INVESTIGATIONS IN THE FIELD OF POLYMEROCYANINES

III. Dimerocyanine Dyes with Electron-Donating Substituents in the Polymethine Chain*

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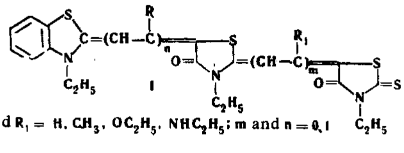
A series of thiadimerocyanine dyes that are derivatives of 3-ethyl-4-oxothiazolidine-2-thione with methyl-, ethoxy-, and ethylamino groups in the α and α' positions of the polymethine chain have been synthesized. The colors and sensitizing properties of these dyes have been studied.

In a preceding communication [2] devoted to dimerocyanine dyes derived from rhodanine we studied the influence of the nature of the heterocyclic nitrogen-containing residues and the length of the polymethine chains on the properties of these dyes. Substituents in the polymethine chains of the merocyanine dyes have a considerable influence on the color [3–7], both bathochromic and hypsochromic displacements of the absorption maximum being found according to the nature and the position of the substituents and also the nature of the nitrogen-containing heterocyclic residue. The question of the influence of substituents in the polymethine chain of dimerocyanines on their color and photographic properties has been little studied up to the present time [8–12].

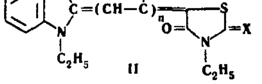
We have carried out the synthesis of thiadimerocyanines with methyl, ethoxy, and ethylamine groups in the α and α' positions of the polymethine chain having the general formula I and have measured their absorption spectra in ethanol.



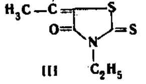
I

R and R_1 = H, CH_3, OC_2H_5, NHC_2H_5; m and n = 0, 1

In the synthesis of dimerocyanines with OC_2H_5 and CH_3 groups in the α and α' positions and the NHC_2H_5 group in the α position of the polymethine chain, we started from the merocyanines (II, X = S), which were converted into quaternary salts by heating with dimethyl sulfate, these being condensed with 3-ethylrhodanine or its ethylidene derivative (III).



II



III

R = H, CH_3, OC_2H_5, NHC_2H_5; R_1 = H, CH_3, OC_2H_5

Dyes with an ethylamino group in position α' of the polymethine chain (table, dyes 8 and 12), like the thiamerocyanines [4], were obtained in good yields by heating the corresponding α-ethoxy-substituted dimerocyanines with ethylamine in absolute ethanol. At the same time, it was impossible to obtain α-ethylamino-substituted dimethine-zeromethine- and bis(dimethine)dimerocyanines (table, dyes 4 and 5, respectively) by this method. The mobility of the ethoxy group in the α position of the merocyanine derivatives of 4-thiazolidinone [4] is due to the displacement of electrons from it to the carbonyl oxygen of the oxomethylene residue which is greater the stronger the electron-accepting properties of the substituent in position 2 are (compare [13]). Accordingly, the reactivity of an ethoxy group in the α' position of the dimerocyanines is the same as that in merocyanine derivatives of 4-oxothiazolidine-2-thione (II, X = S) and is much less in the α position. In the latter case, there is a displacement of electrons from the nitrogen atom of the central thiazolidinone residue to the carbonyl oxygen of the terminal rhodanine nucleus, which is less electronegative than the thione sulfur.

The absorption maxima in ethanol of the dyes synthesized are given in the table (the measurements were carried out on a SF-2 M spectrophotometer). It can be seen from these figures that the introduction of methyl, ethoxy, and ethylamino groups into the α and α' positions of dimethine-zero-methine and zero-methinedimethinedimerocyanines (1–8) and also in the α' position of bis(dimethine)dimerocyanines (9–12) has approximately the same influence on the color as in the case of the thiadimethinemerocyanines [3,4]. When the α-hydrogen atom of a thiabis(dimethine)dimerocyanine is replaced by a methyl or an ethoxy group (13–14), the distribution of the electron density in the chromophoric system apparently becomes more uniform and the color deepens considerably. For the same reason, the hypsochromic shift of the absorption maximum due to the introduction of an ethylamino group is only 24 nm. It is known that the introduction of methyl and ethoxy groups into the α position of the polymethine chain of a thiadimethinemerocyanine leads to a considerable increase in its sensitizing action [14]. In the case of the dimerocyanines that we have studied, the introduction of these substituents does not have such a favorable influence on the sensitizing properties of these dyes.

EXPERIMENTAL

The ethyl methyl sulfate compounds of the thiamerocyanine derivatives of 2-methylthio-4-thiazolinone required for the synthesis

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*For part II, See [1].

Dimerocyanines I

Compound	n	m	R	R_1	Condensation conditions				External form	Mp, °C	λ_{max}	$\Delta\lambda_{max}$*	Empirical formula	Found, %	Calculated, %	Yield, %
					C_5H_5N	$(CH_3CO)_2O$	$(C_2H_5)_3N$, ml	time, min; temp., °C			nm	nm				
1	1	0	H	—	—	—	—	—	—	—	575[2]	—	—	—	—	—
2	1	0	CH_3	—	3	—	—	5; 130	Purple powder	300	585	+10	$C_{22}H_{23}N_3O_2S_4$	N 8.41; 8.46	N 8.58	65.5
3	1	0	OC_2H_5	—	3	—	0.16	5; 100	Purple powder	288	575	0	$C_{23}H_{25}N_3O_3S_4$	S 24.82; 24.93	S 24.68	44.5
4	1	0	NHC_2H_5	—	3	—	0.16	20; 130	Purple powder	252	498	−77	$C_{23}H_{26}N_4O_2S_4$	N 10.68; 10.51	N 10.81	75
5	0	1	—	H	—	3	0.48	5; 100	Black powder	313	565	—	$C_{21}H_{21}N_3O_2S_4$	S 27.07; 26.99	S 27.01	42.1
6	0	1	—	CH_3	3	—	0.16	10; 130	Purple powder	273	571	+6	$C_{22}H_{23}N_3O_2S_4$	S 26.35; 26.22	S 26.17	55
7	0	1	—	OC_2H_5	—	3	0.48	5; 100	Dark brown powder	255	569	+4	$C_{23}H_{25}N_3O_3S_4$	S 24.69; 24.83	S 24.68	84.5
8**	0	1	—	NHC_2H_5	—	—	—	—	Dark purple powder	214—215	466	−99	$C_{23}H_{26}N_4O_2S_4$	N 10.51; 10.68	N 10.81	88.7
9	1	1	H	H	—	—	—	—		—	614[2]	—	—	—	—	—
10	1	1	H	CH_3	3	—	0.16	10; 130	Dark green powder	283	618	+4	$C_{24}H_{25}N_3O_2S_4$	N 7.96; 7.86	N 8.15	62
11	1	1	H	OC_2H_5	—	3	0.48	10; 120	Small dark green needles	245	618	+4	$C_{25}H_{27}N_3O_3S_4$	S 23.16; 23.18	S 23.48	18
12**	1	1	H	NHC_2H_5	—	—	—	—	Dark green powder	232	496	−118	$C_{25}H_{28}N_4O_2S_4$	N 10.24; 10.41	N 10.27	62.5
13	1	1	CH_3	H	3	—	0.16	10; 130	Dark green powder	298	636	+22	$C_{24}H_{25}N_3O_2S_4$	S 24.64; 24.66	S 24.85	50
14	1	1	OC_2H_5	H	—	3	0.48	10; 100	Dark brown powder	245	634	+20	$C_{25}H_{27}N_3O_3S_4$	S 23.66; 23.68	S 23.48	40.5
15	1	1	NHC_2H_5	H	3	—	0.16	15; 130	Dark red powder	282	590	−24	$C_{25}H_{28}N_4O_2S_4$	N 9.97; 10.08	N 10.27	33

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*Displacement of the absorption maximum relative to the dye unsubstituted in the chain.

**For the conditions and synthesis of these dyes, see the Experimental part.

of the dimerocaynines were obtained by heating 1 mole of the corresponding merocyanine (II, X = S) with 3 moles of dimethyl sulfate under the following conditions: for the thia-zero-methinemerocyanines (II, n = 0) at 125°–130° C (here and below the bath temperature is given) for 10 min; for the thiadimethinemerocyanine (II, n = 1, R = H), at 140° C for 15 min; for the α-ethoxythiadimethinemerocyanine (II, n = 1; R = OC_2H_5), at 140° C for 10 min; for the α-methylthiadimethinemerocyanine (II, n = 1, R = CH_3), at 130° C for 15 min; and, finally, for α-ethylaminothiadimethinemerocyanine (II, n = 1, R = NHC_2H_5), at 130° C for 10 min. The quaternary salts obtained were washed with absolute ether and were used for the synthesis of the dimerocyanines without isolation.

Synthesis of the dimerocyanines. The dimerocyanines were obtained by condensing 0.001 mole of one of the above-mentioned quaternary salts with 0.001 mole of 3-ethyl-4-oxo-thiazolidine-2-thione or one of its ethylidene derivatives III. In all cases, the dyes that deposited on cooling were filtered off and purified by being boiled with 100–300 ml of ethanol (2–3 times). The purity of the products obtained was checked by chromatography on activated alumina. The conditions of condensation and the yields, melting points, and analyses of the dyes are given in the table.

3-Ethyl-5-(3'-ethyl-2'-benzothiazolinylidene)-2-(3"-ethyl-4"-oxo-2"-thioxo-5"-thiazolidinylidene-α"-ethylaminoethylidene)-4-thiazolidinone (table, 8). A mixture of 0.52 g (0.001 mole) of 3-ethyl-5-(3'-ethyl-2'-benzothiazolinylidene)-2-(3"-ethyl-4"-oxo-2"-thioxo-5"-thiazolidinylidene-α"-ethoxyethylidene)-4-thiazolidinone, 10.4 ml of 33% ethanolic ethylamine, and 5 ml of absolute ethanol was heated in the boiling water bath for 2 hr and was left overnight. On the following day, the precipitate was filtered off and washed on the filter with ethanol. Yield 0.46 g. For purification, the dye was boiled with ethanol (2 × 50 ml).

3-Ethyl-5-(3'-ethyl-2'-benzothiazolinylideneethylidene)-2-(3"-ethyl-4"-oxo-2"-thioxo-5"-thiazolidinylidene-α"-ethylaminoethylidene)-4-thiazolidinone (table, 12). A mixture of 0.54 g (0.001 mole) of 3-ethyl-5-(3'-ethyl-2'-benzothiazolidinylideneethylidene)-2-(3"-ethyl-4"-oxo-2"-thioxo-5"-thiazolidinylidene-α"-ethoxyethylidene)-4-thiazolidinone, 12 ml of 29% ethanolic ethylamine, and 5 ml of absolute ethanol was heated in the boiling water bath for 40 min and was left overnight. On the following day the precipitate was filtered off and washed with ethanol. Weight 0.5 g, mp 227° C. After purification by boiling with ethanol (60 ml): mp 228° C, weight 0.38 g. To remove a contaminating dye forming a blue band on alumina, the product was chromatographed on alumina in benzene solution. Yield 0.34 g.

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