BISCYANINES WITH UNCONJUGATED CHROMOPHORES FROM 2,4-DIMETHYLTHIAZOLE AND LEPIDINE DERIVATIVES

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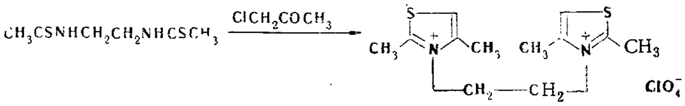
Bisquaternary salts in which the hydrogen atoms of the heterocyclic rings are bonded by polymethylene chains of different lengths were synthesized from lepidine and 2,4-dimethylthiazole. Biscyanine dyes were obtained from salts with an active methyl group. The absorption spectra of the dyes were investigated. It is shown that the unconjugated chromophores linked by a saturated chain of short length have a mutual effect upon one another, and this interaction decreases rapidly as the length of the isolating group increases.

It has recently been shown in a number of cases [1-3] that there is no fundamental difference between bisdyes in which the chromophores are conjugated or isolated. An investigation of the absorption spectra of bisdyes with chromophores isolated by polymethylene chains of short length showed that the chromophores have an appreciable effect on one another, as a consequence of which the absorption band of the dye component is split into two bands of the bisdye. This sort of interaction is realized through space and therefore weakens rapidly as the distance increases [3].

Dyes in which two chromophores are linked through nitrogen atoms of the heterorings of a saturated chain consisting of several methylene groups are the simplest biscyanines with unconjugated chromophores. Despite the fact that dyes of this sort are known [4, 5], their absorption spectra have not been adequately studied, and no one has observed the mutual effect of unconjugated chromophores. This is apparently associated to a considerable degree with the difficulty involved in the isolation of the corresponding bisquaternary salts and the dyes themselves in pure form.

We decided to use biscarbocyanines with polymethylene bridges from bisquaternary salts of 2,4-dimethylthiazole and lepidine as the objects for this investigation. Bisquaternary salts with bridges of short length (for example, $-CH_2CH_2-$) are difficult to obtain and for most of the methyl-substituted heterocycles cannot be obtained by direct quaternization.

We synthesized 3,3'-ethylenedi(2,4-dimethylthiazolium) diperchlorate (I) from dithioacetylethylenediamine [6]:



I

We recently obtained 1,1'-ethylenedi(4-methylquinolinium) di(p-toluenesulfonate) (IIa) and from it biscyanines, for which a rather strong interaction of the two unconjugated chromophores is characteristic [7].

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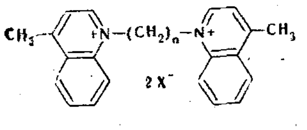
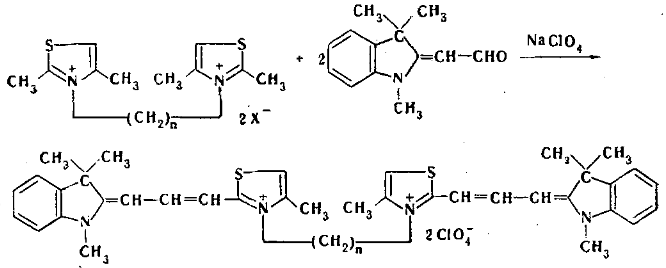


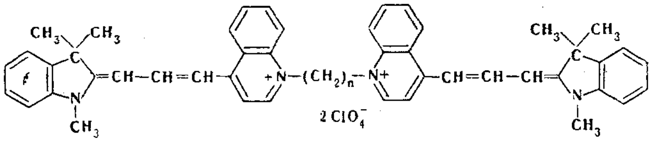
II a-d

II a $n = 2$, $X = p\text{-}CH_3C_6H_4SO_3$,
b $n = 3$, $X = Br$;
c $n = 4$, $X = I$;
d $n = 5$, $X = ClO_4$

Salts of 2,4-dimethylthiazole and lepidine with longer bridges (trimethylene, tetramethylene, etc.) are more accesible, and some of them have been described [5, 8]. Inasmuch as the preparation of bisquaternary salts is usually accompanied by the formation of the corresponding hydrobromide or hydriodide [8] and also monoquaternary salts [7, 9], we used treatment with ammonium hydroxide in the isolation of the required products, after which the salts were washed thoroughly or crystallized. The bisquaternary salts were subjected to condensation with 1,3,3-trimethyl-2-formylmethyleneindoline for the synthesis of the biscyanines. Biscyanines (VII-X) were similarly obtained from lepidine salts (IIa-d).



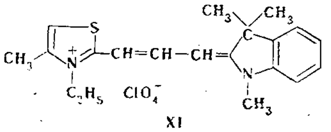
III-VI



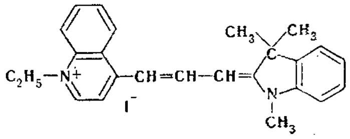
VII-X

III, VII $n=2$; IV, VIII $n=3$; V, IX $n=4$; VI, X $n=5$

It seemed of interest to ascertain how the interaction of the two unconjugated chromophores depends on the length of the polymethylene bridge in the case of typical biscyanine dyes. The absorption maxima and logarithms of the extinctions of the dyes obtained and of the corresponding dye components as well as the degree of the interaction of the chromophores are presented in Table 1.



XI



XII

The following irregularities are observed for the dyes of the thiazole series (Table 1). Biscyanine III has an absorption curve that differs appreciably in form from the curve of dye component XI. The presence of a distinct inflection on the short-wave branch and the considerable shift of the absorption maximum to the long-wave region of the spectrum provide evidence that two chromophores separated by a $-CH_2CH_2-$ group interact in biscyanine III. The degree of interaction is 39 nm. The form of the absorption curve of biscyanine IV recalls the curve of dye III, but the interaction of the chromophores here is weaker and the degree of interaction is 32 nm. The mutual effect of the chromophores is practically absent in biscyanines V and VI, although their absorption maxima are somewhat shifted to the long-wave region as compared with the maximum of dye XI. The interaction of two unconjugated chromophores shows up more distinctly in the lepidine series (Table 1). The spectrum of dye VII shows the characteristic pattern of splitting of the absorption band of dye component XII into two bands of the biscyanine. The degree of interaction is 71 nm. The chromophores in biscyanine VIII have a considerably smaller effect on one another. Both the form of the curve and the degree of interaction (41 nm) attest to this. In the case of a tetramethylene bridge (dye IX), the effect of the chromophores is weakened to an even greater extent, even though it does show up to a certain degree. In dye X with chromophores separated by five methylene groups, the effect of the interaction practically does not show up, although the maximum of the biscyanine is shifted by 16 nm to the long-wave region of the spectrum.

TABLE 1. Biscyanines III-XII

Compound	n	mp, °C	Empirical formula	Cl, %		λ_{max_1}, nm ($\lg \varepsilon_1$)	λ_{max_2}, nm ($\lg \varepsilon_2$)	Degree of interaction, Δ, nm ($\lambda_2 - \lambda_1$)	Yield, %
				found	calc.				
III	2	214—216	$C_{38}H_{44}Cl_2N_4O_8S_2$	8,6	8,7	507 (4,90)	546 (4,98)	39	29
IV	3	168—170	$C_{39}H_{46}Cl_2N_4O_8S_2$	8,7	8,5	500 (4,96)	532 (5,02)	32	42
V	4	267—270	$C_{40}H_{48}Cl_2N_4O_8S_2$	8,3	8,4	—	520 (5,16)	—	30
VI	5	247—250	$C_{41}H_{50}Cl_2N_4O_8S_2$	8,0	8,2	—	517 (5,17)	—	22
XI*							514 (4,95)		
VII	2	207—210	$C_{48}H_{48}Cl_2N_4O_8$	8,1	8,1	576 (5,25)	647 (5,10)	71	50
VIII	3	203—208	$C_{49}H_{50}Cl_2N_4O_8$	8,2	7,9	583 (5,16)	624 (5,31)	41	55
IX	4	200—203	$C_{50}H_{52}Cl_2N_4O_8$	8,1	7,8	590 (5,24)†	621 (5,37)	31	20
X	5	194—197	$C_{51}H_{54}Cl_2N_4O_8$	7,9	7,7	—	618 (5,34)	—	63
XII[13]							602 (5,04)		

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* Obtained from 2,4-dimethylthiazole ethiodide by the method in [12].

† Inflection.

The data that we obtained are in agreement with the data for bismerocyanine [2] and bishemicyanine [3] dyes.

Kiprianov and Buryak [3] linked the degree of interaction of unconjugated chromophores not only with the number of methylene groups but also with the distances between the chromophores, calculated with allowance for the bond length of the isolating groups; however, they pointed out that these distances are overstated. This sort of quantitative evaluation is more descriptive.

However, the differences between the chromophores are apparently determined by the distances between the nitrogen atoms of the heteroring but also depend on the spatial orientation of the chromophores. Thus, judging from the spectrum of biscyanine VII, its two chromophores are situated at an acute angle [11] with respect to one another, and, moreover, the distance between the chromophores should, of course, be smaller. Hence it is understandable why the greatest degree of interaction of the chromophores is observed precisely for dye VII.

The large number of possible conformations that arise as a result of rotation about the C—C and C—N bonds of the bridges is difficult to take into account. The angles between the direction of the chromophores can be taken as different values corresponding to different equilibrium conformations.

EXPERIMENTAL

The absorption spectra of methanol solutions of the synthesized dyes were measured with an SF-10 spectrophotometer.

3,3'-Ethylenedi (2,4-dimethylthiazolium) Diperchlorate (I). A mixture of 0.352 g (2 mmole) of dithioacetylethylenediamine [6] and 1.2 g (13 mmole) of chloroacetone was heated at 100° for 10 min. The oily product was washed with benzene and dissolved in 10 ml of methanol. A solution of 0.75 g (6 mmole) of sodium perchlorate in methanol was added to the solution, and the resulting crystalline precipitate was removed by filtration and washed with methanol to give 0.17 g (19%) of a product that melted above 300° (from water). Found, %: Cl 15.6. $C_{12}H_{18}Cl_2N_2O_8S_2$. Calculated, %: Cl 15.7.

3,3'-Trimethylenedi (2,4-dimethylthiazolium) Diperchlorate (XIII). A mixture of 3.39 g (0.03 mole) of 2,4-dimethylthiazole and 2.02 g (0.01 mole) of 1,3-dibromopropane was heated in a sealed tube at 140-150 for 15 h. The solid mass was pulverized and washed with benzene and ether. Workup gave 1.53 g (36%) of the dibromide with mp 232-236° (from propyl alcohol). The diperchlorate had mp 235-238° (dec.). Found, %: S 14.1. $C_{13}H_{20}Cl_2N_2O_8S_2$. Calculated, %: S 13.7.

3,3'-Tetramethylenedi (2,4-dimethylthiazolium) Diiodide (XIV). A mixture of 2.3 g (0.02 mole) of 2,4-dimethylthiazole and 3.1 g (0.01 mole) of 1,4-diiodobutane was heated in a sealed tube at 140° for 5 h. The salt was washed with ether and dissolved in water. Ammonium hydroxide (0.7 ml) was added to the solution, the impurities were extracted with benzene, and the water was removed by vacuum distillation. The solid residue was washed with boiling propyl alcohol to give 2.17 g (40%) of a product with mp 264-266° (dec., from water). Found, %: I 46.8. $C_{14}H_{22}I_2N_2S_2$. Calculated, %: I 47.3.

3,3'-Pentamethylenedi (2,4-dimethylthiazolium) Dibromide (XV). A mixture of 3.39 g (0.03 mole) of 2,4-dimethylthiazole and 2.30 g (0.01 mole) of 1,5-dibromopentane was heated in a sealed tube at 140° for 11 h. The salt was isolated as in the preparation of diiodide XIV to give 1.58 g (35%) of a product with mp 240-243° from propyl alcohol. Found, %: Br 34.9; S 13.7. $C_{15}H_{24}Br_2N_2S_2$. Calculated, %: Br 35.1; S 14.0.

1,1'-Polymethylenedi (4-methylquinolinium) Salts (IIa-d). These salts were obtained by the method in [7, 8]. Salts IIb and IIc were obtained by refluxing lepidine with the appropriate polymethylene dihalides in propyl alcohol for 12 h, whereas salts IIa and IId were obtained without a solvent.

1,1'-Pentamethylene-4-methylquninolinium Diperchlorate (IId). This compound was isolated from the appropriate dibromide by the action of sodium perchlorate in methanol and had mp 207-210° (dec.). Found, %: Cl 12.7. $C_{25}H_{28}Cl_2N_2O_8$. Calculated, %: Cl 12.8.

Biscyanines III-X (Table 1). A mixture of 1 mmole of the appropriate bisquaternary salt and 2.2 mmole of 1,3,3-trimethyl-2-formylmethyleneindoline in 8-12 ml of acetic anhydride was refluxed for 15 min. Biscyanines V and VI were obtained by fusing 1 mmole of the bisquaternary salt with 3 mmole of 1,3,3-trimethyl-2-formylmethyleneindoline at 200° for 5 min. The dyes were removed by filtration; where necessary, the dyes were precipitated from actic anhydride by the addition of ether, washed with benzene and water, and crystallized from alcohol.

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