POLYMETHINE DYES DERIVED FROM HETEROCYCLIC BASES CONTAINING CONDENSED THIOPHENE RINGS

VII. Thionaphthenopyrid-3-yl and Thienothienopyrid-6-yl Derivatives*

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The synthesis of polymethine dyes of the cyanine and merocyanine series derived from 3-methylthionaphtheno[2,3-b]pyridine, 3-methylthionaphtheno[3,2-b]pyridine, 6-methylthieno[2,3-b]thieno[2,3-b]pyridine, and 6-methylthieno[3,2-b]thieno[2,3-b]pyridine is described. The color of the dyes obtained is discussed. It has been shown that the replacement of vinylene groups by sulfur atoms in one of the two benzene rings of the hetero residue in 2-substituted 5,6-benzoquinolines in cyanine dyes leads to a bathochromic shift of the absorption maxima.

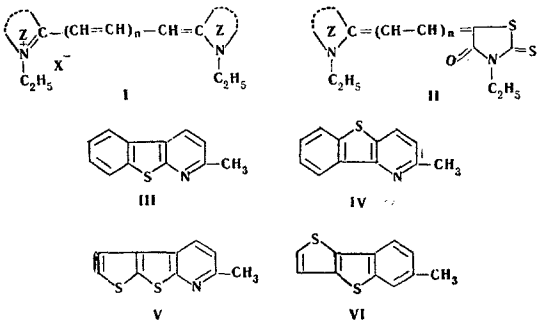
We have described polymethine dyes derived from 5- and 6-substituted thienopyridines previously [1]. It was shown that the absorption maxima of such dyes are displaced into the long-wave part of the spectrum as compared with the corresponding 2-substituted quinoline derivatives. In the present paper we describe the synthesis of polymethine dyes of the cyanine and merocyanine series of structures I and II derived from new heterocyclic bases containing condensed thiophene rings: 3-methylthionaphtheno[2,3-b]- and [3,2-b]pyridines (III, IV) [2] and 6-methylthieno[2,3-b]-thieno[2,3-b]- and -thieno[3,2-b]thieno[2,3-b]pyridines (V, VI) [3].

Table 1

Absorption Maxima of the Carbo- and Dicarbocyanines in Ethanol

Z in formula I	λ_{max}, nm	
	$n=1$	$n=2$
5, 6-Benzoquinol-2-yl	634[4]	–
Thionaphtheno[2, 3-b]pyrid-3-yl	648	743
Thionaphtheno[3,2-b]pyrid-3-yl	668	780
Thieno[2, 3-b]thieno[2, 3-b]pyrid-6-yl	650	742
Thieno[3,2-b]thieno[2, 3-b]pyrid-6-yl	656	760
Thionaphtheno[3, 2-b]pyrid-3-yl	665*	–
Thieno[2, 3-b]thieno[2, 3-b]pyrid-6-yl	646*	–

*Methanol.



The positions of the absorption maxima of the carbo- and dicarbocyanine dyes derived from the bases synthesized, and also from bases isosteric with them are given in Table 1.

The data of Table 1 show that the replacement of vinylene groups by sulfur atoms in one or two benzene rings of the residues of 2-methyl-5,6-benzoquinoline in the cyanines causes a bathochromic shift of the absorption maxima of the dyes. Dyes with residues of thionaphtheno[3,2-b]- or thieno[3,2-b]thieno[2,3-b]-pyridine have somewhat deeper colors than the corresponding derivatives of thionaphtheno[2,3-b]- or thieno[2,3-b]thieno[2,3-b]pyridine. As usual, the replacement of the ethyl group on the heterocyclic nitrogen atom by a methyl group has practically no influence on their coloration. The vinylene shift of the absorption maximum on passing from the carbo- to the dicarbocyanines retains its usual value of about 100 nm.

*For part VI, see [8].

Table 2

Absorption Maxima of the Merocyanines in Ethanol

Z in formula II	λ_{max}, nm			Hypsochromic shifts, nm
	merocyanines		cyanines	
	$n=1$	$n=2$	$n=1$	$n=1$
5, 6-Benzoquinol-2-yl	584	—	635[4]	4.5
Thionaphtheno[2, 3-b]pyrid-3-yl	586	684	648	9.0
Thionaphtheno[3,2-b]pyrid-3-yl	605	706	668	0
Thieno[2, 3-b]thieno[2, 3-b]pyrid-6-yl	581	682	650	15
Thieno[3, 2-b]thieno[2, 3-b]pyrid-6-yl	588	685	656	11

Note: the hypsochromic shifts are the deviations of the absorption maxima of the dimethylmerocyanines from the arithmetic mean values calculated from the absorption maxima of the corresponding carbocyanines (n = 1) and the monomethine oxanine derived from 3-ethylrhodanine [5] (λ_{max} at 542 nm in ethanol).

Table 3

Characteristics of the Cyanine Dyes

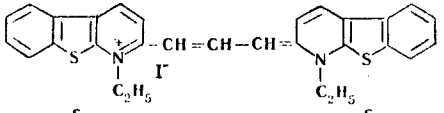
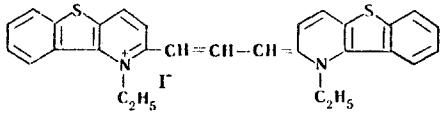
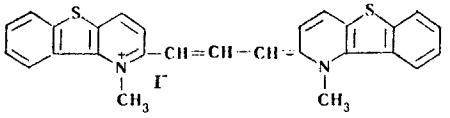
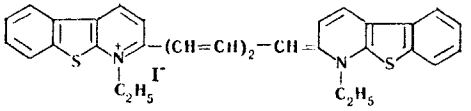
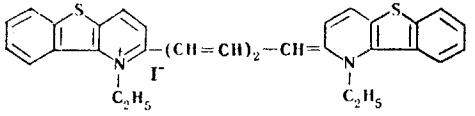
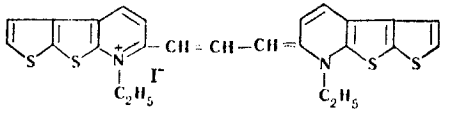
Formula	Amount: quaternary salt	Amount: substance forming the chain	Amount: solvent, ml	External form	Mp, °C (decomp.)	Empirical formula	N, %: found	N, %: calculated	Yield, %
	0.71	0.7	8	Dark blue prisms	277—278	$C_{29}H_{25}IN_2S_2$	4.59 4.61	4.72	31
	0.71	0.7	8	Dark blue prisms	259—260	$C_{29}H_{25}IN_2S_2$	4.62 4.66	4.72	29.3
	0.70	0.6	5	Dark blue prisms	214—215	$C_{27}H_{21}IN_2S_2$	4.78 4.87	4.94	28.6
	0.45	0.75	5	Dark blue prims	220—221	$C_{31}H_{27}IN_2S_2$	4.41 4.47	4.53	21.6
	0.56	0.2	3.0	Dark blue prisms	210—211	$C_{31}H_{27}IN_2S_2$	4.31 4.38	4.53	10.3
	0.72	0.70	5	Dark blue prisms	230—232	$C_{25}H_{21}IN_2S_4$	4.51 4.56	4.63	26.8

Table 3 (Cont'd.)

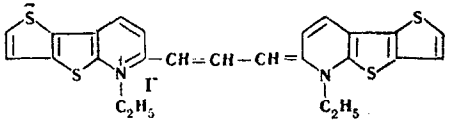
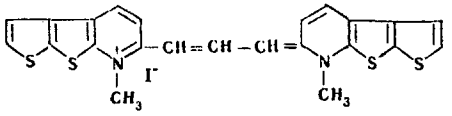
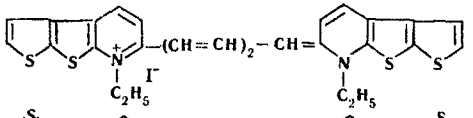
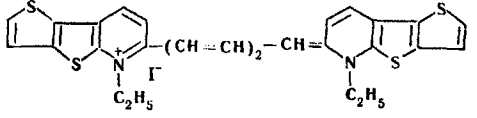
Formula	Amount: quaternary salt	Amount: substance forming the chain	Amount: solvent, ml	External form	Mp, °C (decomp.)	Empirical formula	N, %: found	N, %: calculated	Yield, %
	0.36	0.3	1.5	Green prisms	265—267	$C_{25}H_{21}IN_2S_4$	4.59 4.68	4.63	14.6
	0.68	0.6	3	Dark blue needles	241—243	$C_{23}H_{17}IN_2S_4$	4.71 4.79	4.85	18
	0.96	0.4	7.0	Dark blue prisms	244—246	$C_{27}H_{23}IN_2S_4$	6.39 6.47	6.50	9.6
	0.56	0.24	3.0	Dark blue prisms	217—219	$C_{27}H_{23}IN_2S_4$	6.36 6.43	6.50	10.3

Table 4

Characteristics of the Merocyanine Dyes

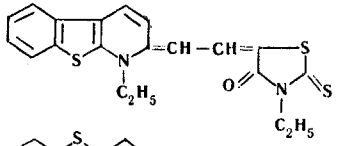
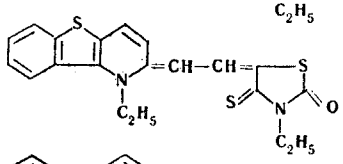
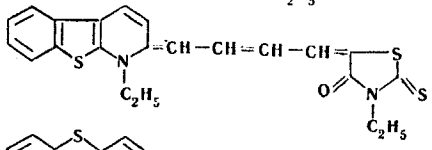
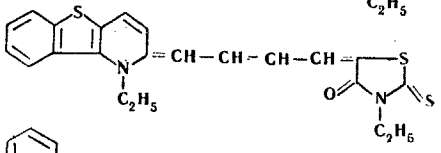
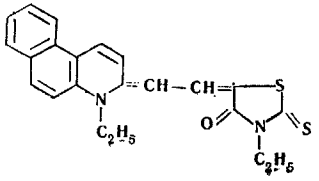
Formula	Amount			External form	Mp (decomp.), °C	Empirical formula	N, %		Yield, %
	quaternary salt, g	3-ethylrhodanine derivative, g	solvent, ml				found	calculated	
	0.71	0.60	10	Violet needles	270—271	$C_{20}H_{18}ON_2S_3$	6.87 6.93	7.03	59
	0.71	0.60	10	Violet needles	264—265	$C_{20}H_{18}ON_2S_3$	6.91 6.97	7.03	56
	0.70	0.65	20	Green prisms	246—247	$C_{22}H_{20}ON_2S_3$	6.41 6.43	6.59	18
	0.70	0.65	30	Light green plates	256—258	$C_{22}H_{20}ON_2S_3$	6.39 6.48	6.59	16
	0.18	0.15	5.0	Violet needles	243—245	$C_{22}H_{20}ON_2S_2$	7.10 7.16	7.13	43

Table 4 (Cont'd.)

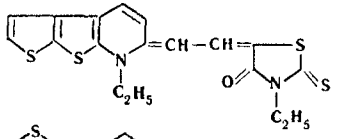
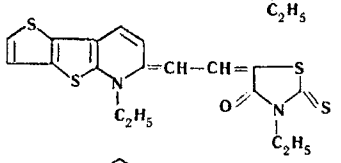
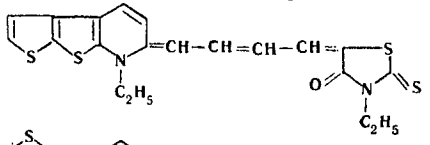
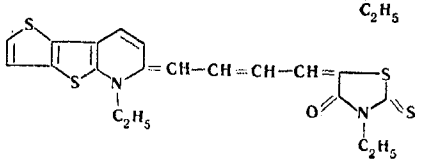
Formula	Amount			External form	Mp (decomp.) °C	Empirical formula	N, %		Yield, %
	quaternary salt, g	3-ethylrhodanine derivative, g	solvent, ml				found	calculated	
	0.72	0.60	10	Dark violet prisms	241—243	$C_{18}H_{16}N_2OS_4$	6.83 6.89	6.92	49.6
	0.72	0.60	10	Dark violet prims	259—261	$C_{18}H_{16}N_2OS_4$	6.81 6.89	6.92	41.3
	0.70	0.65	40	Light green prisms	247—249	$C_{20}H_{18}N_2OS_4$	6.43 6.57	6.50	13.9
	0.70	0.65	40	Green prisms	241—243	$C_{20}H_{18}N_2OS_4$	6.37 6.49	6.50	14.6

Table 2 gives the positions of the absorption maxima of the merocyanine dyes derived from the 3-methylthionaphtheno- and 6-methylthienothienopyridines and also those of dyes isosteric with them and the hypsochromic shifts calculated for them.

It can be seen from Table 2 that the di- and tetramethine merocyanines with a thieno[3,2-b]thieno[2,3-b]pyrid-6-yl residue or with the isomeric thionaphthenopyrid-3-yl residues have a deeper coloration than the dyes derived from 2-methyl-5,6-benzoquinoline that are isosteric with them, just as in the case of the cyanines.

With a decrease in the polarity of the solvent, the absorption maxima of the dimethine merocyanine dyes described shift first in the long-wave direction and then in the short-wave direction. This shows that the structure of these dyes in ethanol approximates to an internally ionic structure. A comparison of the values of the hypsochromic shifts given in Table 2 shows that the basicities both of the thionaphtheno[2,3-b]-pyrid-3-yl residue and of the isomeric thienothienopyrid-6-yl residue are somewhat higher than the basicity of the 5,6-benzoquinol-2-yl residue. However, the thionaphtheno[3,2-b]pyrid-3-yl residue is probably less basic than the residues of the other bases described.

EXPERIMENTAL

Cyanine dyes. The carbocyanines were synthesized by condensing the alkyl iodide derivatives of the bases with ethyl orthoformate in nitrobenzene (see [6]) at 180–185° C for 20–40 min. The dicarbocyanines were obtained by the reaction of the ethiodides of the bases with the hydrochloride of the dianil of malonaldehyde (see [7]) in acetic anhydride at 120–130° C for 30–60 min in the presence of triethylamine. For purification, the dyes were chromatographed on alumina in chloroform and were then crystallized from ethanol. Some constants and the results of the analyses of the dyes are given in Table 3.

The merocyanine dyes (Table 4). The dimethine merocyanines were obtained by condensing the ethiodides of the bases with the 5-acetanilinomethylene derivatives of 3-ethylrhodanine in absolute ethanol in the presence of triethylamine with heating in the boiling water bath for 30–60 min. The tetramethine merocyanines were synthesized similarly by condensing the ethiodides of the bases with 5-(γ-acetanilinoallylidene)-3-ethyl-4-oxothiazolidine-2-thione in absolute ethanol. For purification, before crystallization from ethanol the dyes were chromatographed on alumina in chloroform solution.

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