POLYMETHINE DYES FROM ISOMERIC 2-METHYLTHIONAPHTHENOTHIAZOLES

IV. Derivatives of Thieno[2, 3-g]benzothiazole as Dyes*

Z. I. Moskalenko and M. A. Al'perovich

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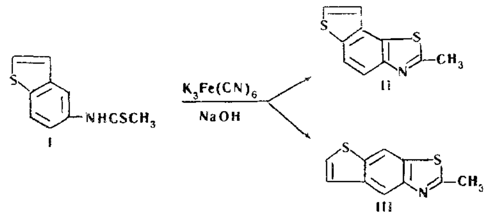
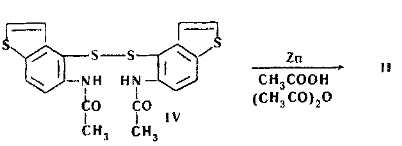
The structure of 2-methylthieno[2, 3-g]benzothiazole, previously obtained by potassium ferricyanide oxidation of 5-thioacetylaminothionaphthene in alkaline solution, is proved. A synthesis of this base is effected by heating 5, 5'-diacetylamino-4, 4'-dithionaphthenyldisulfide with zinc dust in acetic acid—acetic anhydride. Quino-(2)monomethyl-, carbo-, mero-, dimero-, and thiocyanato dyes are obtained, as well as styryl dyes containing a thieno[2, 3-g]benzothiazole group, and their colors are investigated.

Methylthieno[2, 3-g]benzothiazole and some cyanine dyes derived from it have previously been described in the patent literature [2]. 2-Methylthieno[2, 3-g]benzothiazole was prepared by oxidizing 5-thioacetylaminothionaphthene (I) with potassium ferricyanide in alkaline solution. That might be expected to give two isomeric compounds II and III.



The authors of the patent obtained only one base by the reaction, and did not prove its structure.

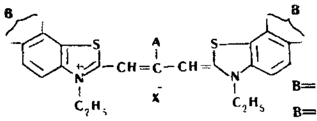
We have repeated the synthesis of the base described in the patent [2]. It led to isolation of a compound melting point 85°–86° C. To show the structure of this compound, 2-methylthieno[2, 3-g]benzothiazole (II) was synthesized by the equation:



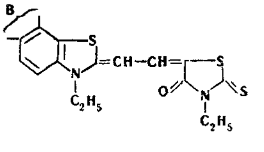
Base II obtained in that way gave an undepressed mixed melting point with the substance obtained by oxidizing 5-thioacetylaminothionaphthene I with potassium ferricyanide in alkaline solution, which results in thiazole ring closure at position 4 of the thionaphthene ring.

Treatment of the benzothiazole II with alkylating agents gave quaternary salts, from which monomethine-2-quino, carbo-, mero-, dimer-, and rhodacyanines, as well as styryl dyes, were synthesized by the usual means.

Positions of absorption maxima of symmetric carbocyanines, dimethinemerocyanines, and thieno-[2, 3-g]benzothiazole derivatives are given below and also, for comparison, those of the corresponding dyes containing a benzothiazole group. A SF-2M spectrophotometer was used to obtain the absorption spectra curves of ethanol solutions of the dyes prepared.



	λ_{max}, mμ A=H	 A=CH₃	 A=C₂H₅
B=H	558[3]	543[4]	547[3]
B=Thieno(2, 3)	584	566	571



	λ_{max}, mμ	Hypsochromic shift, mμ
B=H	524[5]	26[5]
B=Thieno(2, 3)	537	25

On passing from dyes with a benzothiazole group to the corresponding thieno[2, 3-g]benzothiazole derivative, a considerable bathochromic shift of the absorption maximum is observed. This kind of relationship is also found with other classes of dyes containing the thieno[2, 3-g]benzothiazole group.

Comparisons of hypsochromic shifts of absorption maxima of dimethinemerocyanines derived from thieno[2, 3-g]benzothiazole and benzothiazole, calculated on the absorption maxima of the corresponding oxazine (λ_{max} 540 nm [5]) and cyanine dyes, make it possible to infer that the basicities of the thieno-[2, 3-g]benzothiazole and benzothiazole groups are quite close to one another.

EXPERIMENTAL

5-Acetylaminothionaphthene [5] was prepared by acetylating the tin double salt of 5-aminothionaphthene hydrochloride. 2 ml Ac_2O in 3 ml dry ether was added to a vigorously stirred suspension of 3 g (0.007 mole) tin double salt of 5-aminothionaphthene in 10 ml water at 0°–2° C. Then a solution of 3.4 g (0.085 mole) NaOH in 4 ml water was gradually added. The whole was stirred for 30 min, then left for 1 hr. The precipitate was filtered off, washed with water, and dried. Yield 1.15 g (90%), mp 96°–98° C, colorless needles (ex EtOH), mp 107° C (the literature [6] gives mp 106° C).

5-Thioacetylaminothionaphthene (I). A mixture of 1.9 g (0.01 mole) 5-acetylaminothionaphthene and 1.2 g (0.006 mole) P_2S_5 was gradually added to 25 ml stirred, boiling dry benzene, then the mixture was refluxed for 2 hr. After cooling, the benzene layer was poured off and the residue in the flask boiled with 100 ml dry benzene. The combined benzene solutions were extracted with 5% aqueous NaOH, the alkaline solution neutralized with 50% acetic acid and made slighly acid. The precipitate was filtered off, washed with water, and dried. Yield 1.3 g (61.9%), mp 126°–127° C. Colorless needles

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*For Part III see [1]

Dyes Derived from Thieno[2, 3-g]benzothiazole

Compound	Name	Appearance and ml EtOH taken per g of dye for recrystallization	Mp, °C (decomp)	λ_{max}, nm	Formula		Calculated	Yield, %
V	2-p-Dimethylaminostyryl-6, 7-(thieno-2', 3')benzothiazole ethylethyl sulfate	Violet needles 100	263—264	534	$C_{23}H_{26}N_2O_4S_3$	5.82 5.96	5.71	98.9
VI	3, 1'-Diethyl-6, 7-(thieno-2", 3")quino-2'-thiacyanine iodide	Orange needles 400	273—274	498	$C_{23}H_{21}IN_2S_2$	5.45 5.23	5.42	69.2
VII	3, 1'-Diethyl-6'-methyl-6, 7-(thieno-2", 3")quino-2'-thiacyanine iodide	Orange needles 500	276—277	502	$C_{24}H_{23}IN_2S_2$	5.11 5.23	5,28	76,9
VIII	3, 1'-Diethyl-6'-methoxy-6, 7-(thieno-2", 3")quino-2'-thiacyanine iodide	Orange needles 800	283—284	508	$C_{24}H_{23}IN_2OS_2$	4.93 5.00	5.13	81.4
IX	3, 3'-Diethyl-6, 7, 6', 7'-di(thieno-2", 3")-thiacarbocyanine bromide	Dark green prisms 200	190—191	584 578[2]	$C_{25}H_{21}BrN_2S$	4.74 4.75	5.02	82.1
X	3, 3'-Diethyl-9-methyl-6, 7, 6', 7'-di-(thieno-2", 3")thiacarbocyanine bromide	Green needles 180	218—219	566	$C_{26}H_{23}BrN_2S_4$	4.79 4.83	4.89	48.6
XI	3, 3'-Triethyl-6, 7, 6', 7'-di(thieno-2", 3")thiacarbocyanine bromide	Green needles 150	248—249	571	$C_{27}H_{25}BrN_2S_4$	4.78 4.97	4.78	44.8
XII	3-Ethyl-5-[3'-ethyl-6, 7-(thieno-2", 3")-benzothiazolinylidene-2'-ethylidene]-thiazolidine-2-thion-4-one	Reddish-violet needles 2500	266—267	537	$C_{18}H_{16}N_2OS_4$	6.88 6.92	4.93	75.0
XIII	3, 3'-Diethyl-4-keto-4', 5'-diphenyl-5-[3"-ethyl-6", 7"-(thieno-2‴, 3‴)benzothaizolinylidene-2"-ethylidene] thiazolinothiazolocyanine ethyl sulfate	Green needles with metallic iridescence 150	269—270	607	$C_{38}H_{37}N_3O_5S_5$	5.09 5.10	5.39	65.5
XIV	2(3'-Carbethoxyamylthiazolidine-2'-thion-4'-on-5'-ylidene)-3-ethyl-5-[3"-ethyl-6", 7"-(thieno-2", 3")benzothiazolinylidene-2"-ethylidene]thiazolidin-4-one	Green needles 6000	247—248	585	$C_{29}H_{31}N_3O_4S_5$	6.39 6.45	6.50	62.5

(ex 50% EtOH), mp 128°–129° C (the patent [2] does not give the mp of 5-thioacetylaminothionaphthene). Found: N 6. 46; 6. 42%, calculated for $C_{10}H_9NS_2$: N 6. 46%.

5, 5'-Diacetylamino-4, 4'-dithionaphthenyl disulfide (IV). 2.4 g (0.01 mole) 5-Acetylamino-4-nitrothionaphthene in 45 ml 50% H_2SO_4 was added to a solution of 2.7 g (0.01 mole) Na sulfide, 0.36 g (0. 01 mole) S, and 0. 44 g (0. 01 mole) NaOH in 3 ml water at 0° C. Then 0. 75 g (0. 01 mole) $NaNO_2$ in 3 ml water was added at the same temperature, the mixture left for 2 hr at room temperature, the solid filtered off, washed with water, and dried. Yield 1. 5 g (38. 2%), mp 182°–185° C. Pale yellow needles (ex EtOH), mp 190°–191° C. Found: S 28. 53; 28. 41%, calculated for $C_{20}H_{16}N_2O_2S_4$: S 28.24%.

2-Methylthieno[2, 3-g]benzothiazole (II). A solution of 5 g (0. 025 mole 5-thioacetylaminothionaphthene in 300 ml 5% aqueous NaOH was added to 40 ml of vigorously stirred 20% potassium ferricyanide solution. Then the reaction mixture was stirred for 2 hr at 0° C and for 3 hr at room temperature, the precipitate filtered off, washed with water, and dried. Mass 4. 9 g, mp 68°–69° C. Steam distillation followed by recrystallization from petrol ether gave 4 g (80. 8%), colorless plates, mp 85°–86° C. Found: N 6. 58; 6. 74%, calculated for $C_{10}H_7NS_2$: N 6. 83%.

b) 1.32 g (0.03 mole) 5, 5'-Diacetylamino-4, 4'-dithionaphthenyl-disulfide, 2 g Zn dust, 3 ml Ac_2O, and 30 ml AcOH were refluxed together for 3 hr. Then the products were diluted with 60 ml water, and the whole made alkaline with 10% NaOH. The precipitate was filtered off, washed with water, and dried, yield 0. 3 g (50. 0%), mp 85°–86° C (ex petrol ether). Undepressed mixed mp with the base prepared by method (a).

Picrate: yellowish green needles, mp 182°–183° C (ex EtOH). Found: N 13. 11; 13. 16%, calculated for $C_{10}H_7NS_2 \cdot C_6H_3N_3O_7$: N 12. 90%.

2-Methylthieno[2, 3-g]benzothiazole ethiodide. 0. 6 g (0. 003 mole) 2-Methylthieno[2, 3-g]benzothiazole and 0.96 g (0.0007 mole) EtI were heated together for 15 hr on a boiling water bath. The product was washed with dry acetone, yield 0. 45 g (42. 8%), mp 227°–228° C (decomp). Colorless prisms (ex EtOH), mp 236°–237° C (decomp). Found: N 3. 69; 3. 75%, calculated for $C_{12}H_{12}INS_2$: N 3. 87%.

Dyes (Table 3). The styryl dye V was prepared by heating 0. 001 mole 2-methylthieno[2, 3-g]benzothiazole with 0. 001 mole diethyl sulfate at 135° C for 1-1/2 hr, then condensing the resultant quaternary salt with 0. 001 mole p-dimethylaminobenzaldehyde in 2 ml Ac_2O by heating for 30 min at 120° C. The monomethinecyanines **VI–VIII** were synthesized by heating together on a boiling water bath for 10–15 min, 0. 001 mole of the diethyl sulfate of the base and 0. 001 mole 2-ethylmercaptoquinoline ethiodide, or its 6-methyl- or 6-methoxy- derivative, in 2 ml EtOH in the presence of 0. 002 mole Et_3N. Carbocyanines **IX–XI** were prepared by condensing 0. 001 mole 2-methylthieno[2, 3-g]benzothiazole ethylethyl sulfate with 0. 002 mole ethyl orthoformate, orthoacetate, or orthopropionate, respectively, in 3 ml dry pyridine at 135° C for 1–1-1/2 hr. The dimethinemerocyanine **XII** was synthesized by heating a mixture of 0. 001 mole base ethylethyl sulfate with 0. 001 mole 5-acetanilinomethylene-3-ethylrhodanine in 2 ml absolute EtOH, in the presence of 0. 002 mole Et_3N, on a boiling water bath for 10 min. The rhodacyanine **XIII** and dimerocyanine **XIV** were obtained by heating 0. 001 dimethinemerocyanine **XIV** with 0. 002 mole Me_2SO_4 at 125° C for 15 min, then reacting the resultant quaternary salt with 0. 001 mole 2-methyl-4, 5-diphenylthiazole ethylethyl sulfate or 3-ε-carbethoxyaminorhodanine ethylethyl sulfate respectively, in 3 ml dry pyridine at 125°–130° C for 45 min. All the dyes synthesized were purified by recrystallizing from EtOH.

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