THIAZOLOCYANINES.

XIX.* MONO- AND DIQUATERNARY N-PYRIDLTHIAZOLIUM SALTS AND NULLOMETHYLIDYNEMEROCYANINES BASED ON THEM

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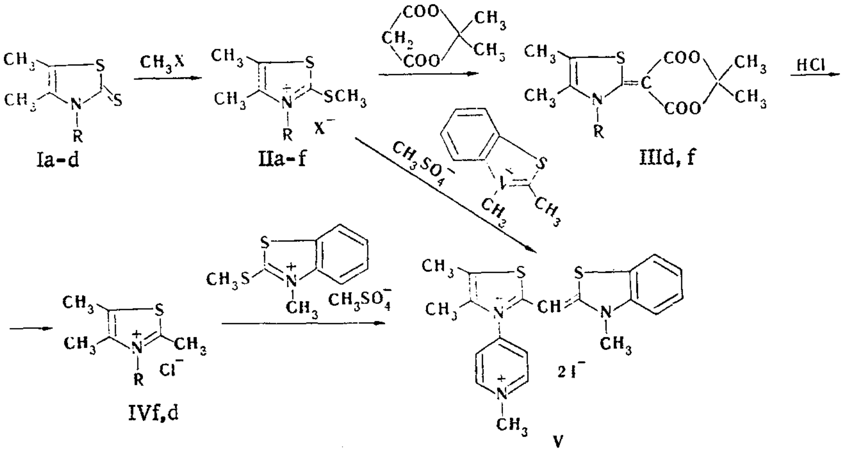
Mono- and diquaternary thiazolium salts with an active methyl or methylthio group containing pyridyl residues attached to the nitrogen atom were synthesized, and nullomethylidynemerocyanines based on them were prepared. The UV spectra of the dyes are discussed.

We have previously shown [2] that alkylation occurs only at the exocyclic sulfur atom (IIa,b) in the case of thiazoline-2-thiones containing 2-hetaryl residues attached to the nitrogen atoms (Ia,b).



I—IV a R=2-thiazolyl; b R=2-pyridyl; c R=3-pyridyl; d R=4-pyridyl, e R=3-pyridyl methiodide; f R=4-pyridyl methiodide

We set out to synthesize thiazolium salts with 3- and 4-pyridyl residues attached to the nitrogen atom of the thiazole ring and cyanine dyes based on them. In the process we observed that thiones with these residues (Ic,d), in which the steric hindrance to alkylation of the pyridine ring is absent, react with methyl iodide at 20°C to give, in addition to monoquaternary salts (IIc,d), diquaternary salts (IIe,f); these transformations take place more readily in the case of the isomer with a 4-pyridyl residue.

The methylthio group in salts IIf and IId was replaced by a methyl group by means of isopropylidene malonate — Meldrum acid — which has advantages over diethyl malonate and other compounds used for similar purposes [3]. The structure of salts IIf, and IVf was confirmed by the identical character of monomethylidynecyanine V obtained by alternative synthesis.

Two bands — shortwave band (λ_{max} 415 nm), close to the absorption maximum (437 nm) of the nullomethylidynecyanine obtained from monoquaternary salt IId, and a less intense long-wave band (λ_{max} 512 nm) associated with the development of a new chromophore arising as a

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*See [1] for communication XVIII.

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TABLE 1. Absorption Maxima of Dye VI in Solvents with Different Polarities

Solvent	$\lambda_{1\max}$, nm	$\lambda_{2\max}$, nm
Ethanol + benzene	415	524
Ethanol	415	512
Dimethylformamide	415	494
Water	417	486

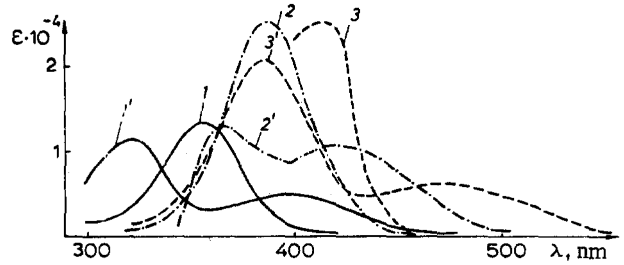
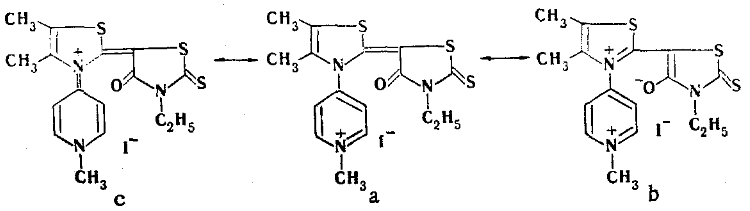


Fig. 1. Absorption spectra of ethanol solutions of dyes IIIf (1), XV (2), and XIV (3), obtained from the diquaternary salt, and of the corresponding dyes (1', 2', and 3') obtained from the monoquaternary salt.

result of intramolecular transfer of electrons from the merocyanine portion of the molecule (as an electron donor) to the pyridinium residue (as an electron acceptor) — were observed in the absorption spectrum of an alcohol solution of nullomethylidynemerocyanine VI obtained from diquaternary salt IIf and N-ethylrhodanine. In fact, nullomethylidynemerocyanine VI, in addition to the nonpolar (VIa) and dipolar (VIb) structures customary for merocyanines, can be represented by a limiting structure (VIc).

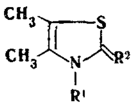


VI

The absorption maxima of dye VI in solvents with different polarities confirm this assumption (Table 1). The long-wave band displays negative solvatochromism, whereas the absorption maximum of the shortwave band remains almost unchanged as the solvent is changed also for the dyes from the monoquaternary salts. The form of the long-wave absorption band and its solvatochromism recall the behavior of the absorption bands associated with charge transfer in derivatives of pyridinium salts [4].

The two chromophores in the molecule evidently interact with one another, since we observe separation of the absorption maxima [5]: if the absorption maximum at 437 nm for the dye from the monoquaternary salt is adopted as the "parent" maximum its shift to the shortwave region on passing to the dye from the diquaternary salt is evidently due to interaction with the other longer-wave chromophore.

We also subjected both the mono- and diquaternary thiazolium salts to condensation with other ketomethylene compounds with various structures: with 3-butyloxazolidine-2-thion-4-one, 1,3-indanedione, and Meldrum acid. The appearance of two absorption maxima (Fig. 1) was observed in all cases in the absorption spectra of the nullomethylidynemerocyanines obtained

TABLE 2. Nullomethylidynemerocyanines 

Compound	R¹	R²	Conds. of reaction		mp, °C	Found, %		Empirical formula	Calc., %		UV spectrum, λmax, nm, in ethanol (log ε)	Yield, %
			temp., °C	time, h		N	S		N	S		
VI'[a]	4-Pyridyl	R[b]	20	3	292c	12,0	27,5	$C_{15}H_{15}N_3OS_3$	12,0	27,5	437 (4,60)	14
XIV'	4-Pyridyl	O	80	3/4	190d	11,5	17,6	$C_{17}H_{19}N_3O_2S_2$	11,6	17,7	417 (4,43)	36
XV'	" "	I	20	1	238e	8,2	9,4	$C_{19}H_{14}N_2O_2S$	8,3	9,5	388 (4,41)	19
III[d]	" "	M	20	5	228f	8,5	9,6	$C_{16}H_{16}N_2O_4S$	8,4	9,6	357 (4,13)	60
XVI'	3-Pyridyl	R	80	3/4	223e	11,8	27,5	$C_{15}H_{15}N_3OS_3$	12,0	27,5	437 (4,57)	30
VI	4-Pyridyl methiodide	R	80	3/4	259e	I 25,7	19,5	$C_{16}H_{18}IN_3OS_3$	I 25,9	19,5	415 (4,40) 512 (3,82)	40
XIV	4-Pyridyl methiodide	O	20	1	223g	I 25,6	12,9	$C_{18}H_{22}IN_3O_2S_2$	I 25,2	12,7	385 (4,32) 472 (3,79)	20
XV	" "	I	80	3/4	252e	I 26,5	6,6	$C_{20}H_{17}IN_2O_2S$	I 26,7	6,7	366 (4,11) 423 (4,03)	46
IIIe	" "	M	20	20	220h	5,9	I 26,6	$C_{17}H_{19}IN_2O_4S$	5,9	I 26,8	322 (4,06) 400 (3,69)	52
XVI	3-Pyridyl methylperchlorate	R	80	3/4	271h	9,0	20,7	$C_{16}H_{18}ClN_3O_5S$	9,0	20,7	435 (4,46)	24

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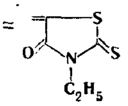
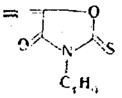
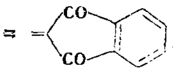
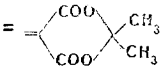
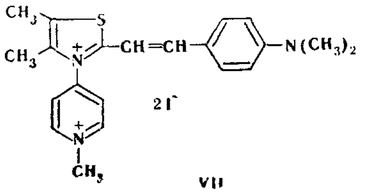
[a] Dyes obtained from the monoquaternary salt are designated by apostrophes.

[b] R =  O =  I =  M = 

[c] From ethanol–nitromethane (1:2). [d] From isopropyl alcohol. [e] From ethanol. [f] From absolute ethanol. [g] From isopropyl alcohol–ethanol. [h] From methanol.

from the diquaternary salt with a 4-pyridyl residue, and the shortwave band is shifted to the shorter-wave region as compared with the dyes from the monoquaternary salt (Table 2). The long-wave band, in conformity with its interpretation as a band with electron transfer from the merocyanine portion of the dye to the pyridinium residue, is shifted to the long-wave side with decreasing acidity of the ketomethylene residue.

The structure of dye XV was confirmed by comparison with the merocyanine obtained by methylation of dye XV' from the monoquaternary salt. A new maximum appeared in the spectrum of the dye formed in this case, and the absorption curves of alcohol solutions of the two dyes coincided. The dyes have identical melting points. The second absorption band was not observed in the spectrum of the dye from the diquaternary salt with a 3-pyridyl residue (XVI), since one cannot imagine extension of the conjugation chain to the nitrogen atom of the 3-pyridyl residue; the absorption maximum of this dye is almost the same as that of base XVI'. Styryl VII was synthesized in addition to monomethylidynecyanine V from diquaternary salt IVf. The corresponding dyes were synthesized from monoquaternary salt IVd. In the spectrum of dye V splitting of the absorption band is only projected (inflection), whereas it is absent in the spectrum of styryl VII, probably because of the very weak electron-donor character of the p-dimethylaminophenyl group. The presence of a saltlike pyridine residue in the styryl dye affects only the decrease in the basicity of the thiazole ring, as a consequence of which the deviation decreases, and dye VII acquires a relatively deep color as compared with the styryl obtained from the monoquaternary salt.



VII

EXPERIMENTAL

The absorption spectra of ethanol solutions of the compounds were recorded with SF-4a and SF-10 spectrophotometers.

α-Acetylethyl 3-(4-Pyridyl)dithiocarbamate (VIII). A 6.04-g (0.04 mole) sample of 3-bromo-2-butanone was added to a solution of 10.84 g (0.04 mole) of triethylammonium 3-(4-pyridyl)dithiocarbamate [6] in 80 ml of water. The exothermic reaction produced an oil, which solidified on standing. Workup gave 8.1 g (84%) of a product with mp 134-135° (from ether). Found: N 11.7; S 26.8%. $C_{10}H_{12}N_2OS_2$. Calculated N 11.7; S 26.7%. Its isomer (IX) with a 3-pyridyl residue was similarly obtained and had mp 133° (from ether). Found: N 11.7; S 26.5%. $C_{10}H_{12}N_2OS_2$. Calculated N 11.7 S 26.7%.

3-(4-Pyridyl)-4,5-dimethylthiazoline-2-thione (Id). A mixture of 4.8 g (0.02 mole) of ester VIII and 14 ml of glacial acetic acid was heated at 90° for 2 h, after which it was cooled and poured into 100 ml of water. The solidified precipitate was removed by filtration to give 2.3 g (52%) of a product with mp 132-133° (from ether). Found: N 12.7; S 28.5%. $C_{10}H_{10}N_2S_2$. Calculated N 12.6; S 28.8%. The isomer (Ic) with a 3-pyridyl residue was similarly obtained in 75% yield and had mp 124° (from isopropyl alcohol). Found: N 12.6; S 28.6%. $C_{10}H_{10}N_2S_2$. Calculated: N 12.6; S 28.8%.

2-Methylthio-4,5-dimethyl-3-(4-pyridyl)thiazolium Iodide Methiodide (IIf). A mixture of 0.22 g (1 mmole) of thione Id and 0.2 ml of methyl iodide in 2 ml of dry acetone was allowed to stand for 2 days, after which it was worked up to give 0.3 g (65%) of a product with mp 223° (from ethanol). Found: I 49.7; S 12.6%. $C_{12}H_{16}I_2N_2S_2$. Calculated: I 50.2; S 12.6%. When the reaction was carried out in nitrobenzene, a mixture of IIf and 2-methylthio-3-(4-pyridyl)-4,5-dimethylthiazolium iodide (IId) precipitated. It was extracted with hot acetone, and the extract was filtered to remove the IIf. The extract was then evaporated to a small volume, and ether was added to precipitate IId (28% yield) with mp 212° (from isopropyl alcohol). Found: I 34.9; S 17.6%. $C_{11}H_{13}IN_2S_2$. Calculated: I 34.9; S 17.6%. 2-Ethylthio-3-(4-pyridyl)-4,5-dimethylthiazolium iodide (XI), with mp 192-194° (precipitation from acetone solution by the addition of absolute ether), was similarly obtained. Found: I 33.6%. $C_{12}H_{15}IN_2S_2$. Calculated: I 33.6%. 2-Methylthio-3-(3-pyridyl)-4, dimethylthiazolium iodide (IIc), with mp 120° (from isopropyl alcohol), was obtained in 56% yield from 3-(3-pyridyl)-4,5-dimethylthiazoline-2-thione (Ic) by the method used to prepare IId. Found: I 35.0; S 17.6%. $C_{11}H_{13}IN_2S_2$. Calculated: I 34.9; S 17.6%. The methiodide (IIe) had mp 196-197° (from ethanol). Found: I 50.1; S 12.7%. Calculated: I 50.2; S 12.6%.

2-Methyl-3-(4-pyridyl)-4,5-dimethylthiazolium Perchlorate Perchlorate. A mixture of 0.16 g (0.5 mmole) of IIId and 0.5 ml of concentrated hydrochloric acid was heated at 85-90° for 1 h, after which the acid was evaporated, and the solid residue, which deliquesced readily in the air, was identified as the hydrochloride of IVd, which was used for the preparation of the cyanine dye without further purification. It was identified in the form of the diperchlorate: the hydrochloride of IVd was dissolved in a few drops of 42% perchloric acid, and a few milliliters of dry acetone were added. The resulting precipitate was washed with hot acetone and crystallized twice from absolute ethanol to give a product with mp 213°. Found: Cl 16.9; N 6.9%. $C_{17}H_{13}ClN_2O_4S \cdot HClO_4$. Calculated Cl 17.5; N 6.9%.

2,4,5-Trimethyl-3-(4-pyridyl)thiazolium Iodide Methiodide (IVf). A mixture of 0.98-g (2 mmole) of IIIf and 7 ml of concentrated hydrochloric acid was heated at 85-90° for 1 h, after which the acid was removed in vacuo, and the residue was dissolved in ethanol. A saturated alcohol solution of sodium iodide was added to the solution, and it was worked up to give 0.7 g (73%) of a product with mp 233° (twice from ethanol). Found: I 53.6; S 6.9%. $C_{12}H_{16}I_2N_2S$. Calculated I 53.6; S 6.7%.

2-(p-Dimethylaminostyryl)-3-(4-pyridyl)-4,5-dimethylthiazolium Perchlorate (XII). A mixture of 0.07-g (0.25 mmole) of the hydrochloride of IVd and 0.037 g (0.25 mmole) of p-dimethylaminobenzaldehyde was fused for 30 min, after which the cooled melt was triturated with ether, and the solid material was removed by filtration and washed with chloroform.

The dye was suspended in chloroform, and a few drops of ammonium hydroxide were added. The chloroform solution of the dye was washed with 1 ml of distilled water and dried over magnesium sulfate. The solvent was evaporated, and the dye was precipitated from alcohol solution by the addition of sodium perchlorate. The dye was removed by filtration, washed with boiling alcohol, and dried to give 0.025 g (25%) of a product with mp 252-254° (from ethanol). UV spectrum (in ethanol): λ_{max} 512 nm (log ε 4.55). Found: N 9.6; S 7.3%. $C_{20}H_{22}ClN_3O_4S$. Calculated: N 9.6; S 7.3%.

2-(p-Dimethylaminostryryl)-3-(4-pyridyl)-4,5-dimethylthiazolium Iodide Methiodide (VII). A mixture of 0.24 g (0.5 mmole) of methylthiazole IVf and 0.08 g (0.5 mmole) of p-dimethylaminobenzaldehyde was fused in the presence of a few drops of acetic anhydride at 175-180° for 2 h, after which the cooled melt was triturated with ethanol, and the solid material was removed by filtration to give 0.03 g (10%) of a product with mp 232° [from ethanol—nitromethane (2:1)]. UV spectrum (in nitromethane): λ_{max} 546 nm (log ε 4.55). Found: I 41.9; N 6.8%. $C_{21}H_{25}I_2N_3S$. Calculated: I 42.0; N 6.9%.

3-(4-Pyridyl)-2-(3-ethylbenzothiazolinylidene-2-methylene)-4,5-dimethylthiazolium Iodide (XIII). A 0.24-g (0.8 mmole) sample of 2-methylbenzothiazole ethyltosylate and 0.08 g (0.8 mmole) of triethylamine were added to a solution of 0.31 g (0.8 mmole) of salt XI in 2 ml of absolute ethanol, and the mixture was allowed to stand for 40 min. Workup gave 0.08 g (19%) of a product with mp >250° (from ethanol). UV spectrum (in ethanol): λ_{max} 430 nm (log ε 4.75). Found: I 25.7; S 12.7%. $C_{20}H_{20}IN_3S_2$. Calculated: I 25.7; S 13.0%.

3-(4-Pyridyl)-2-(3-methylbenzothiazolinylidene-2-methylene)-4,5-dimethylthiazolium Iodide Methiodide (V). A) A mixture of 0.12 g (0.25 mmole) of salt IIf, 0.07 g (0.25 mmole) of 2,3-dimethylbenzothiazolium methylsulfate, 0.03 g (0.3 mmole) of triethylamine, and 8 ml of absolute ethanol was heated at 100° for 1 h, after which it was worked up to give 0.08 g (52%) of a product with mp 274° (from nitromethane). UV spectrum (in ethanol): λ_{max} 430 and 460 nm (inflection) (log ε 4.36). Found: I 40.7; S 10.2%. $C_{20}H_{21}I_2N_3S_2$. Calculated: I 40.9; S 10.3%.

B) A 0.15-g (0.5 mmole) sample of 2-methylthio-3-methylbenzothiazolium methylsulfate and 0.05 g (0.5 mmole) of triethylamine were added to 0.24 g (0.5 mmole) of salt IVf in a mixture of 10 ml of absolute ethanol and 5 ml of DMF, and the mixture was heated at 90° for 2 h. Workup gave 0.06 g (20%) of V. No melting-point depression was observed for a mixture of this product with the dye obtained by method A, and the two dyes had the same absorption curve.

Nullomethylidynemerocyanines (Table 2). These dyes were obtained by reaction of equimolar amounts* (1 mmole each) of the quaternary 2-methylthio-4,5-dimethyl-3-R^1-thiazolium salt,† the ketomethylene compound, and a 10% excess of triethylamine in absolute ethanol (dyes IIId and IIIf were obtained in DMF).

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*A twofold excess of the ketomethylene compound was used for the preparation of dyes IIId and IIIf.

†A thiazolium salt with a 2-ethylthio group was used for the synthesis of dyes VI and XIV.