INVESTIGATIONS IN THE FIELD OF POLYMEROCYANINES

II. Dimerocyanine Dyes that are Derivatives of 3-Alkylrhodanines*

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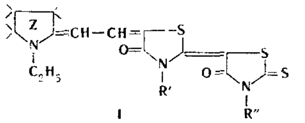
Dimerocyanines containing rhodanine residues with an alkyl or a substituted alkyl group on the nitrogen atom have been synthesized. The influence of these substituents on the color and photo properties of these dimerocyanines and their solubility in ethanol has been studied.

We have previously shown [1–3] that dimethine-zero-methinedimerocyanines that are derivatives of 3-ethylrhodanine, in particular those containing residues of aryl-substituted thiazoles, are extremely effective sensitizers of silver halide emulsions. However, the very low solubility of these dyes in ethanol interferes with their study and practical utilization. It might be assumed that the solubility of these dyes, like that of the dimethinemerocyanines [4, 5], could be increased by introducing onto the nitrogen atoms of the rhodanine residues higher hydrocarbon radicals, either unsubstituted or containing polar substituents.

In this connection it is extremely important that the substituent introduced should not exert an adverse effect on the sensitizing capacity of the dye.

In the present work, in order to obtain ethanol-soluble dimerocyanines we synthesized dyes of the general formula I containing on the nitrogen atoms of the rhodanine nuclei n-butyl, n-amyl, n-heptyl, alkoxy, or alkoxycarbonylalkyl groups. The absorption spectra of these dyes were measured and their photographic properties were studied.



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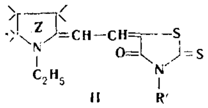

II

Z = Nitrogen-containing heterocycle

R′ and R″ = n-C_4H_9, n-C_5H_{11}, n-C_7H_{15}, $(CH_2)_2OCOC_2H_5$, $(CH_2)_3OCOC_2H_5$ or $(CH_2)_nCOOR'''$, where $n = 2$ or 5; R‴ = H, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9.

The dyes I were synthesized by a known method [2] from the dimethinecyanine dyes II, which were converted by heating with dimethyl sulfate into quaternary salts, the latter then being condensed with the corresponding 3-substituted rhodanines.

The influence of the substituents mentioned on solubility, coloration, and photo properties was studied on the dimerocyanine dyes derived from 4,5-diphenylthiazole (Table 1).

As can be seen from the figures in these tables, the attachment of higher hydrocarbon radicals or acyloxylalkyl groups to the nitrogen atoms of the oxomethylene residues considerably increases the solubility of the dimerocyanines in ethanol and has little effect on their color and zone of sensitization. The greatest solubility is achieved by the introduction of two n-heptyl groups.

The dye with a n-amyl group on the nitrogen atom of the terminal rhodanine residue has a similar sensitizing action of the ethyl derivative. With a further increase in the molecular weight of the alkyl groups and in the number of them in the molecule of the dye, the sensitizing action gradually decreases, and the dye with two n-heptyl groups has practically no sensitizing action on a silver halide emulsion. The attachment of a β-propionyloxyethyl or a γ-propionyloxypropyl group to the nitrogen atom of the terminal rhodanine residue leads to a considerable decrease in sensitizing action.

An alkoxylcarbonyl group in a hydrocarbon radical causes a marked increase in solubility (compare dyes 3 and 13 and 4 and 14).

It is interesting that the attachment of ω-alkoxycarbonylalkyl substituent to the nitrogen atom of the terminal rhodanine residue has a great influence on the solubility (compare dyes 11 and 13).

With respect to their absorption maxima and their photographic properties, the dimerocyanines with ω-alkoxycarbonylalkyl groups on the nitrogen atoms do not differ from the corresponding N-ethyl derivatives.

Similar characteristics are found for the dimerocyanine dyes derived from other nitrogen-containing heterocycles (Table 2).

EXPERIMENTAL

2-(γ-Hydroxypropyl)rhodanine was obtained in a similar manner to 3-(β-hydroxyethyl)rhodanine [6] from 15 g of γ-propanolamine (0.2 mole) and 22.6 g (0.1 mole) of bis(carboxylmethyl) trithiocarbonate. Yield 22g (79%) in the form of a yellow viscous oil. Found, %: N 7.05, 7.19. Calculated for $C_6H_9NO_2S_2$, %: N 7.33.

3-(β-Propionyloxylethyl)rhodanine. A mixture of 8 g (0.045 mole) of 3-(β-hydroxyethyl)rhodanine and 11.7 g (0.09 mole) of propionic anhydride was heated in the water bath for 1 hr and was then distilled in vacuum, a fraction with bp 160°–170° C (4 mm) being collected. Yield 2.25 g (21%), in the form of a yellow viscous oil readily soluble in ethanol, benzene, and ether. Found, %: N 6.09, 6.13. Calculated for $C_8H_{11}NO_3S_2$, %: N 6.22.

3-(γ-Propionyloxypropyl)rhodanine was obtained in a manner similar to that of the preceding compound from 8.6 g (0.045 mole) of 3-(γ-hydroxypropyl)rhodanine and 11.7 g (0.09 mole) of propionic anhydride. Yield 2.5 g (23%), bp 145°–150° C (4 mm) in the form of a dark yellow viscous oil, readily soluble in ethanol, benzene, and ether. Found, %: N 5.67, 5.81. $C_9H_{13}NO_3S_2$, %: N 5.89.

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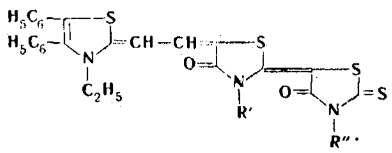
*For part I, see [2].

Table 1

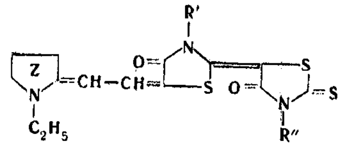


No.	R′	R″	Mp, °C	Solubility in boiling ethanol, ml/g of dye	λ_{max} (in ethanol), nm	Empirical formula	N, % found	N, % calculated	Yield, %
1	C_2H_5	C_2H_5	—	Very sparingly soluble	603[1]	—	—	—	—
2	n-C_4H_9	n-C_4H_9	—	2800	603[1]	—	—	—	—
3	n-C_4H_9	n-C_5H_{11}	252—254	2500	605	$C_{34}H_{37}N_3O_2S_4$	6.32 6.37	6.48	53
4	n-C_5H_{11}	n-C_5H_{11}	220	1400	605	$C_{35}H_{39}N_3O_2S_4$	6.15 6.27	6.34	48
5	n-C_4H_9	n-C_7H_{15}	215—216	1200	605	$C_{36}H_{41}N_3O_2S_4$	6.04 6.33	6.21	49
6	n-C_7H_{15}	n-C_7H_{15}	185	500	605	$C_{39}H_{47}N_3O_2S_4$	5.81 6.09	5.85	72.5
7	n-C_4H_9	$(CH_2)_2OCOC_2H_5$	212—215	1150	602	$C_{34}H_{35}N_3O_4S_4$	6.31 6.40	6.20	20.6
8	n-C_4H_9	$(CH_2)_3OCOC_2H_5$	218—220	1150	602	$C_{35}H_{37}N_3O_4S_4$	6.07 6.22	6.08	21.5
9	n-C_4H_9	n-$C_7H_9OOC(CH_2)_2$	200—201	1500	602	$C_{36}H_{39}N_3O_4S_4$	6.16 6.05	6.03	60
10	n-C_4H_9	i-$C_4H_9OOC(CH_2)_2$	224—225	1400	602	$C_{36}H_{39}N_3O_4S_4$	6.18 6.23	6.03	68.8

Table 1 (Cont'd)

No.	R′	R″	Mp, °C	Solubility in boiling ethanol, ml/g of dye	λ_{max} (in ethanol), nm	Empirical formula	N, %		Yield, %
							found	calculated	
11	$C_2H_5OOC(CH_2)_5$	*n*-C_4H_9	190—191	750	601	$C_{37}H_{41}N_3O_4S_4$	5.61 5.68	5.83	85.3
12	C_2H_5	$C_2H_5OOC(CH_2)_5$	150—182	300	602	$C_{35}H_{37}N_3O_4S_4$	6.11 6.34	6.08	57.1
13	*n*-C_4H_9	$C_2H_5OOC(CH_2)_5$	177—178	200	604	$C_{37}H_{41}N_3O_4S_4$	5.84 5.92	5.83	69.5
14	$C_2H_5OOC(CH_2)_5$	$C_2H_5OOC(CH_2)_5$	124—126	150	602	$C_{41}H_{47}N_3O_6S_4$	5.49 5.38	5.22	76.3
15	C_2H_5	*n*-$C_4H_9OOC(CH_2)_5$	176—178	130	601	$C_{37}H_{41}N_3O_4S_4$	5.79 5.61	5.83	54.2
16	*n*-$C_4H_9OOC(CH_2)_5$	$C_2H_5OOC(CH_2)_5$	119—120	120	603	$C_{43}H_{51}N_3O_6S_4$	5.11 5.15	5.03	50
17	*n*-C_4H_9	*n*-$C_3H_7OOC(CH_2)_5$	157—158	80	602	$C_{38}H_{43}N_3O_4S_4$	5.84 5.77	5.98	65.8
18	*n*-C_4H_9	*i*-$C_3H_7OOC(CH_2)_5$	140—142	70	602	$C_{38}H_{43}N_3O_4S_4$	5.77 5.90	5.98	61.6
19	*n*-C_4H_9	*n*-$C_4H_9OOC(CH_2)_5$	170—172	70	601	$C_{39}H_{45}N_3O_4S_4$	5.78 5.88	5.65	62.6
20	*n*-$C_4H_9OOC(CH_2)_5$	*n*-$C_4H_9OOC(CH_2)_5$	167—168	70	603	$C_{45}H_{55}N_3O_6S_4$	4.95 5.00	4.87	69.5

Table 2



Heterocyclic residue Z	R′	R″	Mp, °C	Solubility in boiling ethanol, ml/g of dye	λ_{max} (in ethanol), nm	Empirical formula	N, % found	N, % calculated	Yield, %
Benzoxazoyl	C_2H_5	$C_2H_5OCO(CH_2)_5$	175	3400	546 (538)*	$C_{27}H_{31}N_3O_5S_3$	7.60; 7.63	7.32	66.2
2-Quinolyl			213	2300	613, 575 (614, 575)	$C_{29}H_{33}N_3O_4S_3$	7.45; 7.57	7.20	69.7
4-Quinolyl			233	2050	633, 613 (617, 664)	$C_{29}H_{33}N_3O_4S_3$	7.46; 7.29	7.20	46.2
Benzothiazolyl			231	2050	572 (575)	$C_{27}H_{31}N_3O_4S_4$	7.13; 7.23	7.13	44.1
Thiazolyl			224—225	650	589 (—)	$C_{23}H_{29}N_3O_4S_4$	7.81; 7.62	7.78	37
Thiazolinyl			220	640	535 (538)	$C_{23}H_{31}N_3O_4S_4$	7.85; 7.83	7.76	48.8
4-Phenylthiazolyl			194	450	589 (591)	$C_{29}H_{33}N_3O_4S_4$**	—	—	55.2
4-Methylthiazolyl			193—194	150	595 (—)	$C_{24}H_{31}N_3O_4S_4$	7.08; 7.06	7.21	25.8
3,3-Dimethylindoleninyl			178	140	556 (556)	$C_{30}H_{37}N_3O_4S_3$	6.94; 6.88	7.01	40
2-Pyridyl			210	120	602 (596)	$C_{25}H_{31}N_3O_4S_3$	7.88; 8.05	7.87	64
5-Ethoxycarbonyl-4-methylthiazolyl			164—165	100	587 (—)	$C_{27}H_{35}N_3O_6S_4$	6.97; 6.83	6.70	84.7
4-Phenylthiazolyl	n-C_4H_9	i-$C_3H_7OCO(CH_2)_5$	170	200	590 (591)	$C_{32}H_{39}N_3O_4S_4$	6.21; 6.25	6.38	45.6

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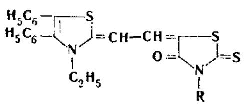
*The absorption maxima of the 3-ethyl-substituted dimerocyanines (R′ and R″ = C_2H_5) are given in brackets [2].

**Found, %: S 20.64, 20.82. Calculated, %: S 20.81.

Table 3



R	Mp, °C	Solubility in boiling ethanol, ml/g of dye	λ_{max}, nm*	Empirical formula	N, %		Yield, %
					found	calculated	
$(CH_2)_2COOH$	184—185	300	552	$C_{25}H_{22}N_2O_3S_3$	5.32; 5.48	5.66	53
$(CH_2)_5COOH$	216—217	200	552	$C_{28}H_{28}N_2O_3S_3$	5.21; 5.29	5.21	44.4
$(CH_2)_2COOC_2H_5$	139—140	200	552	$C_{27}H_{26}N_2O_3S_3$	5.50; 5.64	5.85	62.2
$(CH_2)_2COOC_4H_9$-*n*	114—116	50	552	$C_{29}H_{30}N_2O_3S_3$	4.95; 5.12	5.08	65.4
$(CH_2)_2COOC_4H_9$-*i*	128—130	70	552	$C_{29}H_{30}N_2O_3S_3$	5.22; 5.16	5.08	54.5
$(CH_2)_5COOC_2H_5$	106—107	100	552	$C_{30}H_{32}N_2O_3S_3$	5.02; 5.17	4.95	42.8
$(CH_2)_5COOC_4H_9$-*n*	115—117	60	552	$C_{32}H_{35}N_2O_3S_3$	4.82; 5.00	4.72	57.6
n-C_7H_{15}	155—156	120	553	$C_{29}H_{32}N_2O_3S_3$	5.45; 5.59	5.38	40.4

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*For the 3-ethyl-substituted dimethylmerocyanine (R = C_2H_5), λ_{max} 553 nm.

The dimethylmerocyanines II that were derivatives of 4, 5-diphenylthiazole were obtained by condensing 0.001 mole of the diethyl sulfate derivative of 2-β-anilinovinyl-4, 5-diphenylthiazole with 0.001 mole of one of the appropriate N-substituted rhodanines [7, 8] in acetic anhydride (4 ml) in the presence of 0.003 mole of triethylamine with 30 minutes heating in the boiling water bath.

The dyes were purified by crystallization from ethanol. The yields of the dyes, their properties, and their analyses are given in Table 3. The other merocyanines required for the synthesis of the dimerocyanines have been described previously [9].

3-n-Amyl-5-(3'-ethyl-4', 5'-diphenyl-2'-thiazolinylideneethylidene)-4-oxothiazolidine-2-thione. A mixture of 1 g (0.004 mole) of 2-methyl-4, 5-diphenylthiazole and 0.64 ml (0.048 mole) of diethyl sulfate was heated at 130° C for 30 min. To the resulting quaternary salt were added 1.24 g (0.004 mole) of 3-n-amyl-5-anilinomethylenerhodanine, 8 ml of acetic anhydride, and 1.68 ml (0.012 mole) of triethylamine, and heating was continued at 100° C for another 20 min. The solidifying reaction mixture was diluted with 8 ml of ethanol and left overnight in the refrigerator. Yield 1 g (51%), mp 159°–160° C. After crystallization from ethanol (1 g from 140 ml) it formed fine purple needles with mp 162°–163° C. Weight 0.75 g. Found, %: N 5.71, 5.55. Calculated for $C_{27}H_{28}N_2OS_3$, %: N 5.68.

The dimerocyanines I that were derivatives of 3-alkyl- and 3-acyloxyalkylrhodanines were obtained by condensing 0.001 mole of a quaternary salt of a merocyanine [2] with 0.001 mole of rhodanine in 3 ml of pyridine with boiling for 10 min. The corresponding derivatives of 3-(ω-alkoxycarbonylalkyl)rhodanines were obtained by heating 0.001 mole of one of the above-mentioned quaternary salts with 0.001 mole of rhodanine in pyridine (4 ml) in the presence of 0.001 mole of triethylamine at 105°–110° C for 20 min. In all cases, the solidified reaction mixture was diluted with 3–4 ml of ethanol and left in the refrigerator overnight. The crystals that deposited were filtered off and recrystallized from ethanol. The yields, properties, and analyses of the dyes are given in Tables 1 and 2.

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