SELENONAPHTHENO[2,3-d]THIAZOLE DERIVATIVES AS POLYMETHINE DYES

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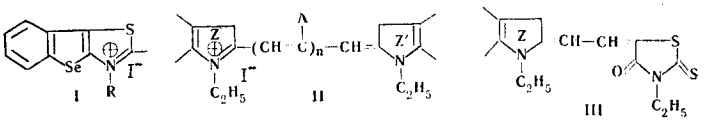
New polymethine dyes – selenonaphtheno[2,3-d]thiazole derivatives – were synthesized. It is shown that all of the synthesized dyes which have a selenonaphtheno[2,3-d]thiazole residue are more deeply colored than the corresponding 6,7-benzobenzothiazole and thionaphtheno-[2,3-d]thiazole derivatives.

It is known that polymethine dyes which contain a thiazole ring condensed with thiophene or thionaphthene rings are considerably more deeply colored than the corresponding benzothiazole and benzobenzothiazole derivatives and are extremely interesting optical sensitizers of photographic materials [1-3]. In this connection, it was of interest to synthesize dyes which contain a selenophene or selenonaphthene ring condensed with a thiazole ring and to study their properties.

In this communication polymethine dyes with selenonaphtheno[2,3-d]-thiazole (I) residues having structures II and III are described:



where Z is a selenonaphtheno[2,3-d]thiazole residue, Z' is a selenonaphtheno[2,3-d]thiazole, 6,7-benzobenzothiazole, benzothiazole, or benzoselenazole residue (or their derivatives), A is H or alkyl, and n = 1 or 2.

The positions of the absorption maxima in ethanol of the synthesized carbo- and merocyanines and the hypsochromic shifts for compounds with unsymmetrical structures are presented in Table 2.

It is apparent from an examination of the absorption maxima of the dyes obtained that all of the selenonaphtheno[2,3-d]thiazole derivatives are more deeply colored than the corresponding 6,7-benzobenzothiazole and thionaphtheno[2,3-d]thiazole derivatives (a shift in the absorption maximum of 43 nm and 16 nm, respectively, in the case of symmetrical carbocyanines).

A comparison of the hypsochromic shifts of unsymmetrical carbocyanines and dimethinomerocyanines indicates that the basicity of the selenonaphtheno[2,3-d]thiazole residue is of about the same order as that of 6,7-benzobenzo- and thionaphtheno[2,3-d]thiazole residues.

EXPERIMENTAL

Cyanines (Table 2). Symmetrical Carbocyanine (IV). This was obtained by heating the ethiodide of methyl-substituted base I with excess ethyl orthoformate in acetic anhydride at 130-135° for 20 min in a glycerine bath.

Symmetrical Dicarbocyanine (V). This was synthesized by heating the ethiodide of methyl-substituted base I with the ethiodide of 2-(δ-anilinobutadienyl)selenonaphtheno[2,3-d]thiazole in acetic anhydride in the presence of triethylamine in a boiling-water bath for 30 min.

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TABLE 1. Cyanine Dyes

Compound	Amount			Appearance	Mp °C	λ max (in ethanol), nm	Empirical formula	I, %		Yield, %
	quaternary salt, g	substance for formation of chain on hemicyanine, g	solvent, ml					found	calc.	
3,3'-Diethylselenonaphtheno[2_1,3_1-d, $2_1'$,$3_1'$-d]-thiazolocarbocyanine iodide (IV)	0,82	0,70	4 †	Dark blue prisms	195—196	636	$C_{25}H_{21}IN_2S_2Se_2$	3,93*	4,01*	46
3,3'-Diethylseneonaphthenol[2_1,3_1-d, $2_1'$,$3_1'$-d]-thiazolodicarbocyanine iodide (V)	0,82	1,20	5 †	Dark green prisms	196—197	729	$C_{27}H_{23}IN_2S_2Se_2$	3,94*	3,86*	63
3,3'-Diethylselenonaphtheno[2_1,3_1-d]-thiazoloselenacarbocyanine iodide (VIII)	0,82	1,00	6 †	Dark violet prisms	237—238	605	$C_{23}H_{21}IN_2SSe_2$	19,71	19,79	44
3,3',7-Triethyl-5'-methoxyselenonaphtheno[2_1,3_1-d]thiazoloselenacarbocyanine iodide (X)	0,82	0,95	8 ‡	Dark violet prisms	242—243	593	$C_{26}H_{27}IN_2OSSe_2$	17,98	18,12	35
3,3',7-Triethylselenonaphtheno-[2_1,3_1-d]thiazoloselenacarbocyanine iodide (XI)	0,82	0,93	8 ‡	Dark violet prisms	244—245	581	$C_{25}H_{25}IN_2SSe_2$	19,07	18,93	40
3,3'-Diethylselenonaphtheno[2_1,3_1-d]-thiazolothiacarbocyanine iodide (VI)	0,40	0,50	3 †	Dark violet prisms	243—244	598	$C_{23}H_{21}IN_2S_2Se$	21,27	21,31	62
3,3'-Diethyl-6',7'-benzoselenonaphtheno[2_1,3_1-d]thiazolothiacarbocyanine iodide (VII)	0,40	0,50	3 †	Green prisms	246—247	611	$C_{27}H_{23}IN_2S_2Se$	19,68	19,66	38
3,3'-Diethyl-7-methylselenonophtheno[2_1,3_1-d]thiazoloselenacarbocyanine iodide (XII)	0,82	0,92	8 ‡	Dark violet prisms	238—239	579	$C_{24}H_{23}IN_2SSe_2$	19,41	19,32	43
3,3'-Diethyl-7-methylselenonaphtheno[2_1,3_1-d]thiazolothiacarbocyanine iodide (XIII)	0,82	0,75	8 ‡	Violet needles	245—246	576	$C_{24}H_{23}IN_2S_2Se_2$	20,91	20,82	56
3,3',7-Triethyl-5',6'-dimethylselenonaphtheno[2_1,3_1-d]thiazolothiacarbocyanine diodide (XIV)	0,82	0,84	5 ‡	Dark violet prisms	204—205	583	$C_{27}H_{29}IN_2S_2Se$	19,56	19,48	36
3-Ethyl-5-[3'-ethylselenonaphtheno-[2_1,3_1-d]thiazolinylidene-2']-ethylidene]thiazolidine-2-thion-4-one (IX)	0,40	0,30	2 ‡	Dark violet needles	88—89	566	$C_{18}H_{16}N_2OS_3Se$	6,13*	6,20*	71

*Analysis for N.

† Acetic anhydride.

‡ Anhydrous ethanol.

TABLE 2. Absorption Maxima of Carbo- and Merocyanines in Ethanol

Dye	Gen. form.	Z in formula II or III	Z' in formula II	λ_{max} (in ethanol), nm when A=H and $n=1$	Hypsochromic shift, nm
IV	II	Selenonaphtheno[2,3-d]-thiazole	Selenonaphtheno[2,3-d]thiazole	636(729)*	—
	II	6,7-Benzobenzothiazole	6,7-Benzobenzothiaz.	593[4]	—
	II	Thionaphtheno[2,3-d]thiazole	Thionaphtheno[2,3-d] thiazole	630[3]	—
VI	II	Selenonaphtheno[2,3-d]thiaz.	Benzothiazole	598†	1,0
		Thionaphtheno[2,3-d]thiazole	Benzothiazole	596[3]	2,0
VII	II	Selenonaphtheno[2,3-d]thiaz.	6,7-Benzobenzothiaz.	611	3,5
		Thionaphtheno[2,3-d]thiazole	6,7-Benzobenzothiaz.	610[3]	1,5
VIII	II	Selenonaphtheno[2,3-d]thiaz.	Benzoselenazole	605†	1,0
IX	III	Selenonaphtheno[2,3-d]thiaz.	—	562	27,0
	III	6,7-Benzobenzothiazole ‡	—	540[5]	27,5
	III	Thionaphtheno[2,3-d]thiazole	—	559[3]	27,0

*λ_{max} of symmetrical dicarbocyanine V.
†λ_{max} (in ethanol) of symmetrical carbocyanines with benzothiazole and benzoselenazole residues at 558 nm [4] and 572 nm [4], respectively.
‡λ_{max} (in ethanol) of the monomethinoxanine derivative of 3-ethylrhodanine at 542 nm [6].

Unsymmetrical Chain-Unsubstituted Carbocyanines (VI, VII, and VIII). These were obtained by heating the ethiodide of methyl-substituted base I with the ethiodides of the 2-(β-acetanilinovinyl) derivatives of 6,7-benzobenzothiazole, benzothiazole, or benzoselenazole for 10 min at 120-125° (in a glycerine bath) in acetic anhydride in the presence of triethylamine.

Mesoalkyl-Substituted Unsymmetrical Carbocyanines (X, XI, XII, XIII, and XIV). These were synthesized by heating the ethiodide of methyl-substituted base I with the ethyl methosulfate of the 2-β-methylmercaptopropenyl or 2-β-methylmercaptobutenyl derivative of benzothiazole or benzoselenazole in anhydrous ethanol for 20-30 min in the presence of triethylamine on a boiling-water bath.

To isolate the dyes, ether was added to the cooled reaction mass, the precipitate or resinous mass was dissolved by heating in ethanol, and 10% aqueous potassium iodide was added to the solution. The carbocyanines were purified by recrystallization from ethanol, and the dicarbocyanines were purified before crystallization by chromatography with a column filled with aluminum oxide (with chloroform as the eluent).

Dimethinomerocyanine (IX). This was obtained by heating a mixture of the ethiodide of methyl-substituted base I, 3-ethyl-5-(acetanilinomethylene)thiazolidine-2-thion-4-one, anhydrous ethanol, and triethylamine on a boiling-water bath for 30 min. It was purified by recrystallization from anhydrous ethanol.

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