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1,9-SUBSTITUTED FLUORENES

IV. Cyanine Dyes, Derivatives of Pyridazino [4,5,6-m,*l*]-Fluorene*

N. S. Dokunikhin and S. A. Mikhalenko

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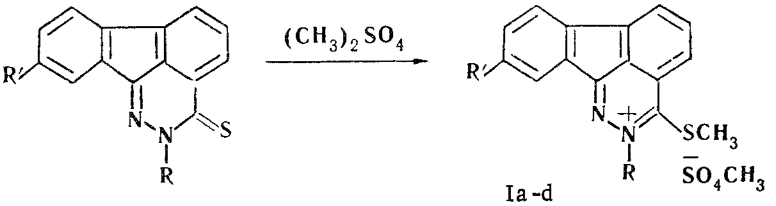
The synthesis of 2-methyl (phenyl)-2, 3H-pyridazino-[4,5,6-m-*l*] fluorene-3-methylthionium methylsulfates and of derivatives with substituents in the fluorene ring, is described. Reaction of the latter with heterocyclic hydrazones, and also with compounds containing an active methylene or methyl group, gives cyanine dyes. The electronic spectra of the dyes are measured.

It has previously been shown [1], that 2,3H-pyridazino [4,5,6-m,*l*]-fluorene-3-thione reacts with substituted 3-hydroxythionaphthenes in boiling trichlorobenzene, to give merocyanine-type dyes.

Attempts to synthesize compounds of similar structure, with the hydrogen at position 2 replaced by an alkyl or aryl group, did not meet with success. Such dyes can be obtained under mild conditions, and in high yield, by using for condensation 2-methyl (phenyl)-2,3H-pyridazino [4,5,6-m,*l*] fluorene-3-methylthionium methylsulfates (Ia-d). These latter can also be successfully used to synthesize other groups of cyanine dyes.

Compounds Ia-d are formed by treating solutions of the appropriate thiones [2] dissolved in aromatic hydrocarbons, with methyl sulfate at 110°–140° C. Some of the compounds formed (Ib, d) are obtained as tarry precipitates, and exhibit instability on standing.

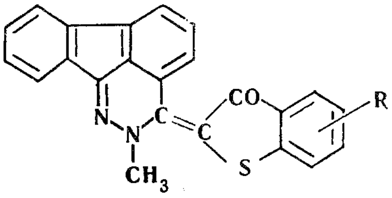


Ia-d

a) R = Me, R' = H
b) R = C_6H_5, R' = H
c) R = Me, R' = Me
d) R = Me, R' = Cl

The reaction with substituted 3-hydroxythionaphthenes takes place in methanol solution, in the presence of added triethylamine. It is of interest to note that traces of moisture (up to 0.05%) must be present for the reaction to start. Dye yields are almost theoretical.

a) R = 6-Cl
b) R = 6-OEt
c) R = 4,5-benzo-



IIa-c

When the absorption maxima for 2-methyl-3-(3-hydroxynaphthenylidene)-2,3H-pyridazino [4,5,6-m,*l*] fluorenes (IIa-c) are compared with those for the corresponding nonmethylated analogs (λ_{max} 485–510 mμ), the maximum is observed to be displaced bathochromically by 40–80 mμ (Table 1); the dyes dye polyester fiber. Under the same conditions, compounds Ia-d condense with quaternary salts of 2-methyl substituted heterocyclic bases, to give a number of

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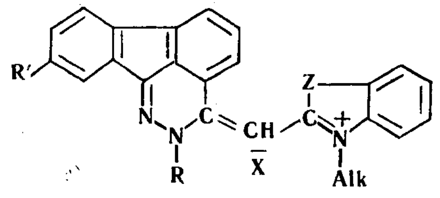
*For Part III see [3].

2, 3H-pyridazino [4, 5, 6-m, *l*] fluorenemonomethinecyanines, of general formula A.



II A I

X = I, ClO_4; Alk = Me, Et; Z = —S—; —CH=CH—, =CMe_2;

R' = H, Me, Cl; R = C_6H_5, Me

Thus, for example, reaction of Ia-b with 2-methylbenzothiazole ethiodide gives red dyes (IIIa, b). Dyes with shades close to these were formed by carrying out the condensation with 2-methylquinoline ethiodide (IVa-d), and 2, 3, 3-trimethylindolenine perchlorate (Va-c). With the exception of IIIa, the dyes formed show marked light absorption maxima. Dye IIIa gives a diffuse absorption band at 510–525 mμ (Table 2). The dyes prepared are soluble in water and ethanol, and they dye polyacrylonitrile fiber.

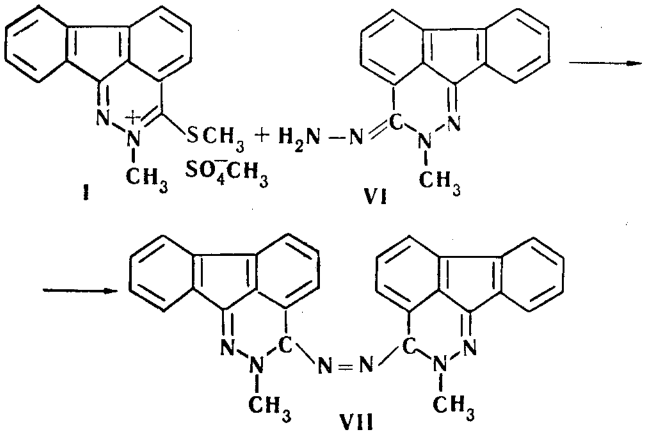


Table 1

Dye number	Mp ° C	λ_{max}, mμ	lgε	Formula	Found, %		Calculated, %		Yield, %
					N	Cl, S	N	Cl, S	
IIa	273—275 (decomp)	555	3.89	$C_{23}H_{13}ClN_2OS$	6.95 7.13	Cl 8.93 8.67	6.69	Cl 8.85	94
IIb	249—252 (decomp)	535—540	4.25	$C_{25}H_{18}N_2O_2S$	6.86 6.64	—	6.83	—	94
IIc	280—282 (ex xylene, decomp)	555—565	3.77	$C_{27}H_{16}N_2OS$	6.96 7.01	S 7.44 7.14	6.73	S 7.70	98

Heating compound Ia with heterocyclic hydrazones, e.g., 2-methyl-3-hydrazino-2, 3H-pyridazino 4, 5, 6-m, *l* fluorene (VI) gives violet bis-[2-methyl-2, 3H-pyridazino [4, 5, 6-m, *l*] fluorenyl]-3, 3'-azine (VII): λ_{max} (lg ε) (m-xylene): 520 (4.34), 545 mμ (4.36); dyes polyester fiber.

Experimental

2-Methyl-2, 3H-pyridazino [4, 5, 6-m, *l*] fluorene-3-methylthionium methylsulfate (Ia). 0.75 g 2-methyl-2, 3H-pyridazino [4, 5, 6-m, *l*] fluorene-3-thione [2], 0.86 g Me_2SO_4, and 15 ml dry toluene were refluxed together for 3 hr.

Table 2

Fluorenomethinecyanines

Dye number	Formula (A)					Mp °C (decomp)	λ_{max}, mμ (MeOH)	lgε	Formula	Found, %						Calculated, %					
	R′	R	X	Alk	Z					C	H	Cl	I	N	S	C	H	Cl	I	N	S
IIIa	H	CH_3	I	C_2H_5	S	279—280 (ex-aqueous MeOH)	510—525	4.40	$C_{25}H_{20}IN_3S$	57.06 57.40	3.91 3.83	—	24.00 23.73	8.00 7.97	6.18 6.53	57.58	3.87	—	24.34	8.04	6.15
IIIb	H	C_6H_5	I	C_2H_5	S	259—261 (ex MeOH)	520	4.12	$C_{30}H_{22}IN_3S$	—	—	—	—	7.59 7.76	5.69 5.43	—	—	—	—	7.20	5.49
IVa	H	CH_3	I	C_2H_5	—CH=CH—	261—263 (ex aqueous MeOH)	535—540	4.30	$C_{27}H_{22}IN_3$	62.81 63.08	4.45 4.48	—	24.20 24.03	8.02 8.06	—	62.92	4.30	—	24.62	8.15	—
IVb	H	C_6H_5	I	C_2H_5	—CH=CH—	244—245.5 (ex benzene-MeOH)	540	4.62	$C_{32}H_{24}IN_3$	66.64 66.34	4.25 4.19	—	21.70 22.04	—	—	66.55	4.19	—	21.98	—	—
IVc	CH_3	CH_3	I	C_2H_5	—CH=CH—	267—268	535	4.32	$C_{28}H_{24}IN_3$	—	—	—	24.46 24.26	7.70 7.89	—	—	—	—	24.03	7.96	—
IVd	Cl	CH_3	I	C_2H_5	—CH=CH—	260—261	540	4.64	$C_{27}H_{21}ClIN_3$	—	—	6.26 6.01	23.25 23.14	—	—	—	—	6.43	23.08	—	—
Va	H	CH_3	ClO_4	CH_3	$>C(CH_3)_2$	261—263 (ex MeOH)	505—510	4.36	$C_{27}H_{24}ClN_3O_4$	—	—	7.15 7.10	—	8.46 8.67	—	—	—	7.25	—	8.59	—
Vb	CH_3	CH_3	ClO_4	CH_3	$>C(CH_3)_2$	278—279 (ex benzene)	505—510	4.04	$C_{28}H_{26}ClN_3O_4$	—	—	7.46 7.32	—	—	—	—	—	7.04	—	—	—
Vc	Cl	CH_3	ClO_4	CH_3	$>C(CH_3)_2$	281—283	510	4.39	$C_{27}H_{23}Cl_2N_3O_4$	—	—	13.14 13.37	—	7.89 7.95	—	—	—	13.52	—	8.01	—

After cooling, the precipitate was filtered off, and washed first with toluene, then with petrol ether. Yield 1.13 g (practically quantitative), yellow prisms, mp 119°–124° C (decomp); readily soluble in water. Found: S 17.45, 17.23%. Calculated for $C_{17}H_{16}N_2O_4S_2$: S 17.03%.

Similarly, 0.93 g 2-phenyl-2, 3H-pyridazino [4, 5, 6-m, *l*] fluorene-3-thione [2] in o-xylene, gave 1.31 g (practically quantitative) Ib, while 0.56 g 2-methyl-9-chloro-2, 3H-pyridazino [4, 5, 6-m, *l*] fluorene-3-thione [2] gave 0.8 g (practically quantitative) Id; the compounds were unstable in the presence of moisture. 0.28 g 2, 9-Me_2-2, 3H-pyridazino-[4, 5, 6-m, *l*] fluorene-3-thione [2] in m-xylene gave 0.41 g (practically quantitative) Ic; flat yellow prisms, mp 190°–192° C (decomp); readily soluble in water. Found: N 7.03, 7.10%. Calculated for $C_{18}H_{18}N_2O_4S_2$: N 7.18%.

3-(6-Chloro-3-hydroxythionaphthylidene)-2-methyl-2, 3H-pyridazino- [4, 5, 6-m, *l*] fluorene (IIa). 1.13 g (0.0034 mole) Ia, 1.1 g (0.0037 mole) 6-chloro-3-hydroxythionaphthene, 0.57 ml (0.0041 mole) Et_3N, and 55 ml MeOH, containing a trace of water, were refluxed together for 3 hr. After cooling, the precipitate was filtered off and washed with EtOH. Yield 1.13 g (94%); violet crystals, soluble in hot xylene, slightly soluble in benzene, insoluble in EtOH.

Table 1 gives the absorption spectrum and analysis of IIa, along with the properties of the dyes similarly prepared.

[2-Methyl-2, 3H-pyridazino [4, 5, 6-m, *l*]fluorene-(3)-[3-ethylbenzothiazole-(2) monomethinecyaniniodide (IIIa). 1.06 g (0.0028 mole) Ia, 0.93 g (0.003 mole) 1-ethyl-2-methylthiazolinium iodide, 0.53 ml (0.039 mole) Et_3N, and 10 ml EtOH containing 0.03% water, were refluxed together for 3 hr. After cooling the solid was filtered off, yield 0.8 g (54%). Red crystals ex aqueous MeOH, mp 279°–280° C (decomp); dyes polyacrylnitrile fiber red, with a blue reflex.

In synthesizing IIIb, double the moles of 1-ethyl-2-methylthiazolinium iodide and 4 times the volume of EtOH were used. Dye yield 74%.

{2-Methyl-2, 3H-pyridazino [4, 5, 6-m, *l*] fluorene-(3)} -[1-ethylquinoline-(2)]-monomethinecyaniniodide (IVa). 0.97 g (0.0026 mole) Ia, 0.78 g (0.0026 mole) 1-ethyl-2-methylquinolinium iodide, 0.48 ml (0.0035 mole) Et_3N, and 15 ml EtOH containing 0.03% water, were refluxed together for 3 hr. The products were cooled, filtered, and 0.98 g (74%) product obtained, dyeing polyacrylonitrile fiber reddish-violet. Similarly boiling together Ib, 1-ethyl-2-methylquinolinium iodide and Et_3N (mole ratios 0.0022 : 0.005 : 0.003) in 50 ml EtOH for 6 hr, gave, after washing the solid with benzene, 0.4 g (31%) IVb; 0.29 g (0.0007 mole) Ic, 0.31 g (0.0007 mole) 1-ethyl-2-methylquinolinium iodide 0.12 ml (0.0009 mole) Et_3N, and 14 ml EtOH gave 0.29 g (74%) IVc, and 0.63 g Id gave 0.41 g (49%) IVd.

{2-Methyl-2, 3H-pyridazino [4, 5, 6-m, *l*]fluorene-(3)}- [1, 3, 3-trimethylindolenine-(2)]monomethylcyanine-perchlorate (Va). 0.97 g (0.0026 mole) Ia, 0.72 g (0.0026 mole) 1-methyl-2, 3, 3-trimethylindoleninium perchlorate, 0.48 g (0.0035 mole) Et_3N, and 15 ml EtOH, were refluxed together for 7 hr. After cooling, the precipitate was filtered off. Yield 0.8 g (64%). Crystallized from MeOH it formed red crystals, mp 261°–263° C (decomp); moderately soluble in EtOH, slightly soluble in water or benzene; dyes polyacrylnitrile fiber bright pink.

Similarly 0.7 g Ic gave 0.2 g (20%) Vb, and 0.82 g Id gave 0.53 g (51%) Vc. Melting points and properties of all dyes synthesized are given in Table 2.

3-Hydrazino-2-methyl-2, 3H-pyridazino [4, 5, 6-m, *l*]fluorene (VI). 1 g (0.003 mole) Ia was added gradually to a mixture of 30 ml dry MeOH and 0.6 ml (0.04 mole) hydrazine hydrate. After refluxing for 2 hr, the products were cooled, the precipitate filtered off, and washed, first with water, then with EtOH. Yield 0.6 g (84.6%), mp 204°–207.5° C (decomp). Recrystallized from EtOH it formed long yellow prisms, mp 206°–207° C (decomp). Found: N 20.82, 21.46%. Calculated for $C_{15}H_{12}N_4 \cdot H_2O$: N 21.04%.

Bis {2-methyl-2, 3H-pyridazino [4, 5, 6-m, *l*] fluorenyl} -3, 3'-azine (VII). 0.38 g (0.001 mole) Ia, 0.19 g (~ 0.0014 mole) Et_3N were added to a suspension of 0.26 g (0.001 mole) VI in 69 ml dry MeOH at 30°–35° C, and the mixture refluxed for 7 hr. The solution was cooled and filtered, the solid washed with EtOH. Yield 0.43 g (95%), mp > 320° C (decomp). Found: C 77.68, 77.59; H 4.17, 4.20; N 17.71, 18.00%. Calculated for $C_{30}H_{20}N_6$: C 77.59; H 4.35; N 18.09%.

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