THE MUTUAL INFLUENCE OF THE CHROMOPHORES OF TWO CYANINE DYES CONNECTED THROUGH A BENZENE NUCLEUS

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Three isomeric biscyanine dyes have been synthesized, each of which forms a pair of indothiazolocarbocyanines attached to a p-phenylene group through the 4, 4' (I), 5, 5' (II), and 3, 3' (III) positions of the thiazole nuclei. It has been found that in the biscyanines II and III the polymethine chromophores are conjugated and influence one another, which is shown by the splitting of the absorption bands of these dyes. In the biscyanines I, no interaction of the chromophores is observed.

In 1965, A. I. Kiprianov and I. L. Mushkalo [1] found that in biscyanine dyes the polymethine chromophores of which are of the same length and are conjugated with one another, these chromophores influence one another as two connected vibrational systems tuned in unison. The two absorption bands of such a biscyanine do not coincide with the absorption bands of the two monocyanine dyes corresponding to them, but are shifted, one in the direction of higher and the other in the direction of lower frequencies.

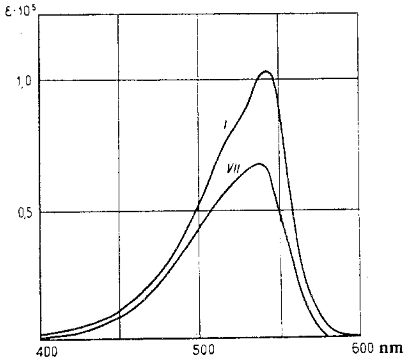
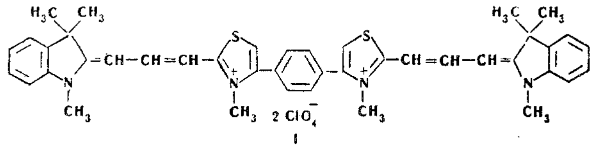


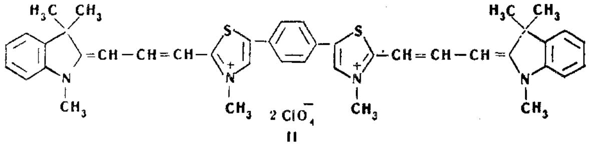
Fig. 1. Absorption curves of the biscyanine **I** and the monocyanine **VII**.

In the case of biscyanines with a completely symmetrical structure, the conjugation of the chromophores must lead to a splitting of the absorption band of the mother monocyanine into two bands, one of longer and one of shorter wavelength. This type of symmetrical biscyanine has been obtained and studied in the present work.

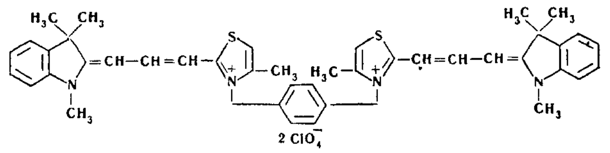
We synthesized three dyes (**I–III**), each of which consisted of a pair of indothiazolocarbocyanines connected with one another through a p-phenylene nucleus:



I



II

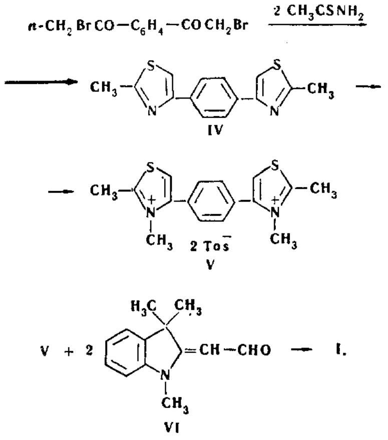


III

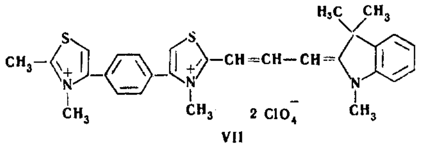
The difference in the structure of these three isomeric biscyanines consists in the fact that in dye **I** the connection between the two monocyanines is effected through the positions 4 of the thiazole nuclei, in dye **II** through positions 5, and in dye **III** through positions 3.

Biscyanines of analogous structure in which the thiazole nuclei of the monocyanines are connected through biphenyl residues have been described by E. D. Sych [2]. In these biscyanines, no splitting of the absorption bands was observed. However, it is known that the biphenyl system is a very poor conductor of electronic influences [3].

The synthesis of the biscyanines **I–III** was carried out by the condensations usual for these types of dyes. It was complicated in the later stages by the difficulty of purifying the relatively high-molecular-weight compounds obtained. The biscyanines **I** were synthesized in the following way:



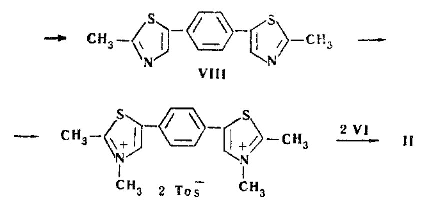
The same salt **V**, on reaction with 1 mole of the aldehyde **VI**, formed the mother dye **VII**:



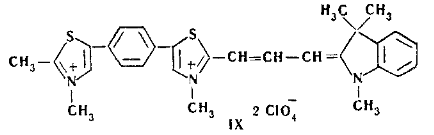
VII

The biscyanine **II** was prepared by a somewhat more complex method:

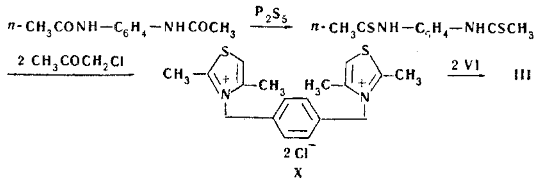
$$n\text{-}CH_3CONHCH_2CO{-}C_6H_4{-}COCH_2NHCOCH_3 \xrightarrow{P_2S_5}$$



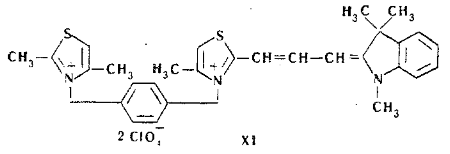
The mother dye **IX** corresponding to the biscyanine **II** was obtained in a similar manner to dye **VII**:



The following route was used for the synthesis of the biscyanine III:



The mother dye **XI** was obtained similarly to VII and **IX**:



The absorption spectra of all the three biscyanines and the monocyanines corresponding to them were determined in ethanolic solutions. Figure 1 gives the absorption curves of the biscyanine I and its mother dye **VII**.

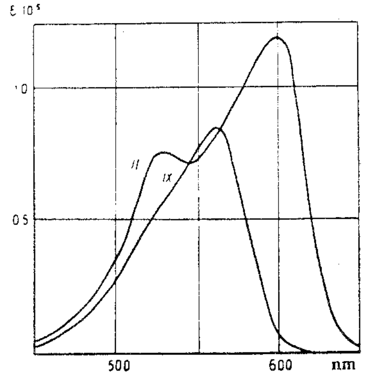


Fig. 2. Absorption spectra of the biscyanine **II** and the dye **IX**.

The absorption curves of the biscyanine I (λ_{max} 544 nm) and the monocyanine **VII** (λ_{max} 538 nm) almost agree both with respect to their shapes and to the positions of the maxima, but the intensity of the absorption band in **I** (ε 1.02 $\times$ 10^5) is far higher than in **VII** (ε 0.66 $\times$ $\times$ 10^5). Hence, it follows that in this case there is practically no interaction between the chromophores of the biscyanine I.

There may be two reasons for this. Apparently, the more important of them is that in the thiazole cyanines, as has been shown by Sych [4], electronic influences are transmitted very feebly to the chromophore (conjugation through the sulfur atom). The second reason is a disturbance of the coplanarity of the benzene nucleus with the two neighboring thiazole nuclei because of steric hindrance [5].

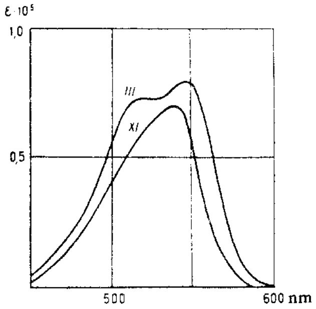


Fig. 3. Absorption spectra of the biscyanine **III** and the dye **XI**.

Figure 2 gives the absorption spectra of the biscyanine **II** and its mother dye **IX**.

Here the picture is different. As we expected, the chromophores of the biscyanine interact. The absorption band of the mother monocyanine **IX** (λ_{max} 562 nm, ε 0.8 $\times$ 10^5) is split in the spectrum of the biscyanine **II** into two bands (λ_{max} 602 nm, ε 1.18 $\times$ 10^5, and λ_{max} 530 nm, ε 0.7 $\times$ 10^5). It is known that position 5 in the thiazole cyanines, unlike position 4, is very sensitive to the electronic influence of substituents (conjugation with the chromophore through the nitrogen atom) [4]. In these dyes the steric hindrance preventing the coplanarity of the benzene nucleus and the thiazole nuclei is also smaller than in the preceding case.

The absorption spectra of the biscyanine III and its mother dye **XI** are given in Fig. 3.

There is also interaction of the chromophores here, but it is not expressed so clearly as in the preceding case. The absorption band of the mother dye **XI** (λ_{max} 540 nm, ε 0.70 $\times$ 10^5) is split in the biscyanine **III** into two bands (λ_{max} 548 nm, ε 0.79 $\times$ 10^5, and λ_{max} 516 nm, ε 0.70 $\times$ 10^5). The conjugation of the chromophores is weakened, probably through steric hindrance.

EXPERIMENTAL

p-Diacetylbenzene [6] **and p-bis(bromoacetyl)benzene** [7] were obtained by published methods.

p-Bis-(2-methyl-4-thiazolyl)benzene (IV). A mixture of 2.15 g of p-bis(bromoacetyl)benzene and 1 g of thioacetamide was heated at 140° C for 1 hr. The product was washed with benzene and dissolved in water, and the base was precipitated with ammonia. Yield 1 g (55%), mp 215–216° C (decomp from ethanol) (the melting points are uncorrected). Found, %: S 23.82, 23.80. Calculated for $C_{14}H_{12}N_2S_2$, %: S 23.52.

The bis(methyl tosylate) derivative (V) was obtained by heating the base IV with methyl p-toluenesulfonate at 170° C for 30 min. Yield 81%, mp 275° C (decomp). Found, %: S 19.88, 19.86. Calculated for $C_{22}H_{22}N_2O_3S_3$, %: S 19.87.

The biscyanine I. A mixture of 0.3 g of the salt V, 0.4 g of 2-formylmethylene-1, 3, 3-trimethylindoline (VI) and 3 ml of acetic anhydride was boiled for 5 min. The dye was precipitated with the ether and was purified by chromatography on alumina in chloroform containing ethanol. The dye was converted into the perchlorate by the action of sodium perchlorate. Yield 35 mg (10%), mp 281° C (decomp). Found, %: S 7.28, 7.10. Calculated for $C_{42}H_{45}Cl_2N_4O_8S_2$, %: S 7.38.

The dye VII was obtained by heating a mixture of 0.6 g of the salt V, 0.07 g of the aldehyde VI, and 3 ml of acetic anhydride, and the dye obtained was purified in the same way as the preceding one. Yield 25 mg (9%), mp 220° C (decomp). Found, %: S 9.35, 9.29. Calculated for $C_{29}H_{31}Cl_2N_3O_8S_2$, %: S 9.35.

p-Bis(acetylaminoacetyl)benzene. p-Bis(aminoacetyl)benzene hydrochloride was obtained from p-bis(bromoacetyl)benzene via the hexamethylenetetramine complex as described by Burns et al. [9]. Two grams of this salt was dissolved in 15 ml of water and, at 0° C, 4.5 ml of acetic anhydride was added. Then, with stirring, sodium hydrogen carbonate was added until a precipitate had formed. The precipitate was washed with ice water and crystallized from ethanol. Yield 1.33 g (65%), mp 234–235° C. Found, %: N 10.21, 10.35. Calculated for $C_{14}H_{16}N_2O_4$, %: N 10.14.

p-Bis(2-methyl-5-thiazolyl)benzene (VIII). The cyclization of the preceding compound to the base VIII was carried out by analogy with [2]. In a mortar, 4.85 g of p-bis(acetylaminoacetyl)benzene was ground with 3.5 g of phosphorus pentasulfide, and then 15 ml of pyridine was added and the mixture was heated at 160° C for 15 min. The pyridine was distilled off in vacuum, the light brown mass was extracted with 15% sodium hydroxide solution, and the residue was crystallized from ethanol. Yield 2 g (42%), mp 258° C (decomp). Found, %: S 23.53, 23.69. Calculated for $C_{14}H_{12}N_2S_2$, %: S 23.52.

The bis(methyl tosylate) derivative of the base was obtained similarly to the bistosylate V, mp 245° C (decomp).

The biscyanine II was obtained from the preceding salt in a similar manner to the biscyanine I. Yield 12%, mp 275° C (decomp). Found, %: S 7.23, 7.18. Calculated for $C_{42}H_{45}Cl_2N_4O_8S_2$, %: S 7.38.

The dye IX was obtained from the same components with a large excess of the bisquaternary salt in a similar manner to dye VII. Yield 12%, mp 205° C (decomp). Found, %: S 9.24, 9.06. Calculated for $C_{29}H_{31}Cl_2N_3O_8S_2$, %: S 9.35.

N, N'-Bis(thioacetyl)-p-phenylenediamine. A mixture of 10 g of N, N'-diacetyl-p-phenylenediamine [9] and 10 g of phosphorus pentasulfide in 15 ml of pyridine was heated at 110–115° C for 20 min. The pyridine was distilled off in vacuum and the residue was dissolved in 5% sodium hydroxide and precipitated from the solution with carbon dioxide. Yield 2 g (17%), yellow needles, mp 229° C (from ethanol, decomp). Found, %: S 28.31, 28.35. Calculated for $C_{10}H_{12}N_2S_2$, %: S 28.57.

2, 2', 4, 4'-p-Phenylene-3, 3'-bisthiazolium dichloride (X). A mixture of 1.7 g of the preceding compound and 1.26 g of chloroacetone was heated at 100° C for 5 min. The melt was washed with benzene and ether and crystallized from ethanol. Yield 1.02 g (35%), mp 292–293° C (decomp). Found, %: S 16.97, 17.04. Calculated for $C_{16}H_{18}Cl_2N_2S_2$, %: S 17.15.

The diperchlorate was obtained from the dichloride by the action of sodium perchlorate. It did not melt below 330° C. Found, %: S 12.73, 12.68. Calculated for $C_{16}H_{18}Cl_2N_2O_8S_2$, %: S 12.77.

The biscyanine III was obtained from the preceding salt and VI in acetic anhydride. The dye was precipitated with ether and recrystallized from a mixture of ethanol and nitromethane. Yield 10%, mp 230° C (decomp). Found, %: S 7.09, 7.09. Calculated for $C_{42}H_{45}Cl_2N_4O_8S_2$, %: S 7.38.

The dye XI was obtained from the same components with an excess of the bisquaternary salt in a similar manner to dye VII. Yield 11%, mp 181° C (decomp). Found, %: S 8.85, 8.97. Calculated for $C_{20}H_{31}Cl_2N_3O_8S_2$, %: S 9.35.

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