POLYMETHINE DYES FROM ISOMERIC 2-METHYLTHIONAPHTHENOTHIAZOLES

V.* THIENO[3,2-e]BENZOTHIAZOLE DERIVATIVES AS DYES

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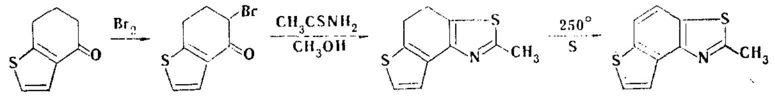
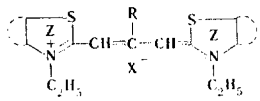
A number of quino(2)monomethylidyne-, carbo-, mero-, dimero-, and rhodacyanines (thieno-[3,2-e]benzothiazole derivatives) were synthesized. It is shown that replacement of the vinylene group by a sulfur atom in one of the benzene rings of the naphtho[1,2-d]thiazole residues in the cyanines and merocyanines does not affect the positions of their absorption maxima.

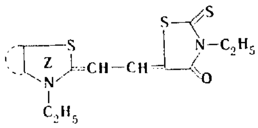
Several cyanine dyes – thieno[3,2-d]benzothiazole derivatives – have been described in the patent literature [2,3]. It seemed of interest to make a more detailed study of the properties of various polymethine dyes with thieno[3,2-e]benzothiazole residues, which are isosteres of the corresponding 2-methylnaphtho[1,2-d]thiazole derivatives, which have been extensively studied and are finding practical application. For this, we synthesized a number of quino(2)monomethylidyne-, carbo-, mero-, dimero-, and rhodacyanines. Of the known [2,3] methods for the preparation of 2-methylthieno[3,2-e]benzothiazole (IV), we selected that presented in the scheme below (I → IV) because of the greater accessibility of the starting compounds. In this case, substantial changes that make it possible to simplify the synthesis were introduced into the individual steps of the synthesis of IV.



I II III IV



X-XII, Xa-XIIa



XXI, XXIa

X R = H, XI R = CH_3, XII R = C_2H_5; X–XII, XXI Z = thieno[3,2-e]benzothiazole; Xa-XIIa, XXIa Z = naphtho[1,2-d]thiazole

Compound IV was converted to quaternary salts (V and VI) by the action of methyl and ethyl tosylates. Dyes based on V and VI were obtained by the usual methods adopted for the synthesis of such types of compounds [4-6]. A comparison of the absorption spectra of the carbocyanines (X-XII) and the dimethylidyne-merocyanines (XXI) of thieno[3,2-e]benzothiazole (Table 1) with the spectra of the corresponding isosteric naphtho[1,2-d]thiazole dyes (Xa-XIIa [7,8] and XIIa [9]) demonstrates that replacement of one vinylene group in the benzene rings of the naphtho[1,2-d]thiazole residues by a sulfur atom has practically no effect on the positions of their absorption maxima. The same dependence is also observed in other classes of dyes that are thieno[3,2-e]benzothiazole derivatives.

The magnitudes of the hypsochromic shifts of merocyanines XXI and XXIa (26.5 and 25.5 nm, respectively), calculated from the absorption maxima of the corresponding symmetrical dyes, demonstrate that the basicities of the thieno[3,2-e]benzothiazole and naphtho[1,2-d]thiazole residues are extremely close.

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*See [1] for communication IV.

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TABLE 1. Thieno[3,2-e]benzothiazole Derivative Dyes

Comp.	Name	Appearance (from ethanol)*	mp dec.(°C)	Empirical formula	Found, %		Calc., %		λ_{max}, nm	Yield, %
					N	S	N	S		
VII	3,1'-Diethyl-4,5-(3,2-thieno)thiaquino-2'-monomethylidynecyanine iodide	Dark orange needles (800	268—269	$C_{23}H_{21}IN_2S_2$	5,5	12,4	5,4	12,4	504	62,3
VIII	3,1'-Diethyl-6'-methyl-4,5-(3,2-thieno)thiaquino-2-monomethylidynecyanine iodide	Orange needles (1000)	267—268	$C_{24}H_{23}IN_2S_2$	5,4	12,0	5,3	12,1	506	77,6
IX	3,1'-Diethyl-6'-methoxy-4,5-(3,2-thieno)thiaquino-2'-monomethylidynecyanine iodide	Orange needles (700)	262—263	$C_{24}H_{23}IN_2OS_2$	5,3	11,7	5,1	11,7	513	74,1
X	3,3'-Diethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine iodide	Dark green needles (1000)	249—250	$C_{25}H_{21}IN_2S_4$	4,6	21,0	4,6	21,2	597	33,6
XI	3,3'-Diethyl-9-methyl-4,5,4',5'-di(3,2-thieno)-thiacarbocyanine iodide	Dark blue needles (1000)	231—232	$C_{26}H_{23}IN_2S_4$	4,7	20,6	4,5	20,7	574	42,7
XII	3,3',9-Triethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine iodide	Dark green plates (700)	255—256	$C_{27}H_{25}IN_2S_4$	4,7	20,1	4,4	20,2	578	44,9
XIII	3,3',9-Trimethyl-4,5,4',5'-di(3,2-thieno)thiacarbocyanine p-toluenesulfonate	Green prisms (1000)	231—232	$C_{31}H_{26}N_2O_3S_5$	4,4	25,0	4,4	25,2	569	56,1
XIV	3,3'-Dimethyl-9-ethyl-4,5,4',5'-di(3,2-thieno)-thiacarbocyanine p-toluenesulfonate	Green needles (400)	263—264	$C_{32}H_{28}N_2O_3S_5$	4,3	24,5	4,3	24,6	575	57,8
XV	3,3'-Diethyl-4',5'-benzo-4,5-(3,2-thieno)thiacarbocyanine p-toluenesulfonate	Green plates (400)	267—268	$C_{34}H_{30}N_2O_3S_4$	4,3	19,8	4,4	20,0	598	62,3
XVI	3,3'-Diethyl-9-methyl-4',5'-benzo-4,5-(3,2-thieno)thiacarbocyanine iodide	Dark blue needles (1000)	239—240	$C_{28}H_{25}N_2S_3$	4,6	15,6	4,6	15,7	575	66,8
XVII	3,3',9-Triethyl-4',5'-benzo-4,5-(3,2-thieno)-thiacarbocyanine iodide	Violet plates (500)	242—243	$C_{29}H_{27}IN_2S_3$	4,6	15,2	4,5	15,2	579	64,1
XVIII	3,3'-Dimethyl-9-ethyl-4',5'-benzo-4,5-(3,2-thieno)thiacarbocyanine bromide	Violet needles (1000)	205—206	$C_{27}H_{23}BrN_2S_3$	5,0	17,3	5,1	17,4	578	91,2
XIX	3,3'-Diethyl-9-methyl-4,5-(3,2-thieno)thiacarbocyanine iodide	Red-violet needles (500)	254—255	$C_{24}H_{23}IN_2S_3$	5,0	17,0	5,0	17,1	559	62,5
XX	3,3',9-Triethyl-4,5-(3,2-thieno)thiacarbocyanine iodide	Green prisms (250)	238—239	$C_{25}H_{25}IN_2S_3$	4,8	16,5	4,8	16,6	564	74,1
XXI	2-Thioxo-3-ethyl-5-(1-ethylthieno[3,2-e]benzothiazolinylidene-2-ethylidene)thiazolidin-4-one	Red needles (6000)	289—290	$C_{18}H_{16}N_2OS_4$	6,8	31,6	6,9	31,7	542	62,3
XXII	2-Thioxo-3-butyl-5-(1-ethylthieno[3,2-e]benzothiazolinylidene-2-ethylidene)thiazolidin-4-one	Dark red prisms (2500)	269—270	$C_{20}H_{20}N_2OS_4$	6,3	29,4	6,5	29,5	542	85,1
XXIII	2-(2-Thioxo-3-butyl-4-oxo-5-thiazolidinylidene)-3-butyl-5-(1-ethylthieno[3,2-e]benzothiazolinylidene-2-ethylidene)thiazolidin-4-one	Green needles (8000)	285—286	$C_{27}H_{29}N_3O_2S_5$	7,2	27,1	7,1	27,2	589	37,0
XXIV	3,3'-Diethyl-4-oxo-4',5'-(3,2-thieno)-5-(1-ethylthieno[3,2-e]benzothiazolinylidene-2-ethylidene)thiazolinothiacyanine ethanesulfonate	Green needles (8000)	292—293	$C_{32}H_{31}N_3O_5S_6$	5,9	26,2	5,8	26,3	623	68,0
XXV	3,3'-Diethyl-4-oxo-4',5'-diphenyl-5-(1-ethylthieno[3,2-e]benzothiazolinylidene-2-ethylidene)thiazolinothiazolocyanine bromide	Green needles (100)	240—241	$C_{36}H_{32}BrN_3OS_4$	5,6	17,4	5,7	17,5	611	81,5
XXVI	3,3'-Diethyl-4-oxo-4',5'-(3,2-thieno)-5-(3-ethyl-4,5-diphenylthiazolinylidene-2-ethylidene)-thiazolinothiacyanine bromide	Blue-green needles (200)	196—197	$C_{36}H_{32}BrN_3OS_4$	5,5	17,3	5,7	17,5	629	75,0

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*The amount of ethanol for the crystallization of the dyes is indicated in parentheses in milliliters per gram.

EXPERIMENTAL

4,5,6,7-Tetrahydro-4-thionaphthenone (I). This compound was obtained by the reaction of γ-(α-thienyl)butyryl chloride with anhydrous stannic chloride in benzene [10].

5-Bromo-4,5,6,7-tetrahydro-4-thionaphthenone (II). This compound was synthesized by the action of bromine on I in absolute ether at 0° [11].

2-Methyl-4,5-dihydrothieno[3,2-e]benzothiazole (III). A solution of 23 g (0.1 mole) of II in 100 ml of methanol was added with stirring in the course of 1 h to a refluxing mixture of 15 g (0.2 mole) of thioacetamide and 15 g (0.17 mole) of anhydrous sodium carbonate in 100 ml of methanol, and the mixture was stirred for 30 min, after which 150 ml of methanol was removed by distillation. Water (500 ml) was added to the residue, and the liberated oil was extracted with ether. The base was extracted from the ether extracts with 3 N hydrochloric acid. The acid extract was neutralized with sodium carbonate, and the resulting oil was extracted with ether. The ether extracts were dried with calcium chloride, and the ether was removed by distillation to give 15 g (71.4%) of colorless crystals of III with mp 49° [3].

2-Methylthieno[3,2-e]benzothiazole (IV). A mixture of 5.2 g (0.025 mole) of III and 0.8 g (0.025 g-atom) of sulfur was heated at 120° for 10 min, and the temperature was then raised to 250° in the course of an hour. Water (30 ml) and 5 ml of 25% sodium hydroxide solution were then added to the dark crystalline product, and IV was removed by steam distillation to give 4 g (80.0%) of colorless plates with mp 86-87° (87.5° [3]). The picrate of IV was obtained as yellow needles (from ethanol) with mp 176-177°. Found: N 13.0%. $C_{10}H_7NS_2 \cdot C_6H_3N_3O_7$. Calculated: N 12.9%.

1,2-Dimethylthieno[3,2-e]benzothiazolium Tosylate (V). A mixture of 0.6 g (0.003 mole) of IV and 0.6 g (0.003 mole) of methyl p-toluenesulfonate was heated at 135° for 2 h. The resulting glassy mass was triturated with 3 ml of anhydrous acetone, and the crystalline product was removed by filtration and washed with 2 ml of acetone to give 0.94 g (80.0%) of V with mp 191-193°. Recrystallization from acetone gave colorless needles with mp 203-204°. Found: C 55.0; H 4.1; N 3.6; S 24.3%. $C_{18}H_{17}NO_3S_3$. Calculated: C 55.1; H 4.3; N 3.6; S 24.5%.

1-Ethyl-2-methylthieno[3,2-e]benzothiazolium Tosylate (VI). A mixture of 2 g (0.01 mole) of IV and 2.5 g (0.012 mole) of ethyl p-toluenesulfonate was heated at 135° for 6 h, and the resulting crystalline mass was triturated with 5 ml of anhydrous acetone, removed by filtration, and washed with 2 ml of acetone to give 3.6 g (90.0%) of VI with mp 178-180°. Recrystallization from ethanol gave colorless needles with mp 190-191° (from ethanol). Found: C 56.2; H 4.6; N 3.7; S 23.6%. $C_{19}H_{19}NO_3S_3$. Calculated: C 56.3; H 4.7; N 3.4; S 23.7%.

Monomethylidynecyanines (VII-IX, Table 1). These compounds were obtained by heating 0.001 mole of VI with 0.001 mole of 1-ethyl-2-ethylmercaptoquinolinium iodide at 95-98° for 10 min and also by heating its 6-methyl and 6-methoxy derivatives in 2 ml of pyridine in the presence of 0.003 mole of triethylamine.

Symmetrical Carbocyanines (X-XIV, Table 1). These compounds were synthesized by the condensation of 0.001 mole of V or VI with 0.002 mole of ethyl orthoformate, ethyl orthoacetate, or ethyl orthopropionate in 3 ml of pyridine at 125° for 30 min.

Unsymmetrical Carbocyanines (XV-XX, Table 1). These compounds were obtained by the reaction of 0.001 mole of quaternary salt IV with 1-ethyl-2-(β-anilinovinyl)naphtho[1,2-d]thiazolium tosylate, 1-methyl- or 1-ethyl-2-(β-methylmercaptopropenyl or butenyl)naphtho[1,2-d]thiazolium methane (or ethane) sulfonate, as well as with the corresponding benzothiazolium salts, respectively, in 2 ml of alcohol or acetic anhydride in the presence of 0.002 mole of triethylamine at 100° for 10 min.

Dimethylidynemerocyanines (XXI and XXII, Table 1). These compounds were synthesized by heating a mixture of 0.001 mole of VI and 0.001 mole of 5-acetanilidomethylene-3-ethyl- or -3-butylrhodanine in 2 ml of alcohol in the presence of 0.002 mole of triethylamine.

Dimerocyanine XXIII and Rhodacyanines XXIV-XXVI (Table 1). These dyes were obtained by heating 0.001 mole of XXI or XXII with 0.002 mole of dimethyl sulfate at 125° for 15 min and condensation of the products with 0.001 mole of 3-butylrhodanine and also by heating 2-methyl-3-ethyl-4,5-diphenylthiazolium ethanesulfonate and VI, respectively, in 3 ml of pyridine at 125° for 10-45 min.

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