; H 4.4; N 10.8; S 24.8.

2-(p-Dimethylaminostyryl)indolo[3,2-d]thiazole Ethobromide (XI). This compound was synthesized in 35% yield by heating 0.34 g (0.001 mole) of 2-methylindolo[3,2-d]thiazole ethiodide with 0.22 g (0.0014 mole) of p-dimethylaminobenzaldehyde in 10 ml of anhydrous ethanol for 1 h on a boiling-water bath in the presence of piperidine. The dark red prisms (from ethanol) had mp 216-217°. Found,%: C 58.8; H 5.0; Br 18.5. $C_{21}H_{22}BrN_3S$. Calculated,%: C 58.9; H 5.1; Br 18.6.

2-(p-Dimethylaminostyryl)-3-(γ-sulfopropyl)indolo[3,2-d]thiazolium Betaine (XXI). This compound was similarly obtained in 26% yield from 0.30 g (0.001 mole) of 2-methyl-3-(γ-sulfopropyl)indolo[3,2-d]-thiazolium betaine and 0.22 g (0.0014 mole) of p-dimethylaminobenzaldehyde. The violet prisms (from anhydrous ethanol) had mp 295-296°. Found,%: C 59.7; H 5.1; S 14.4. $C_{22}H_{23}N_3O_3S_2$. Calculated,%: C 59.8; H 5.2; S 14.5.

LITERATURE CITED

1. N. I. Fisher and F. M. Hamer, J. Chem. Soc., 2502 (1930).
2. B. Beilenson and F. M. Hamer, J. Chem. Soc., 143 (1939).
3. Z. I. Moskalenko, Dissertation [in Russian], Moscow (1965).
4. A. I. Kiprianov, S. G. Fridman, and L. S. Pupko, Sbornik Nauchn. Rabot IOKh Akad. Nauk Ukr SSR, 13, 44 (1947).
5. F. M. Hamer, J. Chem. Soc., 2598 (1929).
6. Z. I. Miroshnichenko and M. A. Al'perovich, Zh. Obshch. Khim., 34, 247 (1964).
7. M. V. Deichmeister, Z. P. Sytnik, and É. B. Lifshits, Zh. Obshch. Khim., 22, 167 (1952).
8. N. S. Spasokukotskii and E. S. Kozlova, Trudy NIKFI, 40, 70 (1960).
9. N. I. Fisher and F. M. Hamer, Proc. Roy. Soc. (London), 154A, 703 (1936).
10. M. V. Deichmeister, I. I. Levkoev, and É. B. Lifshits, Zh. Obshch. Khim., 23, 1529 (1953).
11. P. I. Abramenko, Zh. Vsesoyuzn. Khim. Obshchestva, 16, 231 (1971).