

5-HETARYL-SUBSTITUTED 2-METHYLENEINDOLINES AND POLYMETHINE DYES BASED ON THEM

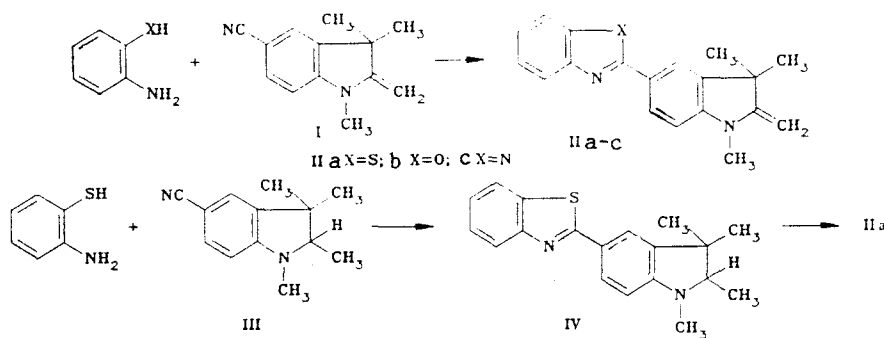
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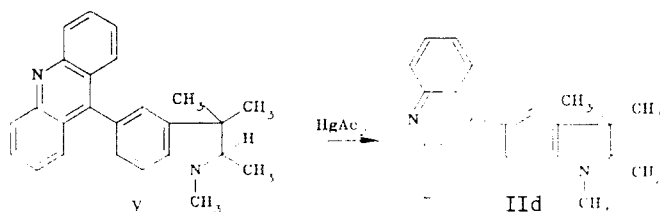
2-Methyleneindolines containing benzazole residues at the 5-position were synthesized and polymethine dyes were obtained from them. The bathochromic shifts induced by the introduction of heterocyclic residues into indocyanines exceed the similar shifts induced by the same heterocycles in thio and quinocyanines.

The influence of heterocyclic substituents on the color of polymethine dyes has been extensively studied using compounds with high and medium basicity as examples, such as imido-, thio-, quino-2-, and quino-4-cyanines [1-5]. The weakly basic indocyanines with heteroaromatic groupings have not yet been described in the literature, while exactly in these compounds the greatest bathochromic shifts might be observed [6]. Among the polymethine dyes, indocyanines are in particular most suitable as working media for lasers [7, p. 173] and are used as sensitizers in electrophotography [8., 9]. The synthesis of these dyes is therefore also of interest from this point of view.

Since it is quite difficult to introduce heteroaromatic substituents into the benzene ring of compounds of the indole series by conventional methods [10], our recently developed method [11, 12] was used for the synthesis of hetaryl-substituted 2-methylene indolines. Using this method nitrile I was also synthesized, which in the form of its salts was frequently mentioned in the patent literature [9], but because of the instability of such has not yet been characterized in the form of a base. From compound I, by condensation with the corresponding ortho-substituted anilines in polyphosphoric acid, 5-(benzothiazol-2-yl)-, 5-(benzoxazol-2-yl)-, and 5-(benzimidazol-2-yl)-2-methyleneindolines (IIa-c) were obtained (Table 1).



Methyleneindoline IIa was also obtained by a countersynthesis from nitrile III via 1,2,3,3-tetramethyl-5-(benzothiazol-2-yl)indole IV, followed by oxidation with mercuric acetate. In a similar way, from the previously described acridyl-substituted 2-methylene indole V [12], 2-methyleneindoline IIId was obtained:



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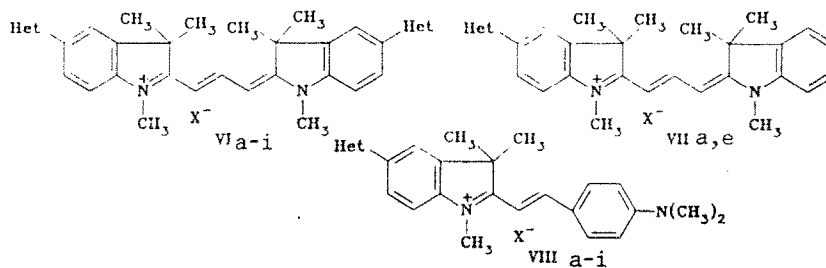
TABLE 1. Physicochemical Characteristics of Compounds I, IIa-d

Com- pound	Empirical formula	mp, °C	IR spectrum, cm ⁻¹	PMR spectrum, ppm				Yield, %
				(CH ₃) ₂ s, 6H	NCH ₃ s, 3H	CH ₂ s, 2H	Ar, m	
I	C ₁₃ H ₁₄ N ₂	85...86	2220 (C=N); 1605 (CHAr)	1.34	3.07	4.01	7.28...7.52 (2H)	66.0
IIa	C ₁₉ H ₁₈ N ₂ S	134...135	1605 (CHAr)	1.13	2.38	4.77	5.78...7.88 (7H)	73.3
IIb	C ₁₉ H ₁₈ N ₂ O	89...90	1605 (CHAr)	1.41	2.80	3.11	6.52...7.98 (7H)	51.1
IIc	C ₁₉ H ₁₉ N ₃	217...218	1605 (CHAr)	1.09	2.97	3.83	6.41...7.98 (7H), 10.0 (s, 1H, NH)	89.2
IIId	C ₂₅ H ₂₂ N ₂	210...211	1605 (CHAr)	1.42	3.17	3.46	7.1...8.4 (10H); 6.75 (d, 1H, 7H)	42.0

TABLE 2. Physicochemical Characteristics of Compounds VIa-i, VIIa, e, VIIIa-i

Com- pound	Empirical formula	mp, °C	λ _{max} , nm	ε · 10 ⁻⁴	ν, cm ⁻¹ (in CH ₃ OH)	ν, cm ⁻¹ (in CH ₃ CN)	λ _{max} , nm	ν, cm ⁻¹ (in CH ₃ CN)	Av. cm ⁻¹ (in CH ₃ CN)	D, nm	λ _{max} , nm	ν, cm ⁻¹ (in CH ₃ CN)	Av. cm ⁻¹ (in CH ₃ CN)	D, nm	Yield, %
VIa	C ₄₃ H ₂₂ N ₄ O ₃ S ₃	233...234	585	13.8	17094	17094	—	1288	17123	1327	—	17123	1327	—	38
VIb	C ₄₆ H ₂₄ N ₄ O ₅ S	220...222	581	11.2	17212	17212	—	1170	17241	1209	—	17241	1209	—	13.1
VIc	C ₄₆ H ₄₄ N ₄ O ₃ S	312...313	583	13.5	17153	17153	—	1229	17123	1327	—	17123	1327	—	8.0
VIId	C ₅₁ H ₄₃ ClN ₄ O ₄	244...245	558	13.5	17921	17921	—	461	—	—	—	—	—	—	28.8
VIe	C ₅₀ H ₄₆ N ₄ O ₃ S	190...192	576	13.0	17361	17361	—	1021	—	—	—	—	—	—	17.0
VIIf	C ₄₈ H ₃₉ ClN ₄ O ₄	207...209	560	11.2	17857	17857	—	525	—	—	—	—	—	—	16.0
VIg	C ₄₉ H ₄₃ ClN ₄ O ₄	222...224	560	9.8	17857	17857	—	525	—	—	—	—	—	—	11.0
VIh	C ₅₅ H ₅₁ ClN ₄ O ₆	216...218	561	13.8	17825	17825	—	557	—	—	—	—	—	—	21.5
VII	C ₅₅ H ₅₁ ClN ₄ O ₆	208...210	556	13.0	17986	17986	—	396	—	—	—	—	—	—	27.2
VIIa	C ₅₀ H ₃₂ ClN ₃ O ₄ S	190...191	563	11.9	17762	17762	2.0	654	—	—	—	—	—	—	74.0
VIIe	C ₃₄ H ₃₄ ClN ₃ O ₄	210...212	559	8.0	17889	17889	1.3	527	—	—	—	—	—	—	30.0
VIIIa	C ₃₅ H ₃₅ N ₃ O ₃ S	310...311	575	10.2	17391	17391	18.7	1025	—	—	—	—	—	—	26.0
VIIIb	C ₃₅ H ₃₅ N ₃ O ₄ S	177...179	577	10.2	17331	17331	14.3	1085	—	—	—	—	—	—	26.0
VIIIc	C ₃₅ H ₃₆ N ₃ O ₃ S	268...270	575	10.9	17391	17391	17.7	1025	—	—	—	—	—	—	54.9
VIIIId	C ₃₁ H ₃₂ ClN ₃ O ₄	268...270	556	9.6	17986	17986	23.5	430	—	—	—	—	—	—	39.2
VIIIe	C ₃₀ H ₃₀ IN ₃	240...242	567	9.8	17637	17637	22.1	779	—	—	—	—	—	—	31.0
VIIIf	C ₃₀ H ₃₀ IN ₃	218...220	558	9.0	17921	17921	23.0	495	—	—	—	—	—	—	25.0
VIIIg	C ₃₀ H ₃₂ ClN ₃ O ₄	184...185	559	7.5	17889	17889	21.7	527	—	—	—	—	—	—	14.5
VIIIh	C ₃₀ H ₃₆ ClN ₃ O ₅	202...204	553	8.5	18083	18083	28.5	333	—	—	—	—	—	—	26.4
VIIIi	C ₃₆ H ₃₆ IN ₃ O	198...200	553	9.2	18085	18085	26.2	333	—	—	—	—	—	—	16.0

From 5-hetaryl-2-methyleneindolines IIa-d, and also from 5-(quinol-2-yl)-, 5-isoquinol-1-yl), 5-(3,4-dihydroisoquinol-1-yl), 5-(N-benzoyl-1,2-dihydroquinol-2-yl), and 5-(N-benzoyl-1,2-dihydroisoquinol-1-yl)-2-methyleneindolines previously described by us [12], the symmetric VIa-i and asymmetric VIIa,e carbocyanines and styryls VIIIa-i were obtained by condensation with ethyl orthoformate or the corresponding aldehyde.



VI-VII: a) Het = 2-benzothiazolyl; b) Het = 2-benzoxazolyl; c) Het = 2-benzimidazolyl; d) Het = 10-acridyl; e) Het = 2-quinolyl; f) Het = 1-isoquinolyl; g) Het = 1-(3,4-dihydroisoquinolyl); h) Het = 2-(1-benzoyl-1,2-dihydroquinolyl); and i) Het = 1-(2-benzoyl-1,2-dihydroisoquinolyl); X = Ts, ClO₄, I⁻.

Our recently published data [6] indicate that the bathochromic shift of the long-wave absorption band, induced by the introduction of heteroaromatic groupings into the weakly basic indocyanines will be greater than similar shifts induced by the introduction of the same substituents into dyes with more basic nuclei. In fact, Table 2 shows that the bathochromic shift induced by introducing 2-benzothiazole into astraflaxine (dye VIa) is much greater than similar shifts induced by the introduction of the same substituent into thio-, quino-2-, and quino-4-carbocyanines, which are equal to 747, 1090, and 1020 cm⁻¹, respectively [1, 2]. Quinoline and benzoxazole were also introduced into thiocarbocyanines [1, 2] and the bathochromic shifts induced by these substituents were smaller than in the present case. It should be noted that, in accordance with the Sych rule [13, 13], the influence of electron-acceptor heteroaromatic groups should, on the contrary, be weakest in weakly basic indocyanines. The greatest bathochromic shifts are observed in benzothiazolyl-, benzoxazolyl-, and benzimidazolyl-substituted carbocyanines (VIa-c) (see Table 2). This can be explained by smaller steric hindrances, meaning greater conjugation of the introduced heterocycles with the overall chromophore system. With increase in the steric hindrances (on transition to quinoline- and isoquinoline indocarbocyanines), the bathochromic shifts decrease noticeably. In the case of the acridine-substituted indocarbocyanine, there is in general no conjugation between the acridine and indolenine parts of the molecule. When acridine is introduced into indocarbocyanine, the bathochromic shift is very small and is practically no different from similar shifts in dyes with nonaromatic N-benzoylquinoline and N-benzoylisoquinoline groupings. Introduction of electron-acceptor substituents into one of the hetero residues of astraflaxine (VIIa,e) slightly disturbs the electronic symmetry. There is practically no deviation in dyes VIIa,e, and the extinction decreases inappreciably. On the contrary, introduction of heteroaromatic groupings, as well as other electron-acceptor substituents [14, 15] into the styryl dyes (VIIIa-i) leads to a considerable decrease in the deviation as the result of decrease in the electronic asymmetry. Since in the series under consideration similar groupings were introduced into the styryls, the deviations decreased synchronously with increase in the electronegativity of the substituents. In our case, the electron-acceptor influence of the heterocycles introduced can be most simply evaluated by using the ¹³C NMR spectra of 2-methyleneindolines (II). The values of shifts of the methylene carbon atom increase symbatically with decrease in the deviation of the corresponding styryls (see Table 3).

EXPERIMENTAL

The UV spectra were run on a Specord M-80 spectrophotometer, the PMR spectra on a Bruker-100 spectrometer (in CDCl₃), using TMS as internal standard, and the ¹³C NMR spectra on a Bruker-200 spectrometer.

1,3,3-Trimethyl-2-methylene-5-cyanoindoline (I) was obtained by the method described in [11], and was isolated by distillation under vacuum in an argon current, bp 133-135°C (0.015 mm Hg).

The characteristics of the compounds are given in Tables 1-3. The results of the elemental analyses of the compounds obtained correspond to the calculated data.

1,3,3-Trimethyl-2-methylene-5-(benzothiazol-2-yl)indoline (Ia); 1,3,3-Trimethyl-2-methylene-5-(benzoxazol-2-yl)indoline (Ib); 1,3,3-Trimethyl-2-methylene-5-(benzimidazol-2-yl)indoline (Ic). A 10-mmol portion of nitrile I and 10 mmoles of o-mercapto-, o-hydroxy-, or o-aminoaniline was added at 120°C to 30 ml of polyphosphoric acid and the mixture was heated with vigorous stirring for 4 h at 200°C. It was then cooled, poured into water, and neutralized with ammonia. The precipitate that separated out was extracted with chloroform, the organic layer was dried over sodium sulfate, the solvent was evaporated, and the remaining oil was recrystallized from hexane (heptane).

TABLE 3. ^{13}C NMR Spectra of II-a,e-g and 1,3,3-Trimethyl-2-methyleneindoline (II)

Compound	Chemical shifts, δ , ppm							
	=CH ₂	CH ₁ N	(CH ₂) ₂	C ₍₂₎	C ₍₃₎	C ₍₇₎	C ₍₈₎	C ₍₉₎
Ila	73.69	26.75	27.86	159.93	41.81	102.83	136.34	146.81
Ilb	73.98	26.84	27.89	159.96	41.84	102.93	136.37	147.26
Ilc	72.96	26.75	27.48	160.25	41.75	103.12	136.44	145.98
Ile	72.57	26.81	27.73	160.60	41.84	102.93	136.88	146.33
Ilf	72.16	—	27.77	160.79	42.19	102.54	135.10	—
Ilg	72.47	26.83	27.93	160.53	41.97	102.02	135.54	145.68
II	71.15	26.61	27.93	160.60	42.04	102.83	135.46	144.28

1,2,3-Tetramethyl-5-(benzothiazol-2-yl)indoline (IV). A mixture of 10 mmoles of nitrile III and 10 mmoles of aminothiophenol was heated for 4 h at 180°C. The cooled melt was recrystallized from heptane. By oxidation with mercuric acetate, according to previously described procedure [11], the compound was converted into IIa.

Symmetric Carbocyanines (VIa-i). A mixture of 0.6 mmole of indoline IIa-i, 0.3 mmole of p-toluenesulfonic acid, and 0.2 ml of ethyl orthoformate was boiled in 1 ml of pyridine for 5-10 min. From the cooled mixture, a precipitate separated out in the case of compounds VIa-e. The dye thus obtained was filtered off, washed with water, ether, and hot benzene, and was purified by reprecipitation with ether from methylene chloride. In the case of compounds VI f-i, 5 ml of water and 5 ml of ether were added to the reaction mixture. The oily dye was extracted with methylene chloride, the solvent was evaporated, the residue was dissolved in 1-2 ml of methanol. A small excess of sodium perchlorate was added, and the product was precipitated by 10 ml of water. The precipitate was filtered, the perchlorate obtained was washed with water, ether, hot benzene, and purified by reprecipitation with ether from methylene chloride.

Asymmetric Carbocyanines (VIIa,e). A mixture of 0.9 mmole of indoline IIa,e, 0.9 mmole of a Fischer aldehyde, and 0.9 mmole of p-toluenesulfonic acid was boiled in 1 ml of pyridine for 5-10 min. The oily dye was extracted with methylene chloride, the solvent was evaporated, and the residue was dissolved in 2 ml of methanol. An excess of sodium perchlorate was added, the product was precipitated with water, washed with ether, hot benzene, and reprecipitated with ether from methylene chloride.

Styryls (VIIIa-i). A mixture of 0.9 mmole indoline IIa-i, 0.9 mmole of p-toluenesulfonic acid, and 1 mmole of p-dimethylaminobenzaldehyde was boiled in 1 ml of pyridine for 5-10 min. Dyes VIIIb,c were filtered off, washed with water, ether, hot benzene, and reprecipitated with ether from methylene chloride. Styryls VIIIa,d,g,h were dissolved in 2 ml of methanol, and excess of sodium perchlorate was added, and the product was precipitated with 10 ml of water. The precipitate was filtered off, washed with hot benzene, and reprecipitated with ether from methylene chloride. Styryls VIIIe,f,i were dissolved in 2 ml of methanol, an excess of potassium iodide was added, and the product was precipitated with 10 ml of water. The precipitate was filtered off, washed with hot benzene, and reprecipitated with ether from methylene chloride.

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