POLYMETHINE DYES CONTAINING CONDENSED THIOPHENE RINGS

VI. Thienothienothiazole Derivatives*

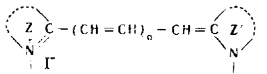
V. G. Zhiryakov and P. I. Abramenko

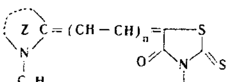
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 3, pp. 488–490, 1969

UDC 547.737'821:541.651.2:668.9

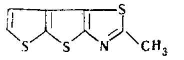
Several new polymethine dyes of the cyanine and merocyanine series with thieno[2',3':5,4]thieno[2,3-d]thiazole residues have been synthesized. It has been shown that the replacement of one vinylene group in the benzene rings of 6,7-benzobenzothiazole by a sulfur atom in the cyanines and merocyanines causes a considerably greater deepening of the color of the dyes than the replacement of two vinylene groups in both condensed rings of 6,7-benzobenzothiazole residues.

We have previously studied polymethine dyes with residues of the isomeric thienothiazoles [1] and thionaphthenothiazoles [2] isosteric with the corresponding 4,5- and 6,7-benzobenzothiazole dyes. In the present paper we describe the synthesis and a study of the coloration of some new cyanine and merocyanine dyes (I, II) derived from 2-methylthieno[2',3':5,4]thieno-[2,3-d]thiazole (III) [3]. Such dyes are isosters of the corresponding derivatives of 2-methyl-6,7-benzobenzothiazole in the condensed benzene rings of which two vinylene groups have been replaced by sulfur atoms.


I


II

n = 1 or 2; z and z' are given in Tables 1 and 2


III

The dyes were obtained by the general methods used for the synthesis of compounds of this type [4–7].

Table 1 gives the absorption maxima of the carbocyanines synthesized and also, for comparison, those of the dyes isosteric with them.

The data of Table 1 show that the thienothienothiazole dyes have colors which are deeper than those of the corresponding 6,7-benzobenzothiazole derivatives but are higher than the analogous dyes with thionaphthenothiazole residues. Thus, the replacement of one vinylene group in the benzene rings of the 6,7-benzobenzothiazole residues by a sulfur atom in the cyanines causes a considerably greater deepening of the color of the dye than the replacement of the vinylene groups by sulfur atoms in both condensed rings of the 6,7-benzobenzothiazole residues. At the same time, on passing from thienothiazole derivatives to the corresponding thienothienothiazole derivatives a deepening of the color of the dyes takes place.

As usual, the replacement of the ethyl group on the hetero atom of nitrogen in the cyanine dyes by a methyl group has practically no influence on the color. The vinylene shift in the absorption maximum on passing from the carbo- to the dicarbocyanine also has its usual value of about 100 nm.

Table 2 gives the positions of the absorption maxima of the merocyanines synthesized and of the corresponding derivatives of 6,7-benzobenzothiazole and thionaphthenothiazole, and also the values of the hypsochromic shifts of the absorption maxima of the merocyanines calculated from the absorption maxima of the corresponding symmetrical dyes. A comparison of the hypsochromic shifts of the merocyanines given in the table shows that they differ little from one another in basicity.

EXPERIMENTAL

Cyanine dyes. Symmetrical carbocyanines were obtained by heating alkyl iodide derivatives of the bases with ethyl orthoformate in acetic anhydride at 120–130° C for 1 hr. The unsymmetrical carbocyanines were synthesized by condensing the ethiodides of the bases with the ethiodide of 2-(β-acetanilinovinyl)benzothiazole (XVI), 6,7-benzobenzothiazole (XVII), or 3,3-dimethylindolenine (XVIII) in acetic anhydride in the presence of triethylamine at 120–125° C for 10–20 min. The dicarbocyanines were obtained by heating the ethiodides of

Table 1

Absorption Maxima in the Spectra of the Carbocyanines in Ethanol

Compound	In formula I, n = 1		λ_{max}, nm
	Z	Z'	
IV	6,7-Benzobenzothiazole	6,7-Benzobenzothiazole	593[2]
V	Thionaphtheno[2,3-d]thiazole	Thionaphtheno[2,3-d]thiazole	630*[2]
VI	Thieno[2',3' : 5, 4]thieno[2, 3-d]-thiazole	Thieno[2', 3' : 5, 4]thieno[2, 3-d]-thiazole	618**
VII	Thieno[2', 3' : 5, 4]thieno[2, 3-d]thiazole	Benzothiazole	588
VIII	Thieno[2', 3' : 5, 4]thieno[2, 3-d]thiazole	3, 3-Dimethylindolenine	566
IX	Thieno[2', 3' : 5, 4]thieno[2, 3-d]thiazole	6, 7-Benzobenzothiazole	602

*In the dicarbocyanine, at 725 nm [2].

**In the dicarbocyanine (VIa) at 711 nm and in the methyl derivative (VIb) at 616 nm.

---

*For part V, see [8].

Table 2

Parameters of the Absorption Spectra of the Dyes in Ethanol

Compound	Z in formula II	λ_{max}, nm		Hypsochromic shifts, nm	
		$n=1$	$n=2$	$n=1$	$n=2$
X, XI	6,7-Benzobenzothiazole	540	631	27.5	—
XII, XIII	Thionaphtheno[2, 3-d]thiazole	559[2]	644	27	25
XIV, XV	Thieno[2′, 3′ : 5, 4]thieno[2, 3-d]thiazole	558	648	24	14

Note: the absorption maximum of the corresponding oxanines in ethanol are at 542 nm (n = 1) and at 613 nm (n = 2) [5].

Table 3

Characteristics of the Dyes

Compound	Amount			External form	Mp (decomp.), °C	Empirical formula	N, %		Yield, %
	quaternary salt, g	substance for the formation of the chain, g	acetic anhydride, ml				found	calculated	
VI	0.74	0.6	5	Dark blue prisms	257—259	$C_{21}H_{17}IN_2S_6$	4.39; 4.46	4.54	21.3
VIb	0.70	0.6	5	Blue prisms	300	$C_{19}H_{13}IN_2S_6$	4.57; 4.64	4.76	19.6
VIa	0.72	0.36	6	Dark green prisms	234—236	$C_{23}H_{19}IN_2S_6$	4.29; 4.41	4.36	9.7
VII	0.35	0.45 XVI	5	Light green prisms	251—253	$C_{21}H_{19}IN_2S_4$	4.89; 4.96	5.06	44
IX	0.35	0.5 XVII	5	Dark green prisms	257—259	$C_{25}H_{21}IN_2S_4$	4.53; 4.56	4.63	48.4
VIII	0.36	0.46 XVIII	3	Violet needles	243—245	$C_{24}H_{25}IN_2S_3$	4.89; 4.93	4.96	46
XIV	0.70	0.6 XIX	10*	Violet needles	201—203	$C_{16}H_{14}N_2OS_5$	6.65; 6.79	6.82	64.6
XV	0.72	1.3 XX	50*	Green prisms	251—253	$C_{18}H_{16}N_2OS_5$	6.24; 6.38	6.41	12.8

---

*Ethanol

the bases with the hydrochloride of the dianil of malonaldehyde in acetic anhydride in the presence of triethylamine at 120–125° for 30 min.

Merocyanine dyes. The di- and tetramethine merocyanines were obtained by heating mixtures of the ethiodides of the bases with 5-acetanilinomethylene-3-ethyl- (XIX) or 5-(γ-acetanilinoallylidene)-3-ethyl-4-oxathiazolidine-2-thione (XX) in anhydrous ethanol in the presence of triethylamine in the boiling water bath for 30–60 min. For purification, the dyes were chromatographed on alumina and crystallized from ethanol. Before analysis, the dyes were dried in vacuum over phosphorus pentoxide to constant weight. Some constants of the dyes and the results of their analyses are given in Table 3.

REFERENCES

1. V. G. Zhiryakov, I. I. Levkoev, N. N. Sveshnikov, and K. I. Pokrovskaya, USSR patent no. 113291; Byull. izobr., no. 5, 1958; V. G. Zhiryakov, ZhOKh, **34**, 2034, 1964.

2. U. S. patent no. 2424483; C. A., **41**, 6483, 1947; Z. I. Miroshnichenko and M. A. Al'perovich, ZhOKh, **34**, 241, 247, 1964.

3. V. G. Zhiryakov and P. I. Abramenko, USSR patent no. 166702; Byull. izobr., no. 25, 1964; KhGS [Chemistry of Heterocyclic Compounds], **1**, 619, 1965.

4. W. König, Ber., **55**, 3293, 1922; W. König and W. Meyer, J. pr. Chem., **109**, 324, 1925.

5. M. V. Deichmeister, Thesis [in Russian], Moscow, 1951.

6. M. V. Deichmeister, I. I. Levkoev, and E. B. Lifshits, ZhOKh, **23**, 1529, 1953.

7. T. Ogata, Proc. Imp. Acad. Tokyo, **8**, 42, 1932.

8. V. G. Zhiryakov and P. I. Abramenko, KhGS [Chemistry of Heterocyclic Compounds], **3**, 830, 1967.

19 July 1966

All-Union Scientific-Research
Motion-Picture Institute,
Moscow