BISCYANINES FROM ISOMERIC BENZODIPYRROLENINES

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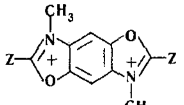
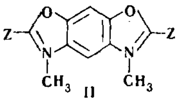
Biscyanines and their corresponding "mother" monocyanines were obtained from the three isomeric benzodipyrrolenines. Splitting of the absorption band of the "mother" monocyanine into two new bands, viz., a long-wave and a short-wave band, is observed for the biscyanines. The degree of splitting of the maxima for a para orientation of the chromophores in the benzene ring is about twice that for the meta position.

Two maxima, which arise as a result of splitting of the absorption band of the "mother" cyanine corresponding to this cyanine, are observed in the absorption spectrum of a symmetrical biscyanine [1]. The degree of interaction of two chromophores of a biscyanine is determined by the magnitude of the difference between its maxima [1]. It is natural to assume that the maximum interaction between the chromophores should be observed when they are conjugated. Experiments indicate, however, that the presence of formal conjugation, i.e., alternation of simple and double bonds between the chromophores, is not necessary for their interaction. Thus, we recently pointed out [2] that the degree of interaction of chromophores ($\Delta\lambda_{max}$) in biscyanines (I and II) obtained from isomeric benzobisoxazoles is almost the same although the chromophores of I are bonded through nitrogen atoms in the para positions of the benzene ring, while the chromophores of II are bonded through nitrogen atoms in the meta positions. Precisely the same sort of thing was observed in the analogously constructed biscyanines from benzobisthiazoles [3].



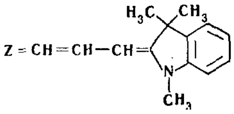
I

$\Delta\lambda_{max}$ 132 nm



II

$\Delta\lambda_{max}$ 124 nm



One can assume that conjugation of the chromophores in biscyanines from benzobisoxazoles or benzobisthiazoles is accomplished not only through the nitrogen atoms but also through the oxygen or sulfur atoms. In order to exclude this possibility, we have now synthesized biscyanines III-V, which are analogous to dyes I and II, from diquaternary salts of the isomeric benzodipyrrolenines described in our previous paper [4]. The "mother" cyanines (VI-VIII), which correspond to biscyanines III-V, were obtained from the monoquaternary salts of the same benzodipyrrolenines. (See scheme on page 579.)

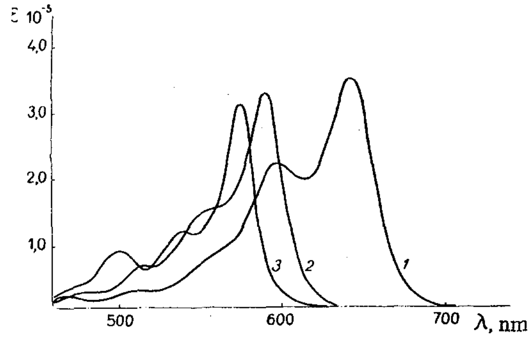


Fig. 1. Absorption spectra of dyes III-V in nitromethane: 1) III; 2) IV; 3) V.

A comparison of the spectral characteristics of III-VIII (Table 1) indicates that the absorption band of the "mother" monocyanines (VI-VIII) is split into two new bands in the absorption spectra of biscyanines III-V. It is readily noted that two trimethine chromophores are conjugated in

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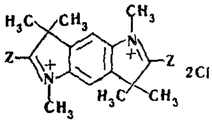
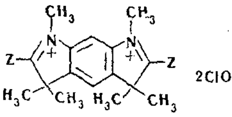
TABLE 1. Spectral and Analytical Characteristics of the Dyes Obtained

Compound	Name	mp, °C*	Absorp. spec. in nitromethane		Empirical formula	Found, %	Calc., %	Yield, %
			λ_{max}, nm	$\varepsilon \cdot 10^{-5}$				
III	2,6-Bis[(1,3,3-trimethyl-2-indolinylidene)propenyl]-1,3,3,5,7,7-hexamethyl-3H,7H-benzo[1,2-b:4,5-b']dipyrrolium diperchlorate	>300	507 646	0.22 3.52	$C_{44}H_{52}Cl_2N_4O_8$	Cl 8.4	Cl 8.5	42
IV	2,6-Bis[(1,3,3-trimethyl-2-indolinylidene)propenyl]-1,3,3,5,5,7-hexamethyl-3H,5H-benzo[1,2-b:5,4-b']dipyrrolium diperchlorate	>300	515 592	0.62 3.28	$C_{44}H_{52}Cl_2N_4O_8$	N 6.9	N 6.7	62
V	2,7-Bis[(1,3,3-trimethyl-2-indolinylidene)propenyl]-1,3,3,6,8,8-hexamethyl-3H,8H-benzo[1,2-b:3,4-b]dipyrrolium diperchlorate	>300	503 577	0.88 3.13	$C_{44}H_{52}Cl_2N_4O_8$	Cl 8.4	Cl 8.5	53
VI	2-[(1,3,3-Trimethyl-2-indolinylidene)propenyl]-1,3,3,6,7,7-hexamethyl-3H,7H-benzo[1,2-b:4,5-b']dipyrrolium perchlorate	>300	567	1.03	$C_{30}H_{36}ClN_3O_4$	N 7.5	N 7.8	14
VII	2-[(1,3,3-Trimethyl-2-indolinylidene)propenyl]-1,3,3,5,5,6-hexamethyl-3H,5H-benzo[1,2-b:5,4-b']dipyrrolium perchlorate	240	557	1.12	$C_{30}H_{36}ClN_3O_4$	N 7.4	N 7.8	12
VIII	7-[(1,3,3-Trimethyl-2-indolinylidene)propenyl]-2,3,3,6,8,8-hexamethyl-3H,8H-benzo[1,2-b:3,4-b']dipyrrolium iodide	260	548	1.60	$C_{30}H_{36}IN_3$	I 22.3	I 22.4	67

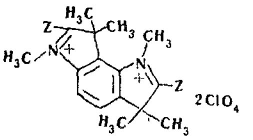
*Compounds III and IV from methanol, V-VII from ethanol, and VIII from water containing NaI.


III

$\Delta\lambda_{max}$ 139 nm


IV

$\Delta\lambda_{max}$ 77 nm


V

$\Delta\lambda_{max}$ 74 nm

III, while conjugation is absent between them in IV and V. It turns out that, in accordance with this, the splitting of the maxima ($\Delta\lambda_{max}$) of III is about twice that for IV and V.

Observations of the interaction of two chromophores associated through the meta position of the benzene ring were also made in bishemicyanines [5], although the splitting of the maxima there is weaker than in biscyanines IV and V. In all of these sorts of cases we are apparently dealing with a dipole–dipole interaction [6]. It was recently shown [6] that the chromophores of two cyanine dyes can also interact with splitting of the absorption bands in those cases in which they are not chemically bonded but are in direct proximity in the monomolecular layers situated one upon the other.

It is known that the ratio of the intensities of the absorption bands of symmetrical biscyanines depends on the angle formed by the directions of the interacting chromophores. If this angle is 180°, one observes only an intense long-wave band in the spectrum of the biscyanine, and the short-wave band disappears almost completely. It is precisely this sort of thing that we observed with III (Fig. 1),* which was ob-

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*The maxima of average intensity (they are not presented in Table 1) in the spectra of the majority of the indacyanines on the absorption curves of each of the biscyanines correspond to vibrational rather than electronic transitions [8].

tained from a centrosymmetrical base. The absorption curve of this dye recalls the absorption curve of dye I. However, in the case of dyes IV and V the short-wave band already has an appreciable intensity. The ratio of the intensities of the two bands attests to the fact that the directions of the chromophores of these dyes form an obtuse angle which is somewhat smaller for dye V.

EXPERIMENTAL

Dyes III-VIII (Table 1) were obtained by heating 1 mole of the appropriate quaternary salt [4] with 2.5 mole of 1,3,3-trimethyl-2-formylmethyleneindoline in acetic anhydride for 1 h at 140°. After removal of the acetic anhydride in vacuo, the residue was washed with ether and crystallized from a suitable solvent. Dyes VI and VIII were chromatographed with chloroform on aluminum oxide before crystallization.

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