RESEARCH ON POLYMEROCYANINES

V.* DIMEROCYANINES WITH VARIOUS TERMINAL KETOMETHYLENE RESIDUES

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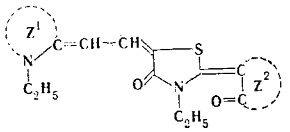
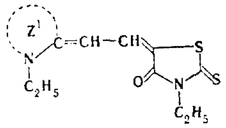
A number of dimethylidynenullomethylidynedimerocyanines that are derivatives of 1-methyl-2-thioketo-3-ethylimidazolidin-4-one, 2-thioketo-3-n-butyloxazolidin-4-one, and 1-phenyl-3-methylpyrazol-5-one were synthesized. The color of the dyes depends on the acidity of the terminal ketomethylene residue. The most effective sensitizers are dimerocyanines that are derivatives of 4,5-diphenylthiazole with terminal residues of 2-thioketo-3-alkylthiazolidin-4-ones.

We have previously described the properties of dimethylidynenullomethylidynedimerocyanines that are derivatives of 2-thioketo-3-alkylthiazolidin-4-one with various nitrogen-containing heterocyclic residues [2, 3]. It seemed of interest to study the effect of the nature of the terminal ketomethylene residues, particularly their acidities [4], on the color and sensitizing ability of dimerocyanines. The literature data on dimerocyanines of this sort are limited primarily to patent data [5-10], on the basis of which it is not possible to draw any conclusions regarding the relationship between the properties of these dyes and their structures.

In the present research we obtained dimethylidynenullomethylidynedimerocyanines (I) that are derivatives of 1-methyl-2-thioketo-3-ethylimidazolidin-4-one, 2-thioketo-3-n-butyloxazolidin-4-one, and 1-phenyl-3-methyl-5-pyrazolone. The synthesis of dimerocyanines I was accomplished by a known method [3] starting from the corresponding dimethylidynemerocyanines (II).

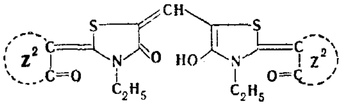


I



II

It is evident from the data in Table 1 that in the case of derivatives of the slightly basic 3,3-dimethylindolenine that the color deepens somewhat as the acidity of the terminal ketomethylene residue (Z^2) increases. Deepening followed by an increase in the coloration occurs in the case of dyes with more basic benzothiazole, 4,5-diphenylthiazole, and pyridine residues as the acidity of the terminal ketomethylene ring increases. The effect of the acidity of the terminal ketomethylene residue on the color becomes more understandable if the hypsochromic shifts ($\Delta\lambda_{max}$, Table 1) for the investigated dimerocyanines I are examined. The absorption maxima of alcohol solutions of four-ring dyes III with 2-thioketo-3-ethyloxazolidin-4-one,† 2-thioketo-3-ethylthiazolidin-4-one, and 1-phenyl-3-methyl-5-pyrazolone residues necessary for the calculation of the hypsochromic shifts are found at 633, 650 [3], and 616 nm, whereas the absorption maxima of alcohol solutions of



III

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* See [1] for communication IV.

† Replacement of the C_2H_5 group by $n\text{-}C_4H_9$ does not affect the position of the absorption maximum.

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TABLE 1. Absorption Maxima and Hypsochromic Shifts ($\Delta\lambda_{max}$) of Alcohol Solutions of Dimerocyanines I*

Z^2 Z^1	2-Thioketo-3-n-butyl-4-oxazolidon-5-ylidene		1-Methyl-2-thioketo-3-ethyl-4-imidazolidon-5-ylidene	2-Thioketo-3-ethyl-4-thiazolidon-5-ylidene [2, 3]		1-Phenyl-3-methyl-5-oxopyrazol-4-ylidene	
	λ_{max}, nm	$\Delta\lambda_{max}$, nm	λ_{max}, nm	λ_{max}, nm	$\Delta\lambda_{max}$, nm	λ_{max}, nm	$\Delta\lambda_{max}$, nm
1-Ethyl-3,3-dimethyl-2-indolenylidene	543	47,5	553	556	43	555	26
3-Ethylbenzo-2-thiazolinyl.	556	39,5	580	575	29	574	13
3-Ethyl-4,5-diphenyl-2-thiazolinylidene	588†	22,5	609	603	16	599	3
1-Ethyl-1,2-dihydro-2-pyridylidene	589 (582)	9	604	596 (597)	10,5	574 (587)	15,5

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* The adsorption maxima in benzene are indicated in parentheses.

† Z^2 = 2-Thioketo-3-ethyl-4-oxazolidon-5-ylidene.

TABLE 2. Dimerocyanines I

Z^1	Z^2	mp, °C (from alcohol)	Found, %		Empirical formula	Calc., %		Yield, %
			N	S		N	S	
1-Ethyl-3,3-dimethyl-2-indolinylid.	1-Methyl-2-thioketo-3-ethyl-4-imidazolidon-5-ylidene	222	11,6	13,2	$C_{25}H_{30}N_4O_2S_2$	11,6	13,3	33
	2-Thioketo-3-n-butyl-4-oxazolidon-5-ylid.	221—222	8,4	12,8	$C_{26}H_{31}N_3O_3S_2$	8,4	12,9	42
	1-Phenyl-3-methyl-5-oxopyrazol-4-ylidene	192	11,1	6,6	$C_{29}H_{30}N_4O_2S$	11,2	6,4	32
3-Ethylbenzo-2-thiazolinylidene	1-Methyl-2-thioketo-3-ethyl-4-imidazolidon-5-ylidene	270	11,9	20,4	$C_{22}H_{24}N_4O_2S_3$	11,9	20,3	50
	2-Thioketo-3-n-butyl-4-oxazolidon-5-ylidene	246—248	8,5	19,8	$C_{23}H_{25}N_3O_3S_3$	8,6	19,7	81
	1-Phenyl-3-methyl-5-oxopyrazol-4-ylidene	253*	11,6	13,0	$C_{26}H_{24}N_4O_2S_2$	11,5	13,1	61
3-Ethyl-4,5-diphenyl-2-thiazolinyl.	1-Methyl-2-thioketo-3-ethyl-4-imidazolidon-5-ylidene	200	9,8	16,9	$C_{30}H_{30}N_4O_2S_3$	9,8	16,7	51
	2-Thioketo-3-ethyl-4-oxazolidon-5-ylidene	269*	7,3	17,0	$C_{29}H_{27}N_3O_3S_3$	7,5	17,1	64
	1-Phenyl-3-methyl-5-oxopyrazol-4-ylidene	158	9,6	10,9	$C_{34}H_{30}N_4O_2S_2$	9,5	10,8	40
1-Ethyl-1,2-dihydro-2-pyridylidene	1-Methyl-2-thioketo-3-ethyl-4-imidazolidon-5-ylidene	215—217	13,7	15,5	$C_{20}H_{24}N_4O_2S_2$	13,5	15,4	39
	2-Thioketo-3-n-butyl-4-oxazolidon-5-ylid.	240	9,8	14,7	$C_{21}H_{25}N_3O_3S_2$	9,7	14,8	52
	1-Phenyl-3-methyl-5-oxopyrazol-4-ylidene	247	12,7	7,4	$C_{24}H_{24}N_4O_2S$	13,0	7,4	64

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* The dye was purified by refluxing with ethanol.

symmetrical indo-, thia-, 4,5-diphenylthiazolo-, and pyridocarbocyanines are found at 548 [3], 558 [3], and 563 [3], respectively.

As expected, the hypsochromic shifts decrease as the basicities or acidities of the terminal heteroresidues increase. Pyridine derivatives in which the hypsochromic shift increases as the acidity of the terminal ketomethylene group increases constitute an exception to this. In this connection, it was of interest to study the behavior of 2-substituted pyridine derivatives in solvents with different polarities. It might have been expected that the structure of the 2-substituted pyridine derivatives with a terminal pyrazolone residue would be closer to dipolar and that in this case negative solvatochromism should be displayed. As seen from Table 1, this is actually the case. In the case of the dimerocyanine with a weakly acidic 2-thioketo-3-n-butyloxazolidin-4-one ring the color in alcohol is 7 nm deeper than in benzene; this constitutes evidence that its molecular structure is closer to covalent. The electron density distribution in the chromophore becomes more uniform as the acidity of the terminal ketomethylene residue increases further. However, in the case of the most acidic 1-phenyl-3-methyl-5-pyrazolone the uniformity of the electron-density distribution again is disrupted, and the structure of the dye approaches the dipolar ion form, in connection with which it displays negative solvatochromism.

Of the examined dyes, the most effective sensitizers are dimerocyanines that are 4,5-diphenylthiazole derivatives with terminal 2-thioketo-3-ethylthiazolidin-4-one [11] and 2-thioketo-3-n-butyloxazolidin-4-one residues. Replacement of the terminal 2-thioketo-3-ethylthiazolidin-4-one ring by the 1-methyl-2-thioketo-3-ethylimidiazolidin-4-one ring leads to a sharp decrease in the sensitizing effect, and 1-phenyl-3-methyl-5-pyrazolone derivatives do not have sensitizing ability at all; this is evidently associated with the high tendency of these dyes to form photographically slightly active H aggregates on the silver halide surface.

EXPERIMENTAL

Quaternary Salts of Dimethylidynemerocyanines (2-Methylthiothiazolin-4-one Derivatives). These compounds were obtained by the method in [3].

Dimerocyanines (I, Table 2). A 1 mmole sample of the above-indicated quaternary salts was heated with 1 mmole of the corresponding ketomethylene compound in 3 ml of pyridine in the presence of triethylamine (0-16 ml) at 130-140°C (in the bath) for 10.15 min, after which the mixture was diluted with 3 ml of ethanol and cooled. The precipitated dyes were crystallized from ethanol. The purity of the products was monitored by chromatography on aluminum oxide.

3-Ethyl-4-hydroxy-2-(1-phenyl-3-methyl-5-oxopyrazol-4-ylidene)-5-[3-ethyl-2-(1-phenyl-3-methyl-5-oxopyrazol-4-ylidene)-4-thiazolidon-5-ylidenemethylene]thiazoline (III, Z^2 = 1-Phenyl-3-methyl-5-oxopyrazol-4-ylidene). A mixture of 0.44 g (1 mmole) of the triethylamine salt of 2-thioketo-3-ethyl-5-(2-thioketo-3-ethyl-4-hydroxythiazolin-5-ylmethylene)-4-thiazolidone (IV) and 0.64 ml (6 mmole) of dimethyl sulfate was heated at 135-140° for 15 min, after which the resulting quaternary salt was washed with 15 ml of dry ether and mixed with 0.36 g (2 mmole) of 1-phenyl-3-methyl-5-pyrazolone and 3 ml of pyridine, and the mixture was heated at 130-135°C for 60 min. It was then allowed to stand at room temperature. After 16 h, the pyridine was removed by vacuum distillation, the residue was refluxed with 17 ml of ethanol, and the mixture was allowed to stand overnight in a refrigerator. The precipitate was removed by filtration and washed with ether to give 0.48 g (81%) of a product with mp 228-230°C. Found: N 13.6; S 10.5%. $C_{31}H_{28}N_6O_4S_2$. Calculated: N 13.7; S 10.5%.

Triethylamine Salt of 3-Ethyl-4-hydroxy-2-(2-thioketo-3-ethyl-4-oxazolidon-5-ylidene)-5-[3-ethyl-2-(2-thioketo-3-ethyl-4-oxazolidon-5-ylidene)-4-thiazolidon-5-ylidenemethylene]thiazoline (III, Z^2 = 2-Thioketo-3-ethyl-4-oxazolidon-5-ylidene). A 0.28-g (2 mmole) sample of 2-thioketo-3-ethyloxazolidin-4-one, 4 ml of pyridine, and 0.32 ml (~2 mmole) of triethylamine were added to 1 mmole of the quaternary salt IV obtained as indicated above, and the mixture was heated at 130°C for 60 min. After 16 h, the mixture was diluted with 90 ml of benzene, and the resulting precipitate was removed by filtration and washed with alcohol and ether to give 0.18 g (27.5%) of a product with mp 208-210° (from ethanol, 1 : 140) in the form of fine dark-green crystals. Found: N 10.6; S 19.5%. $C_{27}H_{37}N_5O_6S_4$. Calculated: N 10.7; S 19.5%.

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