POLYMETHYLENE DYES DERIVED FROM HETEROCYCLIC BASES CONTAINING CONDENSED THIOPHENE RINGS

IV. Derivatives of Thienopyridines-5 and -6

V. G. Zhiryakov and P. I. Abramenko

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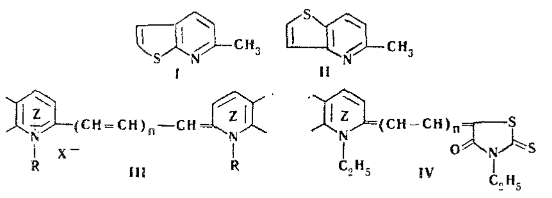
Some new polymethine dyes of the cyanine and merocyanine series which are derivatives of 5- and 6- thienopyridines are synthesized. Replacement of a vinyl group at a sulfur atom in the condensed benzene ring of quinoline in dyes which are derivatives of this base, always leads to a bathochromic shift of the absorption maximum of the corresponding dyes.

We have previously described [1–4] polymethine dyes which are derivatives of 4- and 7-thienopyridines and of 1-thionaphthenopyridines. It was shown that the absorption maxima of such dyes are shifted towards the short wave part of the spectrum in comparison with the compounds isosteric to them.

The present paper describes the synthesis of some polymethine dyes in the cyanine and merocyanine series, having structures III–IV, of derivatives of 6-methylthieno[2,3-b]pyridine (I) and 5-methylthieno[3,2-b]pyridine (II) previously described by us [5, 6].



Z = thieno[2, 3-b]- or -[3, 2-b]pyridine groups
n = 1 or 2, X = acid group
R = CH_3 or C_2H_5

Such dyes are isosteres of the corresponding 2-quinoline derivatives.

The carbocyanines (n = 1) were synthesized by condensing quaternary salts of the appropriate bases with ethyl orthoformate by heating in nitrobenzene (see [7]). The dicarbocyanine dyes (n = 2) were obtained by reacting the ethiodides of the appropriate bases with malonaldehyde dianil hydrochloride (see [8]), the reaction being run in acetic anhydride solution, in the presence of triethylamine.

Table 1

Absorption Maxima in the Spectra of Carbo- and Dicarbocyanines

Z in formula IV	n	R	λ_{max} (in EtOH), nm
quinoline-2	1	C_2H_5	607
thieno[2, 3-b]pyridine-6	1	C_2H_5	618
thieno[3, 2-b]pyridine-5	1	C_2H_5	614
thieno[3, 2-b]pyridine-5	1	CH_3	614
quinoline-2	2	C_2H_5	707
thieno[2, 3-b]pyridine-6	2	C_2H_5	718
thieno[3, 2-b]pyridine-5	2	C_2H_5	708

Di- and tetramethinemerocyanines were synthesized by condensing the ethiodides of the appropriate bases with 3-ethyl-5-(α-acetanilinomethylene)- or 3-ethyl-5-(γ-acetanilinoallylidene)thiazolidine-2-thion-4-one in absolute ethanol in the presence of triethylamine with heating (cf. [9, 10]).

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

The data of Table 1 shows that replacement of a vinyl group by a sulfur atom in the benzene ring of quino[2]cyanines leads to bathochromic displacement of the absorption maxima for the corresponding carbo- and dicarbocyanines. The dyes which are derivatives of 6-thieno[2, 3-b]pyridine are somewhat more deeply colored than the corresponding isomeric dyes.

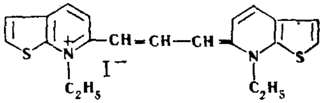
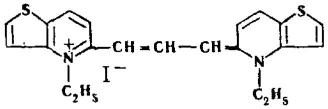
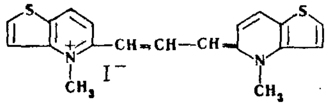
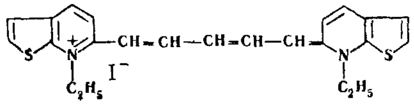
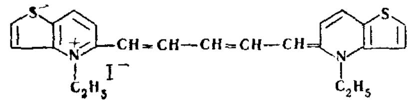
The vinyl shift of the absorption maximum on passing from carbo- to dicarbocyanines in the cases of the dyes which are derived from 5- and 6-thienopyridines, respectively, generally amounts to about 100 nm. Replacement of ethyl by methyl at the nitrogen hetero-

Table 2

Parameters of Spectra of Di- and Tetramethinemerocyanines

Z in formula IV	n	λ_{max} (in EtOH), nm			Hypsochromic shift, nm
		merocyanines	oxazines	cyanines	
2-quinoline	1	565	542	607	9.5
6-thieno[2, 3-b]pyridine	1	576	542	618	4.5
5-thieno[2, 3-b]pyridine	1	570	542	614	8.0
2-quinoline	2	660	613	707	0
6-thieno[2, 3-b]pyridine	2	668	613	718	2.5
5-thieno[2, 3-b]pyridine	2	655	613	708	4.5

Table 3

Dye formula	Amounts			Appearance	Mp (decomp), ° C	Formula	N, %		Yield, %
	Quaternary salt	Chain-forming compound	Solvent, ml				Found	Calculated	
	0.60	0.5	1.5	Dark blue needles	244—246	$C_{21}H_{21}IN_2S_2$	5.78 5.96	5.69	30.6
	1.20	1.2	1.0	Blue prisms	246—247	$C_{21}H_{21}IN_2S_2$	5.53 5.62	5.69	30.0
	0.6	0.5	1.5	Dark violet prisms	236—238	$C_{19}H_{17}IN_2S_2$	27.16**	27.15**	36
	0.61	0.35	3.5*	Dark blue prisms	229—231	$C_{23}H_{23}IN_2S_2$	5.36 5.43	5.40	25
	0.61	0.35	3.5*	Dark green needles	203—204	$C_{23}H_{23}IN_2S_2$	5.53	5.40	48.4

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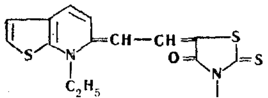
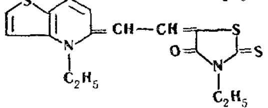
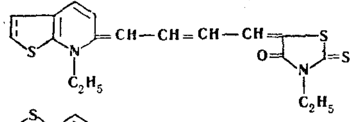
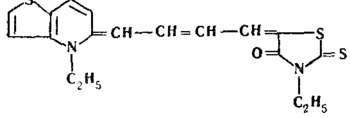
* 1.5 ml Et_3N added.

** I analysis.

Table 4

Dye formula	Amount			Appearance	Mp (decomp), °C	Formula	N, %		Yield, %
	Quaternary salt, g	Rhodanine derivative	Solvent, ml				Found	Calculated	
	0.61	0.61	10	Violet prisms	263—265	$C_{16}H_{16}N_2OS_3$	7.88	8.04	65.0
	0.61	0.61	10	Violet needles	239—241	$C_{16}H_{16}N_2OS_3$	8.07	8.04	72.0
	1.22	1.30	50	Green prisms	234—235	$C_{18}H_{18}N_2OS_3$	7.43	7.49	20.0
	1.22	1.30	50	Dark violet prisms	231—233	$C_{18}H_{18}N_2OS_3$	7.47	7.49	25.0

atom is, furthermore, practically without effect on the colors of the dyes.

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

From Table 2 it is evident that isomeric di- and tetramethinemerocyanines, derivatives of 5- and 6-thienopyridines are somewhat more deeply colored than the dyes isosteric to them just as in the case of cyanine dyes. The hypsochromic shifts of the absorption maxima of dimethinemerocyanines which are derivatives of thienopyridines are somewhat less than for quino[2, 2']carbocyanine, while on the other hand, with tetramethinemerocyanines the hypsochromic shifts of the absorption maxima of derivatives of 5- and 6-thienopyridines somewhat exceed the analogous shifts for quino[2, 2']dicarbocyanine. Evidently this indicates that the structure of the dimethinemerocyanine dyes which are derivatives of 5- and 6-thienopyridines, in ethanol solutions, can be more accurately described as an intraionic one.

EXPERIMENTAL

Carbocyanine dyes were synthesized by condensing the ethiodides of the appropriate heterocyclic compounds with ethyl orthoformate in nitrobenzene at 180° C for 30–40 min. To isolate the dyes, ether was added to the reaction products after cooling, the precipitated solid or resinous mass dissolved in EtOH with heating, and the dye isolated as iodide by precipitation with a 10% KI solution. To purify the dye it was recrystallized from EtOH, or first chromatographed on alumina, and then recrystallized to constant mp from EtOH. Prior to analysis the dye was vacuum dried to constant weight over P_2O_5.

The conditions for preparing the dyes, their appearances, some of their physical constants, and analytical data are given in Table 3.

Dicarbocyanine dyes were prepared by condensing the ethiodides of the appropriate heterocyclic bases with malonaldehyde dianil hydrochloride in acetic anhydride or pyridine, at respectively 125°–130° C or 105°–110° C, in the presence of Et_3N. The methods used for isolating and purifying the dyes were similar to those used for the carbocyanines. Reaction conditions, appearances, some physical constants, and analytical data are given in Table 3.

Dimethinemerocyanine dyes were synthesized by condensing ethiodides of the appropriate heterocyclic bases with 3-ethyl-5-(acetanilinomethylene)thiazolidine-2-thion-4-one in absolute EtOH in the presence of Et_3N, heating on a boiling water bath for 30 min. The dye that precipitated on cooling was filtered off, washed with EtOH, and dried in air. To purify the dye it was recrystallized from EtOH, to constant mp. Prior to analysis it was vacuum dried to constant weight over P_2O_5. Reaction conditions, appearances, some physical constants, and analytical data are given in Table 4.

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

To purify the dyes they were chromatographed on alumina and recrystallized to constant mp from EtOH. Prior to analysis a dye was vacuum dried to constant weight over P_2O_5.

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

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