SYNTHESIS OF BENZIMIDAZOLE DERIVATIVES.

11.* IMIDATRICARBOCYANINES WITH SUBSTITUENTS IN THE POLYMETHINE CHAIN

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In order to investigate their optical properties, imidatricarbocyanines of the benzimidazole series containing methyl, methoxy, and cyano groups as substituents in the polymethine chain have been synthesized.

We have applied a method suggested earlier for the synthesis of imidatricarbocyanines of symmetrical structure [2] to the production of imidatricarbocyanines which have so far remained unknown containing various substituents in the meso position (position 11) of the polymethine chain. To elucidate the influence of substituents introduced into the polymethine chain on the color of the imidatricarbocyanines we have synthesized dyes with substituents of electron-donating and electron-accepting natures.

The initial compounds for the synthesis of these dyes were quaternary salts of substituted 2-methylbenzimidazoles and salts of N,N'-dialkyldianils of β-substituted glutaconaldehydes. Of the latter, the β-methyl-substituted compound was obtained by the cleavage of the pyridine nucleus of γ-picoline by the action of cyanogen bromide and N-methylaniline, in a similar manner to the reaction of γ-picoline with cyanogen bromide and aniline [3]. The salt of the N,N'-dimethyldianil of β-methoxyglutaconaldehyde was obtained as described in an Inventor's Certificate [6]. A salt of β-cyanoglutaconaldehyde is not formed by the action of cyanogen bromide and N-methylaniline on γ-cyanopyridine, and we therefore obtained the hydrobromide of the dianil of β-cyanoglutaconaldehyde by the method described above [3] and converted it into the base — the dianil of β-cyanoglutaconaldehyde and then alkylated this with triethyloxonium tetrafluoroborate. This route to salts of N,N'-dialkyldianils of β-substituted glutaconaldehydes — the alkylation of the corresponding bases — may prove useful in other cases as well; it is also applicable to the dianil of unsubstituted glutaconaldehyde, dimethyl sulfate being suitable as the alkylating agent in this case.

The cyanine condensation of the quaternary benzimidazolium salts with the N,N'-dialkdianils of β-substituted glutaconaldehydes was carried out in anhydrous DMSO in the presence of powdered sodium ethanolate [2]; the yields of the majority of the dyes were from 20 to 35%, the higher yields being observed for dyes with a cyano group in the chain.

As follows from the figures in Table 1, the introduction of a methoxy group — a substituent with an electron-donating character — into the meso position of the polymethine chain of an imidotricarbocyanine causes a lightening in the color of the dye, the shift in the main absorption maximum Δ towards the shortwave part of the spectrum averaging 29 nm. Conversely, the introduction of an electron-accepting substituent — the cyano group — leads to a deepening of the color, the shift of the absorption maximum towards the long-wave part of the spectrum averaging 46 nm. This influence of methoxy and cyano groups is in harmony with the Dewar–Knott rule [4, 5], while, contrary to this rule, the electron-donating methyl group does not lighten but considerably deepens the color of the dye, causing a shift of the main absorption maximum by an average of 24 nm. The anomalous influence of a methyl group in the polymethine chain of a polycarbocyanine on its color has been reported repeatedly, e.g., [1], but has not been explained.

Dyes with methoxy groups in the chain possess higher solubilities than dyes with methyl and cyano groups. It has been reported [2] that imidotricarbocyanines with unsubstituted

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*For communication 10, see [1].

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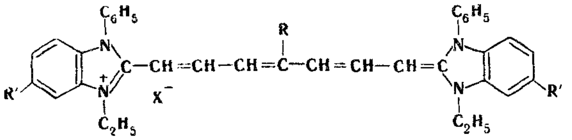
TABLE 1



Dye	Initial sub-stances	R	R¹	X	mp, °C[a]	Found, %		Empirical formula	Calculated, %		λ_{max}[b], mm	Δ[c], nm	$\varepsilon\cdot10^{-5}$[d]	Yield, %
						Hal	N		Hal	N				
I	A, E	CH_3	$COOC_2H_5$	I	182	15,3		$C_{44}H_{45}IN_4O_4$	15,5		748 (724)[d]	+24	1,79 (1,99)	33
II	A, F	CH_3	CN	I	194	17,1	10,9	$C_{40}H_{35}IN_6\cdot H_2O$	17,1	10,9	749 (725)	+24	1,76 (1,98)	22
III	A, G	CH_3	BO	I	213	13,8	8,8	$C_{52}H_{43}IN_6O_2$	14,0	9,2	762 (737)	+25	2,17 (2,28)	25
IV	A, H	CH_3	BT	I	244	13,4	8,9	$C_{52}H_{43}IN_6S_2$	13,5	8,9	765 (742)	+23	2,24 (2,41)	27
V	B, F	OCH_3	CN	I	208	17,0	11,1	$C_{40}H_{35}IN_6O$	17,1	11,3	692 (725)	−33	0,75 (1,98)	23
VI	B, G	OCH_3	BO	I	200		8,9	$C_{52}H_{43}IN_6O_3$		9,1	711 (737)	−26	0,77 (2,28)	21
VII	B, H	OCH_3	BT	I	205		8,6	$C_{52}H_{43}IN_6OS_2$		8,7	715 (742)	−27	0,98 (2,21)	13
VIII	C, F	CN	CN	ClO_4	216	4,7	14,1	$C_{40}H_{32}ClN_7O_4$	5,0	13,8	770 (725)	+45	1,86 (1,98)	47
IX	C, G	CN	BO	ClO_4^-	232	3,9	10,7	$C_{52}H_{40}ClN_7O_6$	4,0	11,0	785 (737)	+48	2,01 (2,28)	35
X	C, H	CN	BT	BF_4	226		10,6	$C_{52}H_{40}BF_4N_7S_2$[f]		10,7	786 (742)	+44	2,30 (2,41)	21

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[a] All the compounds melted with decomposition.
[b] In parentheses are given the absorption maxima taken from the literature [2] of imidotricarbocyanines differing from the given compounds by the absence of substituents in the polymethine chain.
[c] The magnitudes of hypsochromic shifts are denoted by the symbol (−) and bathochromic shifts by the symbol (+).
[d] In parentheses are given the extinctions of imidatricarbocyanines differing from the given compounds by the absence of substituents in the chain.
[e] The dye without the substituent in the polymethine chain having λ_{max} 724 nm (XI) is described in the present paper for the first time.
[f] Found: S 6.8%. Calculated: S 7.0%.

polymethine chains undergo solvolysis so rapidly in dilute solutions in ethanol and some other organic solvents that their extinction could not be measured with sufficient accuracy; however, we have now found that in solution in pure anhydrous DMSO these measurements can be performed: The extinctions of imidotricarbocyanines both with unsubstituted and with substituted chains in this solvent either do not change or change to the extent of only 0.5-1% over 20 min, while the measurement of the extinction of one dye takes about 10 min. Thus, we have determined the extinctions of dyes synthesized previously with unsubstituted chains [2] and those described in the present work with substituted chains. A consideration of the extinction values found (Table 1) for the dyes with substituted chains and their comparison with the extinction values of dyes with unsubstituted chains shows that the introduction of both electron-donating and electron-accepting substituents into the meso position of the polymethine chain of an imidotricarbocyanine causes qualitatively similar changes in extinction — with a decrease in it.

In the pure form, all the dyes obtained can be stored for a long time unchanged. Solutions of the imidotricarbocyanines with substituents in the meso position of the polymethine chain exhibit appreciable fluorescence under UV irradiation in organic solvents.

EXPERIMENTAL

The positions of the main absorption maxima were determined in ethanol solution and the extinctions in DMSO solution in a SF-8 spectrophotometer. DMSO of "pure" grade was dried with anhydrous potassium carbonate and was distilled in vacuum.

The N,N'-dialkylanilide salts of β-methylglutaraldehyde were obtained as described by Vompe et al. [3] with methylaniline in place of aniline, and those of β-methoxyglutaraldehyde as described by Sveshnikov and Stokovskaya [6].

Table 1 gives information on the synthesis of dyes (I-X) and their properties. For the hetaryl substituents in the benzimidazole nucleus and for the initial compounds the following arbitrary abbreviations are used: BO) benzoxazol-2-yl; BT) benzothiazol-2-yl; A) methylphenyl(5-methylphenylamino-3-methylpenta-2,4-dienylidene)ammonium bromide; B) methylphenyl(5-methylphenylamino-3-methoxypenta-2,4-dienylidene)ammonium methosulfate; D) methylphenyl(5-methylphenylaminopenta-2,4-dienylidene)amminium chloride; E) 5-ethoxycarbonyl-3-ethyl-2-methyl-1-phenylbenzimidazolium iodide; F) 5-cyano-3-ethyl-2-methyl-1-phenylbenzimidazolium iodide; G) 5-(benzoxazol-2-yl)-3-ethyl-2-methyl-1-phenylbenzimidazolium iodide; H) 5-(benzothiazol-2-yl)-3-ethyl-2-methyl-1-phenylbenzimidazolium iodide; I) 5-ethoxycarbonyl-3-ethyl-2-methyl-1-phenylbenzimidazolium tosylate; J) (3-cyano-5-phenylaminopenta-2,4-dienylidene)phenylammonium bromide.

Ethylphenyl(5-ethylphenylamino-3-cyanopentadienylidene)ammonium Tetrafluoroborate (C). A suspension of 2 g (5.6 mmole) of salt J prepared by the method of Vompe et al. [3] in 15 ml of acetone was treated with 100 ml of 1 N caustic soda solution. The resulting precipitate of 3-cyano-1-phenylamino-5-phenyliminopenta-1,3-diene was filtered off and washed with water until the wash-waters were neutral. Yield 1.0 g (65%). With stirring, to a solution of the resulting product in 4 ml of dried and redistilled methylene chloride was added in small portions a solution of 2.08 g (10 mmole) of triethyloxonium tetrafluoroborate in 3 ml of the same solvent. After 2 h, a precipitate of compound C was filtered off and it was repeatedly washed with ether. Yield 0.9 g (57.5%); for analysis it was crystallized from glacial acetic acid. Small dark crystals with a violet tinge and luster, mp 200-204°C (decomp.). Found: N 10.2%. $C_{22}H_{24}BF_4N_3$. Calculated: N 10.1%.

Symmetrical Imidatricarbocyanines Each with a Substituent in Position 11 (I-X). To a solution of 1 mmole of a quaternary salt of a substituted 2-methylbenzimidazole and 0.33 mmole of an alkylphenyl(5-alkylphenylamino-3R-penta-2,4-dienylidene)ammonium salt (bromide, iodide, methosulfate, or tetrafluoroborate; R = CH_3, OCH_3, or CN) in 8 ml of DMSO heated to 70-90°C was added 0.1 g of anhydrous powdered sodium ethanolate, and the mixture was carefully stirred for 7-10 min with the temperature maintained between 80 and 90°C. The DMSO was eliminated completely by decantation with ether, the resulting viscous mass was triturated with 10-15 ml of water, and the precipitate was filtered off and was washed on the filter with water and ether or with water, ethanol, and ether. The dye was purified by crystallization from pyridine or by precipitation from a hot solution in pyridine with an aqueous solution of sodium iodide or perchlorate.

5-Ethoxycarbonyl-2-[7-(5-ethoxycarbonyl-3-ethyl-1-phenylbenzimidazol-2-ylidene)hepta-1,3,5-trien-1-yl]-3-ethyl-1-phenylbenzimidazolium Iodide (XI). This was synthesized by the method described above from 0.7 g (1.5 mmole) of the salt I and 0.16 g (0.5 mmole) of the salt D in 8 ml of DMSO with 0.14 g (2 mmole) of sodium ethanolate. After purification of the crude dye by precipitation with a hot solution of sodium iodide from a hot solution in pyridine (15 ml), 0.2 g (33%) of the dye (XI) was obtained. Green crystals with a metallic luster mp 223-225°C (decomp.). For analysis, the purification was repeated. Found: I 15.6; N 7.0%. $C_{43}H_{43}IN_4O_4$. Calculated: I 15.8; N 7.0%.

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