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RESEARCH ON POLYMEROCYANINES

IV.* SOME NULLOMETHYLIDYNEDIMETHYLIDYNE- AND BIS(NULLOMETHYLIDYNE)DIMEROCYANINE DYES

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UDC 547.789.3.5:668.819.45

A number of bis(nullomethylidyne)- and nullomethylidynedimethylidynedimerocyanines that are rhodanine derivatives with 3,3-dimethylindolenine, benzothiazole, 4,5-diphenylthiazole, and pyridine residues were obtained. The color of the dimerocyanines depends on the basicity of the nitrogen-containing heterocyclic residue and the length and position of the external polymethine chain. A sharp increase in the sensitizing ability is observed on passing from nullomethylidynedimethylidynedimerocyanines to dimethylidynenullomethylidynedimerocyanines.

We have previously investigated the dependence of the color and sensitizing ability of dimerocyanine dyes on the nature and relative basicity of nitrogen-containing heterocyclic residues [2, 3] and electron-donor substituents in the α and α' positions of the polymethine chain [1]. It seemed of interest to ascertain the dependence of the indicated properties on the length and position of the external polymethine chain. With this end in mind we obtained bis(nullomethylidyne)- (I) and nullomethylidynedimethylidynedimerocyanines (II). The cor-

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[*] See [1] for communication III.

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1209-1212, September, 1977. Original article submitted June 20, 1976.

0009-3122/77/1309-0975$07.50

TABLE 1. Absorption Maxima (nm) of Alcohol Solutions of Dimerocyanines I–IV

Z	R		R'*		I	II	III[2,3]	IV[2,3]
	I	II	I	II				
1,Ethyl-3,3-dimethyl-2-indol.	C_2H_5	C_2H_5	C_2H_5	C_2H_5	487	550	556	596
3-Ethylbenzo-2-thiazolinylidene	C_2H_5	C_2H_5	$(CH_2)_5COOC_3H_7$-iso	C_2H_5	491	565	575	614
3-Ethyl-4,5-diphenyl-2-thiazolinylidene	C_4H_9	C_4H_9	$(CH_2)_5COOC_3H_7$-iso	C_2H_5	504	587	603	643
1-Ethyl-1,2-dihydro-2-pyridylidene	C_2H_5	C_2H_5	C_4H_9	C_2H_5	524	608	596	650

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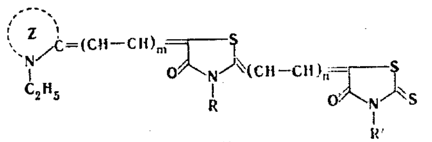
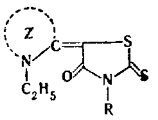
*For dimerocyanines III and IV R = R' = C_2H_5.

responding dimethylidynenullomethylidyne- (III) and bis(dimethylidyne)dimerocyanines (IV) were previously synthesized in [2, 3]. Dimerocyanines I and II were obtained by a known method [3] by heating nullomethylidynemerocyanines (V) with dimethyl sulfate and subsequent condensation of the resulting quaternary salts with 2-thioketo-3-alkylthiazolidin-4-one or 2-thioketo-3-ethyl-5-ethylidenethiazolidin-4-one.


I–IV


V

I $m=n=0$; II $m=0$, $n=1$; III $m=1$, $n=0$; IV $m=n=1$; $R=R'=C_2H_5$, C_4H_9, $(CH_2)_5COOC_3H_7$-i; Z — 3,3-dimethylindolenine, benzothiazole, 4,5-diphenylthiazole, and pyridine residues

As seen from Table 1, the color of dimerocyanines I and II becomes deeper as the basicity of the nitrogen-containing heterocyclic residue (Z) increases. As expected, a bathochromic shift of the absorption maximum, the magnitude of which, however, depends on the position of the external polymethine chain, occurs when the polymethine chain of dimerocyanines I is lengthened by one vinylene group in the left or right portion of the molecule. Thus a somewhat greater deepening of the color occurs when the polymethine chain in the left portion of the molecule of the dimerocyanines I is lengthened. An exception to this is found in the case of 2-pyridyl derivatives, in which case II is 12 nm more deeply colored than the corresponding III. Further lengthening of the polymethine chain on passing from dimerocyanines II and III to dimerocyanines IV gives rise to considerably less deepening of the color. The attenuation of the vinylene shift that is observed in this case has also been previously noted in a number of merocyanines with a 2-thioketo-3-ethylthiazolidin-4-one residue on passing from di- to tetra- and hexamethylidyne derivatives [4, 5].

In contrast to III, which are active panchromatic sensitizers [2, 3], the effectiveness of their vinylene analogs (IV) is low. It is known that a decrease in the effectiveness of the sensitizing action of dyes as the length of the external polymethine chain increases also occurs in the series of cyanine and merocyanine dyes, in which trimethylidynecyanines and dimethylidynemerocyanines, as a rule have the maximum sensitizing effect [4, 6-8]. The change in the position of the external polymethine chain on passing from III to II leads to a sharp decrease in the sensitizing ability. As compared with the corresponding nullomethylidynedimethylidynedimerocyanines II, bis(nullomethylidyne)dimerocyanines I have considerably greater effectiveness and are rather active orthochromatic sensitizers.

EXPERIMENTAL

2-Thioketo-3-ethyl-5-(1-ethyldihydro-2-pyridylidene)thiazolidin-4-one. A mixture of 0.56 g (4 mmole) of 1-ethyl-2-thiapyridone and 0.6 ml (4.8 mmole) of diethyl sulfate was heated at 120-130°C (in a bath) for 2 h, and the resulting quaternary salt was washed with absolute ether (three 5-ml portions) and mixed with 0.64 g (4 mmole) of 2-thioketo-3-ethylthiazolidin-4-one, 3 ml of pyridine, and 1.68 ml of triethylamine. After 16 h, the solvent was removed by vacuum distillation, and the residue was refluxed with 3 ml of ethanol. The mixture was then allowed to stand overnight, and the precipitate was removed by filtration and washed with ethanol to give 0.78 g (72%) of a product with mp 147°C. Crystallization from ethanol (1 : 10) gave shiny dark-orange leaflets with mp 149°C. Found: N 10.5; S 24.0%. $C_{12}H_{14}N_2OS_2$. Calculated: N 10.5; S 24.1%.

TABLE 2. Dimerocyanines I and II

Z	R	R′	n	Appearance*	mp, °C	Found, %		Empirical formula	Calc., %		Yield, %
						N	S		N	S	
1-Ethyl-3,3-dimethyl-2-indolinylidene	C_2H_5	C_2H_5	0	Small bright-orange needles (135)	277–278	9,1	21,0	$C_{22}H_{25}N_3O_3S_3$	9,2	20,9	52
3-Ethylbenzo-2-thiazolinylidene	C_2H_5	$(CH_2)_5COOC_3H_7$-*i*	0	Light-orange powder	261–262	7,2	22,2	$C_{26}H_{31}N_3O_4S_4$	7,3	22,2	62
3-Ethyl-4,5-diphenyl-2-thiazolinylidene	C_4H_9	$(CH_2)_5COOC_3H_7$-*i*	0	Light-orange powder (110)	183	5,9	18,1	$C_{36}H_{41}N_3O_4S_4$	5,9	18,1	80
1-Ethyl-1,2-dihydro-2-pyridylidene	C_2H_5	C_4H_9	0	Small red needles (200)	221	10,1	22,6	$C_{19}H_{23}N_3O_2S_3$	10,0	22,8	71
1-Ethyl-3,3-dimethyl-2-indolinylidene	C_2H_5	C_2H_5	1	Dark-brown needles	227	8,6	19,7	$C_{24}H_{27}N_3O_2S_3$	8,7	19,8	43
3-Ethylbenzo-2-thiazolinylidene	C_2H_5	C_2H_5	1	Black powder	313	8,8	27,0	$C_{21}H_{21}N_3O_2S_4$	8,8	26,9	42
3-Ethyl-4,5-diphenyl-2-thiazolinylidene	C_4H_9	C_2H_5	1	Small blue-green needles	260	7,1	21,0	$C_{31}H_{31}N_3O_2S_4$	6,9	21,1	82
1-Ethyl-1,2-dihydro-2-pyridylidene	C_2H_5	C_2H_5	1	Purple powder (950)	269	10,1	22,8	$C_{19}H_{21}N_3O_3S_3$	10,0	22,9	57

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* The amount of ethanol for recrystallization of the dyes is given in parentheses (in milliliters per gram); the remaining dyes were purified by refluxing with ethanol until they had constant melting points.

2-Thioketo-3-ethyl-5-(1-ethyl-3,3-dimethyl-2-indolinylidene)thiazolidin-4-one. A mixture of 0.41 g (2 mmole) of 1-ethyl-3,3-dimethyl-2-thioxindole and 0.5 ml (~5 mmole) of dimethyl sulfate was heated at 120°C (in a bath) for 90 min, and the resulting quaternary salt was washed with 15 ml of absolute ether and mixed with 0.32 g (2 mmole) of 2-thioketo-3-ethylthiazolidin-4-one, 3.5 ml of pyridine, 1.1 ml of acetic anhydride, and 0.7 ml of triethylamine. After 16 h, the solvents were removed by vacuum distillation, and the residue was treated with 3 ml of ethanol. The precipitate was removed by filtration and washed with cold alcohol to give (45%) of a product with mp 140°C. Crystallization from alcohol (1 : 15) gave fine yellow needles with mp 141°C. Found: N 8.4; S 19.1%. $C_{17}H_{20}N_2OS_2$. Calculated: N 8.4; S 19.3%.

2-Thioketo-3-butyl-5-(3-ethyl-4,5-diphenyl-2-thiazolinylidene)thiazolidin-4-one. A mixture of 1.8 g (6 mmole) of 3-ethyl-4,5-diphenylthiazolidine-2-thione and 0.9 ml (7.2 mmole) of diethyl sulfate was heated at 120-130°C (in a bath) for 2 h, and the resulting quaternary salt was washed with absolute ether and mixed with 1.14 g (6 mmole) of 2-thioketo-3-butylthiazolidin-4-one, 20 ml of absolute ethanol, and 0.96 ml of triethylamine, and the mixture was refluxed for 10 min and allowed to stand overnight in a refrigerator. The resulting precipitate was removed by filtration and washed with alcohol to give 1.96 g (69.5%) of a product with mp 196-197°C. Crystallization from alcohol (1 : 170) gave fine light-yellow needles with mp 198°C. Found: N 6.1; S 21.3%. $C_{24}H_{24}N_2OS_3$. Calculated: N 6.2; S 21.2%.

Quaternary nullomethylidynemerocyanine salts of V were obtained by heating 1 mmole of the corresponding nullomethylidynecyanine V with 3 mmole of dimethyl sulfate at 120-130°C (in a bath) for 10.15 min.

Dimerocyanines I and II (Table 2). These dyes were obtained by heating 1 mmole of the corresponding quaternary salt with 1 mmole of 2-thioketo-3-ethyl-5-ethylidenethiazolidin-4-one in pyridine in the presence of 1 mmole of triethylamine at 130-140°C (in a bath) for 15 min. At the end of the heating period, the mixture was diluted with 3 ml of alcohol, and the mixture was allowed to stand in a refrigerator for 16 h. The precipitated crystals were washed on the filter with ethanol and crystallized from alcohol or washed by refluxing with 100-300 ml of ethanol until they had a constant melting point. Dimerocyanine II (Z = 3-ethylbenzo-2-thiazolinylidene) was obtained by heating 1 mmole of the corresponding quaternary salt with 2-thioketo-3-ethyl-5-ethylyidenethiazolidin-4-one in acetic anhydride (3 ml) in the presence of triethylamine (0.48 ml) at 100°C (in a bath) for 5 min. The purity of the compounds was monitored by chromatography on activated aluminum oxide.

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