SYNTHESIS OF BENZIMIDAZOLE DERIVATIVES.

VII.* IMIDADICARBOCYANINES WITH SUBSTITUENTS IN THE POLYMETHINE CHAIN

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Imidadicarbocyanines containing a chloro, bromo, or methyl group in the polymethine chain were synthesized in order to investigate their optical properties.

Owing to the peculiarities of the configuration of imidacarbocyanine molecules [2], the introduction of any substituent into their polymethine chains should be considerably difficult because of steric hindrance. Imidacarbocyanines substituted in the polymethine chain probably have not been obtained for this reason. Chain-substituted imidicarbocyanines, which, however can be synthesized, inasmuch as steric hindrance does not develop on introduction of substituents into the meso position of the polymethine chain (the 10 position), also have remained unknown.

We have obtained imidadicarbocyanines with chloro or bromo groups in the polymethine chain by condensation of salts of α-chloro- or α-bromo-β-anilinoacrolein anils in pyridine with quaternary salts of 2-methylbenzimidazoles having electron-acceptor substituents, the overall effect of which considerably activates the methyl group. Thus, for example, dyes were obtained from 1-phenyl-2-methyl- 5-acetyl- and 1-phenyl-2-methyl-5-(2-benzothioazolyl)benzimidazole ethiodides, whereas 1-phenyl-2-methylbenzimidazole ethiodide proved to be unsuitable for our purposes.

In order to synthesize imidadicarbocyanines with a methyl group in the meso position of the polymethine chain we used the condensation of 1,1,3,3-tetraethoxy-2-methylpropane with quaternary salts of substituted 2-methylbenzimidazoles in nitrobenzene as in [3, 4]. The yields of meso-methylimidadicarbocyanines are lower than the yields of meso-halo-substituted compounds.

In the case of dyes VI and XII it was shown that the introduction of a substituent into the meso position of the polymethine chain does not create steric hindrance: the intensities of the light absorption of these dyes and the corresponding chain-unsubstituted dye – 1,1'-diphenyl-3,3'-diethyl-5,5'-di(2-benzoxazolyl) imidadicarbocyanine iodide – are almost identical (ε $2.9 \cdot 10^{-5}$, and $3.1 \cdot 10^{-5}$, respectively).

The maxima of the light absorption of all of the imidadicarbocyanines containing a substituent in the polymethine chain are shifted by 3-17 nm to the short-wave portion of the spectrum as compared with the values for the corresponding symmetrical imidadicarbocyanines without substituents in the polymethine chain. The hypsochromic shift (Δ) induced by the introduction of bromo, chloro, or methyl groups into the polymethine chain of the imidadicarbocyanines decreases in the order $Br > Cl > CH_3$, and the shift induced by the introduction of halogen atoms are close to one another but are, on the average, double the shift induced by the introduction of a methyl group.

If it is assumed that for halogen atoms as substituents in the polymethine chain of the imidadicarbocyanine the inductive effect predominates over the electron-donor properties, in conformity with the rule of the change in the color of polymethine dyes that stems from the introduction of electron-donor or elec-

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*See [1] for communication VI.

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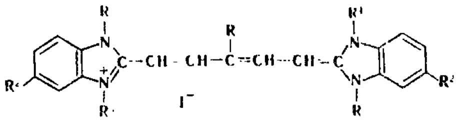
TABLE 1



Dye	Starting materials	R	R¹	R²	R³	mp, °C[a]	Empirical formula	Found, %			Calc., %			λ_{max}[b], nm	Δ, nm	Yield, %
								Cl	I	N	Cl	I	N			
I	A, J	Br	C_6H_5	CH_3CO—	C_2H_5	224	$C_{39}H_{36}BrIN_4O_2$			6,9			7,0	605 (623[4])	18	20
II	A, D	Br	C_6H_5	BT	C_2H_5	177	$C_{49}H_{38}BrIN_6S_2$		12,9	8,7		12,9	8,6	619 (637[3])	18	15
III	B, E	Cl	C_6H_5	H	C_6H_5	253	$C_{43}H_{32}ClIN_4$		16,4			16,6		606 (616[4])	10	25
IV	B, J	Cl	C_6H_5	CH_3CO—	C_2H_5	218	$C_{39}H_{36}ClIN_4O_2$	4,5	16,7		4,7	16,8		608 (623[4])	15	13,5
V	B, D	Cl	C_6H_5	BT	C_2H_5	211	$C_{49}H_{38}ClIN_6S_2$	3,6	13,3		3,7	13,5		620 (637[3])	17	21,5
VI	B, F	Cl	C_6H_5	BO	C_2H_5	228	$C_{49}H_{38}ClIN_6O_2$			9,5			9,3	622 (634[3])	12	25
VII	B, G	Cl	C_6H_5	CN	C_2H_5	236	$C_{37}H_{30}ClIN_6$			11,6			11,7	607 (618[d])	11	24,3
VIII	B, H	Cl	C_6H_5	C_2H_5OOC—	C_2H_5	220	$C_{41}H_{40}ClIN_4O_4$		15,4	6,9		15,6	6,9	604 (617[4])	13	22
IX	B, I	Cl	C_2H_5	CF_3SO_2—	C_2H_5	216	$C_{29}H_{30}ClF_6IN_4O_4S_2$		15,3			15,2		605 (622[8])	17	13
X[c]	C, J	CH_3	C_6H_5	CH_3CO—	C_2H_5	258	$C_{40}H_{39}ClN_4O_6$	5,0			5,0			617 (623[4])	6	12
XI	C, D	CH_3	C_6H_5	BT	C_2H_5	210	$C_{50}H_{41}IN_6S_2$		13,7			13,9		628 (637[3])	9	5
XII	C, F	CH_3	C_6H_5	BO	C_2H_5	209	$C_{50}H_{41}IN_6O_2$		14,1			14,4		625 (631[3])	9	7,5
XIII	C, G	CH_3	C_6H_5	CN	C_2H_5	260	$C_{38}H_{33}IN_6$		18,0			18,1		613 (618[d])	5	10,5
XIV	C, H	CH_3	C_6H_5	C_2H_5OOC—	C_2H_5	271	$C_{42}H_{43}IN_4O_4$		15,6	6,6		16,0	6,9	610 (617[4])	7	9,5
XV	C, E	CH_3	C_6H_5	H	C_6H_5	212	$C_{44}H_{35}IN_4$		16,8	7,2		17,0	7,5	613 (616[4])	3	10

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[a] All of the compounds melt with decomposition.

[b] The absorption maximum of the imidadicarbocyanines that differs from the given compound with respect to the absence of a substituent in the polymethine chain is presented in parentheses; the literature source in which this dye is described is also given.

[c] Dye X was obtained as the perchlorate.

[d] A dye without a substituent in the polymethine chain – 1,1'-diphenyl-3,3'-diethyl-5,5'-dicyanoimidadicarbocyanine iodide (XVI) – is described for the first time in this paper.

tron-acceptor substituents into various positions of their polymethine chains [5, 6], they should induce precisely a hypsochromic shift. Insofar as the methyl group is concerned, the hypsochromic shift induced by it is not explained by this rule, but a similar sort of shift is also observed for the analogously constructed thiadicarbocyanines [7].

Solutions of all of the imidadicarbocyanines, both those with unsubstituted polymethine chains and those containing substituents, in alcohol and many other organic solvents have considerable luminescence.

EXPERIMENTAL

The absorption spectra of ethanol solutions of the compounds in the visible region were recorded with an SF-10 spectrophotometer.

Symmetrical Imidadicarbocyanines with a Substituent in the 10 Position. A) With a halogen atom (I-IX). A 1-mmole sample of α-chloro-β-anilinoacrolein anil hydrochloride or α-bromo-β-anilinoacrolein anil hydrobromide and 1 ml of piperidine were added to a warm solution of 2 mmole of substituted 2-methylbenzimidazole ethiodide in 15 ml of anhydrous pyridine, and the mixture was refluxed for 40 min. The dye was precipitated by the addition of excess ether and washed repeatedly with ether. It was then treated with hot water in order to remove the unchanged starting quaternary salts and purified by chromatography on Al_2O_3 (elution with chloroform) or by precipitation from a hot solution in pyridine by the addition of aqueous sodium iodide solution.

B) With a Methyl Group (X-XV). A mixture of 2 moles of the starting quaternary substituted 2-methylbenzimidazole salt, 2 moles of 1,1,3,3-tetraethoxy-2-methylpropane, and 15-20 ml of nitrobenzene was refluxed for 2 h, after which the dye was precipitated by the addition of 300-350 ml of ether purified as in method A.

Data on the synthesis of dyes I-XV and their properties are presented in Table 1. The following arbitrary symbols for the starting materials and the nitrogen heterocyclic residues – substituents in the benzimidazole rings – were adopted: BO is 2-benzoxazolyl, BT is 2-benzothiazolyl, A is α-bromo-β-anilinoacrolein anil hydrobromide [9], B is α-chloro-β-anilinoacrolein anil hydrochloride [10], C is 1,1,3,3-tetraethoxy-2-methylpropane [16], D is 1-phenyl-2-methyl-5-(2-benzothiazolylbenzimidazole ethiodide [11], E is 1,3-diphenyl-2-methylbenzimidazolium chloride [4], F is 1-phenyl-2-methyl-5-(2-benzoxazolyl)benzimidazole ethiodide [13], G is 1-phenyl-2-methyl-5-cyanobenzimidazole ethiodide [14], H is 1-phenyl-2-methyl-5-ethoxycarbonylbenzimidazole ethiodide [11], I is 1-ethyl-2-methyl-5-trifluoromethylsulfonylbenzimidazole ethiodide [15], and J is 1-phenyl-2-methyl-5-acetylbenzimidazole ethiodide [12].

1,1'-Diphenyl-3,3'-diethyl-5,5'-dicyanoimidadicarbocyanine Iodide (XVI). A 0.1-g (0.55 mmole sample of 1,3,3-triethoxy-1-propene [17] was added to a hot solution of 0.3 g (1 mmole) of ethiodide G in 10 ml of nitrobenzene, and the mixture was refluxed for 4 min. The resulting solution was stirred with 200 ml of ether for 1.5 h, after which the precipitated dye was removed by filtration and washed repeatedly with ether to give 0.18 g (50%) of fine green crystals with a golden luster and mp 285° (dec., from alcohol) and λ_{max} 618 nm. Found: N 12.4%. $C_{37}H_{31}IN_6$. Calculated: N 12.3%.

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