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.

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:

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:

The biscyanine II was prepared by a somewhat more complex method:
The mother dye IX corresponding to the biscyanine II was obtained in a similar manner to dye VII:

\[
\text{CH}_3\text{2} \text{ Tos CH}_3
\]

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

\[
\text{CH}_3\text{CO NH}--\text{C}_6\text{H}_4--\text{NH COCH}_3 \rightarrow S \text{ S}
\]

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

\[
\text{CH}_3\text{2} \text{ ClO}~ \text{XI}
\]

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.

\[
\text{Fig. 2. Absorption spectra of the biscyanine II and the dye IX.}
\]

The absorption curves of the biscyanine II (\(\lambda_{\text{max}} 544 \text{ nm}\)) and the monocyanine VII (\(\lambda_{\text{max}} 538 \text{ nm}\)) almost agree both with respect to their shapes and to the positions of the maxima, but the intensity of the absorption band in I (\(\varepsilon 1.02 \times 10^5\)) is far higher than in VII (\(\varepsilon 0.66 \times 10^5\)). 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].

\[
\text{Fig. 3. Absorption spectra of the biscyanine III and the dye XI.}
\]

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 (\(\lambda_{\text{max}} 562 \text{ nm}\), \(\varepsilon 0.8 \times 10^5\)) is split in the spectrum of the biscyanine III into two bands (\(\lambda_{\text{max}} 548 \text{ nm}\), \(\varepsilon 0.79 \times 10^5\), and \(\lambda_{\text{max}} 516 \text{ nm}\), \(\varepsilon 0.70 \times 10^5\)). 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 (\(\lambda_{\text{max}} 540 \text{ nm}\), \(\varepsilon 0.70 \times 10^5\)) is split in the biscyanine XI into two bands (\(\lambda_{\text{max}} 548 \text{ nm}\), \(\varepsilon 0.79 \times 10^5\), and \(\lambda_{\text{max}} 516 \text{ nm}\), \(\varepsilon 0.70 \times 10^5\)). 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 28.82, 23.80. Calculated for C14H12N2S2, %: 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 273 °C (decomp). Found, %: S 19.88, 19.86. Calculated for C18H18N2O4S2, %: S 19.87.

The biscyanine II. A mixture of 0.8 g of the salt V, 0.4 g of 2-formylmethylene-1,3,3-trimethylindoline (VI) and 3 ml of acetic an-