SOME MEROCYANINE DYES DERIVED FROM 3-ETHYL-4-THIOXOTHIAZOLIDINE-2-ONE

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A number of dimethine and γ-alkoxytetramethine merocyanines derived from 3-ethyl-4-thioxothiazolidin-2-one have been synthesized by the condensation of 5-anilinomethylene-3-ethyl-4-thioxothiazolidin-2-one, obtained by the action of phosphorus pentasulfide on the corresponding 2,4-dione, with quaternary salts of some 2-methyl- and 2-β-alkoxypropenyl-substituted heterocyclic bases. The color and photographic properties of the dyes obtained have been studied.

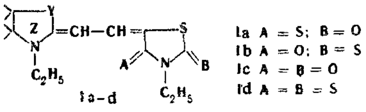
Merocyanines derived from 3-alkyl- or 3-aryl-4-thioxothiazolidin-2-ones (**Ia**), unlike the isomeric dyes with 3-alkyl- or 3-aryl-2-thioxothiazolidin-4-one residues (**Ib**) [1] have been little studied so far. In 1954, Nys [2, 3] proposed a method for obtaining the dimethine merocyanines **Ia** by the action of phosphorus pentasulfide on the corresponding dyes derived from 3-alkyl- and 3-arylthiazolidine-2,4-diones (**Ic**) and described some of their properties. According to these papers [2, 3], the reaction takes place in boiling pyridine, requiring 60 hr in some cases, and is sometimes accompanied by the formation of derivatives of 3-alkyl- or 3-arylthiazolidine-2,4-dithiones (**Id**).

Table 1

Absorption Maxima of the Dimethine Merocyanines **Ia** and b, nm

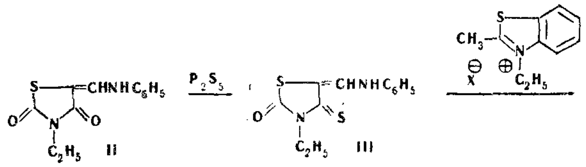
Compound	Z in formulas I	Type of merocyanine	
		Ia	Ib [11]
1	3,3-Dimethylindolenine	550*	503
2	Benzoselenazole	578	524
3	Benzothiazole	576**	524***
4	5-Methyl-1,3,4-thiadiazole	558	514
5	4,5-Diphenylthiazole	591	553^{12}
6	2-Quinoline	604	565

*N-Methyl derivative
**570 nm [3]
***527 nm [3]

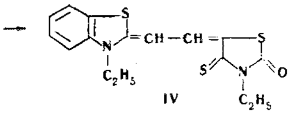


Ia–d

We decided to attempt to obtain the dimethine merocyanines **Ia** in a simpler manner, starting from the readily available [4, 5] 5-anilinomethylene-3-ethylthiazolidine-2,4-dione (**II**).



II III



IV

It was found that **II** reacts readily with phosphorus pentasulfide in pyridine at 100° C and the reaction product differs from 5-anilinomethylene-3-ethylrhodanine. Even at the ordinary temperature, it condenses with 2-methylbenzothiazole methiodide to form the known 3-ethyl-5-(3'-ethyl-2'-benzothiazolinylideneethylidene)-4-thioxothiazolidin-2-one (**IV**) [2, 3]. It is evident that in the action of phosphorus pentasulfide on **II**, as in the case of the corresponding dimethine merocyanines [2, 3], the replacement of the carbonyl oxygen in position 4 by an atom of sulfur takes place with the formation of a 4-thioxothiazolidin-2-one derivative with the structure **III**. The synthesis of dimethine merocyanines with 3,3-dimethylindolenine, benzoselenazole, 5-methyl-1,3,4-thiadiazole, 4,5-diphenylthiazole, and 2-quinoline residues was carried out similarly.

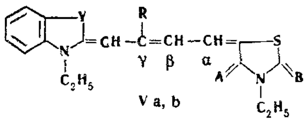
In this way we have been able to develop a new, considerably more convenient, general method for obtaining dimethine merocyanines derived from 3-ethyl-4-thioxothiazolidin-2-one [6], and it was found that the dyes separated from the reaction mixture in the practically pure state.

Table 2

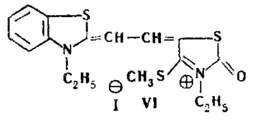
Absorption Maxima of the Tetramethine Merocyanines **Va** and **b**, nm

Compound	Formulas V		Type of dye	
	V	R	Va	Vb [14]
1	S	OCH_3	634	584
2	S	OC_2H_5	635	584
3	Se	OCH_3	637	585

Furthermore, by using the considerable mobility of the hydrogens of the methyl group in the quaternary salts of 2-β-alkoxypropenyl-substituted heterocyclic bases (cf. [7–9]), by their condensation with **III** we have synthesized some previously unknown γ-alkoxy-substituted tetramethine merocyanines derived from 3-ethyl-4-thioxothiazolidin-2-one (**Va**).



V a, b



I VI

Table 3

Characteristics of the Merocyanine Dyes

Type of compound	Quaternay salt used*	Mp, °C	External form	Empirical formula	Found, %		Calculated, %		Yield	
					N	S	N	S	г	%
Ia	QS-1	209—210	Lustrous blue prisms	$C_{18}H_{20}N_2OS_2$	8.17 8.19	18.63 18.59	8.16	18.61	0.18	52.5
Ia	QS-2	260—261	Golden green prisms	$C_{16}H_{16}N_2OS_2Se$	7.07 7.29	—	7.08		0.25	63.0
Ia	QS-2	258—259[2] (264—265[3])	Golden green prisms	$C_{16}H_{16}N_2OS_3$	7.99 7.89	27.73 27.80	8.04	27.60	0.21	60.0[a]
Ia	QS-4	249—250	Golden green needles	$C_{12}H_{15}N_3OS_3$	13.45 13.21	—	13.41		0.17	57.0
Ia	QS-5	224—225	Golden green prisms	$C_{24}H_{22}N_2OS_3$	6.18 6.09	—	6.21		0.22	49.0
Ia	QS-6	244—245 (244[2])	Golden green prisms	$C_{18}H_{18}N_2OS_3$	7.97 7.93	18.65 18.81	8.18	18.72	0.21	61.5
Va	QS-1	236—237	Gray-blue needles	$C_{19}H_{20}N_2O_2S_3$	6.98 6.85	23.80 23.69	6.92	23.78	0.24	59.9[b]
Va	QS-2	201—202	Golden green needles	$C_{20}H_{22}N_2O_2S_3$	6.75 6.90		6.69		0.26	62.0
Va	QS-3	220—221	Golden green needles	$C_{19}H_{20}N_2O_2S_2Se$	6.12 6.12		6.20		0.22	50.0[c]

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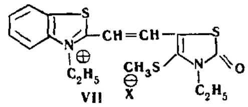
[a] At 15-20° C with a time of 20 hr, the yield was also 60%. [b] 30 min in the boiling water bath. [c] 20 hr at 15-20° C.

*or Quaternay salt component.


VII

Y=S, Se; R=OCH_3, OC_2H_5,
Va A=S; B=O
Vb A=O; B=S
X=SO_4CH_3, I, ClO_4

When **IV** was heated for a long time with methyl iodide and methanol in a sealed tube, the salt-like product of methylation at the thione sulfur [3, 10] was obtained, and to this, the structure of 5-(3'-ethyl-2'-benzothiazolinylideneethylidene)-4-methylthiothiazolidin-2-one methiodide (**VI**) was assigned. This quaternary salt, the structure of which, in view of the low basicity of the nitrogen atom of the thiazolinone nucleus, is obviously close to that of formula **VII** (X = I), we easily obtained by the action of the dimethyl sulfate on the dye **IV** with subsequent treatment of the product formed (**VII**, X = SO_4CH_3) with potassium iodide in aqueous methanolic solution.

The absorption spectra of the dyes obtained, and also of compounds **III** and **VII**, were measured on an SF-10 spectrophotometer in 1×10^{-4}/M solutions in ethanol. Table 1 gives the absorption maxima of the dimethine merocyanines derived from 3-methyl-4-thioxothiazolidin-2-one (**Ia**), and also, for comparison, those of the corresponding isomeric dyes **Ib**.

As can be seen from these figures, the dimethine merocyanines **Ia** have a considerably deeper coloration (by 38–54 nm) than the corresponding isomeric dyes **Ib**, which confirms the observations made previously [3] on the basis of the same merocyanines with a benzothiazole residue and also on the basis of derivatives of 4-thioxoimidazolidin-2-one and the corresponding 2-thioxo-4-one compound [13]. Analogous characteristics have been found in a number of γ-alkoxytetramethine merocyanines (**Va** and **b**)(Table 2).

The merocyanines obtained, with the exception of the dyes with 5-methyl-1,3,4-thiadiazole and 4,5-diphenylthiazole residues proved to be very weak sensitizers of silver halide emulsions (cf. [2,3]).

EXPERIMENTAL*

5-Anilinomethylene-3-ethylthiazolidene-2,4-dione (II) was obtained by a published method [4, 5].

5-Anilinomethylene-3-ethyl-4-thioxothiazolidin-2-one (III). At 90–100° C, 2.47 g (0.02 mole) of **II** was dissolved in 50 ml of anhydrous pyridine and gradually, with stirring, 4.4 g (0.02 mole) of finely ground phosphorus pentasulfide was added, and then the mixture was stirred at the same temperature for 3 hr and was left overnight. The solution was decanted off and the sludge was washed 2–3 times with pyridine. After the pyridine had been distilled off in vacuum, the residue was mixed with 300 ml of water, and the precipitate that separated was filtered off, washed with water and dilute (1 : 1) ethanol, carefully triturated with 10 ml of 50% ethanol, filtered off again, and washed with ethanol and petroleum ether (bp 60–80° C). Yield 1.87 g (71%), mp 136–139° C. For purification, the product was crystallized from a mixture of benzene and petroleum ether (bp 60–80° C) (1 : 1) and then from petroleum ether (bp 85–95° C). Yellow prisms with mp 150–151° C. λ_{max} 437 nm. Found, %: N 10.59, 10.61. Calculated for $C_{12}H_{12}N_2OS_2$, %: N 10.60.

Synthesis of the dyes (Table 3). The merocyanines **Ia** and **Va** were obtained from 0.26 g of **III** in a mixture of 3 ml of pyridine, 0.4 ml of acetic anhydride, and 0.2 ml of triethylamine and the appropriate quaternary salt (QS) with heating in the boiling water bath for 1 hr. In Table 3, the following symbols are used for the initial QSs: 2,3,3-trimethylindolenine ethiodide—QS-1; 2-methylbenzoselenazole ethiodide—QS-2; 2-methylbenzothiazole ethiodide—QS-3; 2,5-dimethyl-1,3,4-thiadiazole ethyl tosylate derivative—QS-4; 2-methyl-4,5-diphenylthiazole ethiodide—QS-5; quinaldine ethiodide—QS-6; 2-β-methoxypropylbenzothiazole ethyl methyl sulfate derivative—QS-7; 2-β-ethoxypropenylbenzothiazole ethyl ethosulfate—QS-8; 2-β-methoxypropenylbenzoselenazole ethyl methyl sulfate derivative—QS-9.

All the dyes were purified by crystallization from ethylene glycol monoethyl ether.

3-Ethyl-2-[β-(3'-ethyl-4'-ethylthio-2'-thiazolinon-5'-yl)vinyl]-benzothiazolium methyl sulfate (VII; X = SO_4CH_3). A solution of 0.35 g (0.001 mole) of 3-ethyl-5-(3'-ethyl-2'-benzothiazolinylidene-ethylidene)-4-thioxothiazolidin-2-one (**IV**) in 3 ml of anhydrous xylene was treated with 0.42 ml (0.004 mole) of dimethyl sulfate and the mixture was heated for 1.5 hr at 110–120° C (bath temperature). The red color of the solution gradually changed to light orange, and an oil collected on the bottom of the flask. On dilution with absolute ether and trituration, crystallization set in. The solid matter was filtered off and washed with absolute ether. Yield 0.42 g (90%). Orange crystals with mp 248–249° C. λ_{max} 443 nm. The substance was used without further purification for the preparation of the ethiodide and ethyl perchlorate derivatives.

Iodide VII (X = I). A hot solution of 0.48 g (0.001 mole) of the methyl sulfate **VII** in 12 ml of absolute methanol was mixed with an equal volume of 15% aqueous potassium iodide. The crystalline precipitate that deposited on cooling was filtered off and washed with water, ethanol, and ether. Yield 0.39 g (80%), mp 220–223° C. Brown prisms from absolute methanol, mp 229–230° C [3, 10], λ_{max} 443 (440 [3]) nm. Found, %: I 25.91; 26.05. Calculated for $C_{17}H_{19}IN_2OS_3$, %: I 25.88.

Perchlorate VII (X = ClO_4). In a similar manner to the preceding experiment, 6 ml of a 15% aqueous solution of sodium perchlorate was added to a solution of 0.24 g (0.0005 mole) of the methyl sulfate **VII** in 6 ml of absolute methanol. Yield 0.20 g (86%), mp 245–246° C. After crystallization from absolute ethanol–orange crystals with the same melting point. Found, %: Cl 7.54, 7.50. Calculated for $C_{17}H_{19}ClN_2O_5S_3$, %: Cl 7.66.

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REFERENCES

1. F. M. Hamer, The Cyanine Dyes and Related Compounds, New York, London, 1964.

2. J. M. Nys and T. H. Ghys; British patent 788901.

3. J. M. Nys, Compte rendu du XXVII Congres Intern. de chimic. industr., Bruxelles, 1954.

4. Z. P. Sytnik, I. I. Levkoev, M. V. Deichmeister, and L. D. Zhilina, ZhOKh, **22**, 1228, 1952.

5. Z. P. Sytnik, A. A. Abdullaev, L. D. Zhilina, and S. S. Kagan, in the collection Kinotekhnika, **4**, 81, 1963.

6. S. A. Kheifets, N. N. Sveshnikov, and A. V. Butuzova, USSR patent 179616; Byull. izobr., no. 5, 1966.

7. N. N. Sveshnikov, I. I. Levkoev, A. F. Bompe, and B. S. Portnaya, DAN, **88**, 281, 1953.

8. S. A. Kheifets and N. N. Sveshnikov, DAN, **163**, 1177, 1965.

9. S. A. Kheifets and N. N. Sveshnikov, KhGS [Chemistry of Heterocyclic Compounds], 1040, 1967.

10. J. M. Nys, Gevaert Photo-Production N. V., British patent 789077.

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*With the participation of A. V. Butuzova.

11. M. V. Deichmeister, E. P. Sytnik, and E. B. Lifshits, ZhOKh, **22**, 166, 1952.
12. M. S. Lyubich, Z. P. Sytnik, R. V. Timofeeva, and M. A. Al'perovich, in collection: Kinotekhnika, **4**, 64, 1963.
13. E. A. Shott-L'vova, Ya. K. Syrkin, I. I. Levkoev, and M. V. Deichmeister, DAN, **145**, 1321, 1962.
14. V. G. Zhiryakov, Thesis [in Russian], Moscow, 1952.

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