POLYMETHINE DYES WHICH ARE DERIVATIVES OF HETEROCYCLIC BASES CONTAINING CONDENSED THIOPHENE RINGS

V. Derivatives of Thienothienopyridines-4 and -8*

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Some new polymethine dyes of the cyanine and merocyanine series, containing thieno[2, 3-b]thieno[2, 3-b]pyridine-4 and thieno[3, 2-b]thieno[2, 3-b]pyridine-8 groups are synthesized. Replacement of the vinylene group by a sulfur atom in the condensed benzene rings of the 5, 6-benzoquinoline-4 group in dyes which are derivatives of this base, results in a marked hypsochromic shift of the absorption maximum of the corresponding dyes.

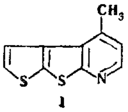
We have previously described [1, 2] polymethine dyes which are derivatives of thienopyridines-4 and -7, and of thionaphthenopyridines-1. It was shown that the absorption maxima of such dyes are displaced towards the short wavelength part of the spectrum as compared with compounds isosteric with them.

Table 1

Absorption Maxima in the Spectra of Carbo- and Dicarbocyanines in Ethanol

Z in Formula III	n	R	λ_{max}, nm
5,6-Benzoquinoline-4	1	C_2H_5	736
5,6-Benzoquinoline-4	1	CH_3	734
Thionaphtheno[2,3-b]pyridine-1	1	C_2H_5	642
Thieno[2,3-b]thieno[2,3-b]pyridine-4	1	C_2H_5	632
Thieno[2,3-b]thieno[2,3-b]pyridine-4	1	CH_3	629
Thieno[3,2-b]thieno[2,3-b]pyridine-8	1	C_2H_5	650
Thieno[3,2-b]thieno[2,3-b]pyridine-8	1	CH_3	644
5,6-Benzoquinoline-4	2	C_2H_5	848
Thieno[2,3-b]thieno[2,3-b]pyridine-4	2	C_2H_5	730
Thieno[3,2-b]thieno[2,3-b]pyridine-8	2	C_2H_5	750

The present paper describes the synthesis of some polymethine dyes of the cyanine and merocyanine series, structures III-IV, which are derivatives of the thienothienopyridines-4 and -8 (I, II) previously obtained by us [3, 4].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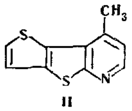
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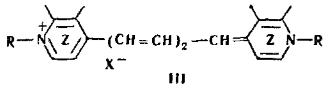
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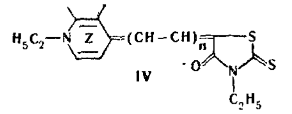
IV

Z is the thieno[2, 3-b]thieno[2, 3-b]pyridine-4 or thieno[3, 2-b]thieno[2, 3-b]pyridine-8 group, n = 1 or 2, X^- is the acid group, R is the CH_3 or C_2H_5 group.

Such dyes are isosteric with the corresponding derivatives of 5, 6-benzoquinoline-4.

The carbocyanines (n = 1) were synthesized by condensing quarternary salts of the appropriate bases with ethyl orthoformate by heating in nitrobenzene (cf. [5]). The dicarbocyanine dyes (n = 2) were prepared by reacting the ethiodides of the appropriate bases with the hydrochloride of the dianil of malonaldehyde (cf. [6]), by heating in acetic anhydride containing triethylamine.

Di- and tetramethinemerocyanines were synthesized by condensing, with heating, the ethiodides of the appropriate bases with 3-ethyl-5-(α-acetanilinomethylene)-or 3-ethyl-5-(α-acetanilinoallyidene)thiazolidine-2-thion-4-one in dry ethanol in the presence of triethylamine (cf. [7]).

Table 1 gives the positions of the absorption maxima of the carbo- and dicarbocyanine dyes synthesized.

The results in Table 1 show that replacement of 2 vinylene groups by a sulfur atom in the condensed benzene rings of the 5, 6-benzoquinoline-4 group in cyanine dyes, gives rise to a hypsochromic shift of the absorption maxima of the corresponding carbo- and dicarbocyanines. Dyes which are derivatives of thieno[3, 2-b]thieno[2, 3-b]pyridine-8 are somewhat more deeply colored than the corresponding isomeric dyes. The vinylene shift of the absorption maximum on passing from carbo- to dicarbocyanines in the cases of dyes which are derivatives of thienothienopyridines-4 and -8, amounts, as usual to about 100 nm. Replacement of the ethyl group by methyl at the nitrogen heteroatom is also practically without effect on dye color.

Table 2 gives positions of absorption maxima, and hypsochromic shifts of absorption maxima of di- and tetramethylenemerocyanines synthesized, calculated on the values of the absorption maxima of the corresponding oxanine and cyanine dyes.

From Table 2 it can be seen that the isomeric di- and tetramethinemerocyaines, which are derivatives of thienothienopyridine-4 and -8 are somewhat more highly colored than the dyes isosteric with them. Table 2 also shows that the values of the hypsochromic shifts of the absorption maxima of dyes containing thienothienopyridine groups and the 5, 6-benzobenzquinoline-4 group differ negligibly, evidently indicating that there is little difference between the basicities of such groups.

EXPERIMENTAL

Carbocyanine dyes. These were synthesized by condensing quaternary salts of the appropriate heterocyclic bases with ethyl orthoformate in nitrobenzene at 180° C for 30–40 min. To isolate the dyes, ether was added to the cold reaction products. The solid or resinous mass which came down was dissolved in hot ethanol, and the dyes were iso-

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*For Part IV see [8].

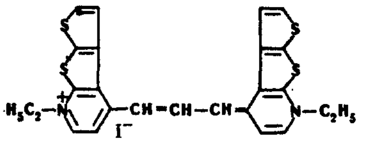
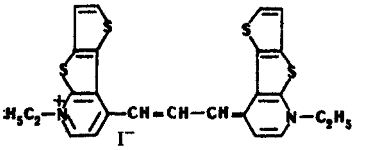
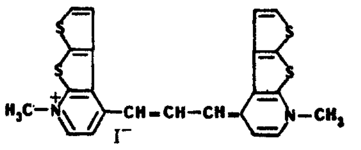
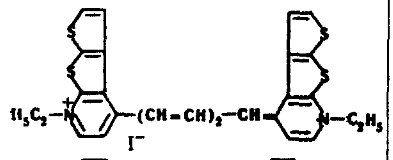
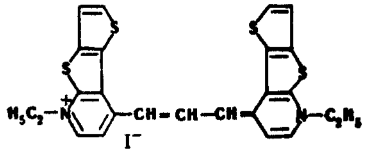
Table 2

Parameters of Spectra of Di- and Tetramethinemerocyanines

Z in formula IV	n	λ_{max} in EtOH, nm			Hypsochromic shift
		Merocyanines	Oxazines	Cyanines	
5,6-Benzoquinoline-4	1	631	542	736	8
Thieno[2,3-b]thieno[2,3-b]pyridine-4	1	578	542	632	9
Thieno[3,2-b]thieno[2,3-b]pyridine-8	1	586	542	650	10
5,6-Benzoquinoline-4	2	731	613	848	0.5
Thieno[2,3-b]thieno[2,3-b]pyridine-4	2	674	613	730	2.5
Thieno[3,2-b]thieno[2,3-b]pyridine-8	2	682	613	750	0.5

Table 3

Properties of Carbocyanine Dyes

Formula	Quaternary salt, g	Chain-forming compound, g	Solvent, ml	Appearance	Mp (decomp), °C	Formula	N, %		Yield, %
							Found	Calculated	
	0.36	0.3	1.5	Dark-blue plates	246—248	$C_{25}H_{21}IN_2S_4$	4.41 4.49	4.63	9.4
	0.36	0.3	1.5	Dark-blue prisms	269—270	$C_{25}H_{21}IN_2S_4$	4.54	4.63	11.6
	0.68	0.6	3	Dark-blue prisms	231—233	$C_{23}H_{17}IN_2S_4$	4.71	4.85	13.0
	0.24	0.12	2.0*	Dark-blue prisms	245—247	$C_{27}H_{23}IN_2S_4$	6.39	6.50	7.9
	0.24	0.12	2.0*	"	269—270	$C_{27}H_{23}IN_2S_4$	6.34 6.41	6.50	8.1

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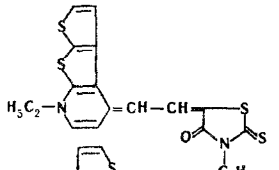
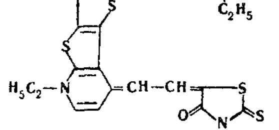
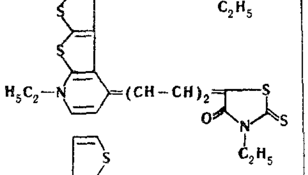
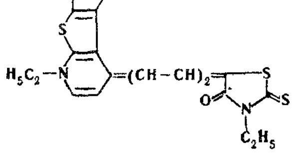
*With addition of 0.8 ml Et_3N.

Table 1

Properties of Merocyanine Dyes

Formula	Quaternary salt, g	Rhodanine derivative, g	Solvent, ml	Appearance	Mp (decomp), °C	Formula	N, %		Yield, %
							Found	Calculated	
	0.18	0.15	2	Violet prisms	234—236	$C_{18}H_{16}N_2OS_4$	6.73 6.81	6.92	35.0
	0.18	0.15	2	Violet prisms	259—261	$C_{18}H_{16}N_2OS_4$	6.71 6.79	6.92	30.0
	0.72	0.66	10	Pale green prisms	259—261	$C_{20}H_{18}N_2OS_4$	6.39 6.47	6.50	6
	0.72	0.66	10	Green prisms	241—243	$C_{20}H_{18}N_2OS_4$	6.33 6.41	6.50	5

lated as their iodides by precipitation with 10% KI solution. To purify a dye it was recrystallized from EtOH or chromatographed on alumina, then recrystallized to constant mp from EtOH. Before analysis it was dried to constant weight under vacuum over P_2O_5.

Reaction conditions, dye appearances, some of their physical properties, and the results of analyses are given in Table 3.

Dicarbocyanine dyes were prepared by condensing alkyliodides of the appropriate heterocyclic bases with the hydrochloride of the dianil of malondialdehyde in Ac_2O or pyridine, at 125°–130° C or 105°–110° C respectively, in the presence of Et_3N. The dyes were isolated and purified by methods analogous to those used for the carbocyanines. Reaction conditions, dye appearances, some of their properties, and analytical data are given in Table 3.

Dimethinemerocycanine dyes were synthesized by condensing ethiodides of the appropriate heterocyclic bases with 3-ethyl-5-(acetanilinomethylene)thiazolidin-2-thion-4-one, in absolute EtOH containing Et_3N, by heating together on a steam bath for 30 min. The dyes which came out on cooling the reaction products were filtered off, washed with EtOH, and air dried. They were purified by recrystallizing to constant mp from EtOH. Prior to analysis a dye was dried to constant weight over P_2O_5 in a vacuum. Reaction conditions, appearances, some physical constants, and analytical data are given in Table 4.

Tetramethinemerocyanine dyes were prepared by condensing ethiodides of the appropriate heterocyclic bases with 3-ethyl-5-(acetanilinoallylidene)thiazolidine-2-thion-4-one in absolute EtOH, in the presence of Et_3N by heating on a steam bath for 1 hr.

The dyes were purified by chromatographing on alumina and recrystallizing from EtOH to constant mp. Before analysis a dye was vacuum dried to constant weight over P_2O_5.

Reaction conditions, appearance, some constants, and analytical data, are given in Table 4.

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