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STUDY OF THE ELECTRONIC INFLUENCE OF SUBSTITUENTS AND THE NATURE OF ELECTRONIC TRANSITIONS IN CYANINE DYES BASED ON PERCHLORATE N-BENZYL-4-METHYL-6-STYRYLQUINOLINE

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Abstract. *Cyanine dyes were synthesized by the interaction of N-benzyl-4-methyl-6-styrylquinolinium perchlorate with p-dimethylaminobenzaldehyde, p-diethylaminobezaldehyde, 1,3,3-trimethyl-2-formyl-methyleneindoline. In order to study the degree of electronic influence of the styryl fragment in the system of dyes, a comparison of their absorption spectra with similar dyes, which contain hydrogen and a sulfamide group in the sixth position of the quinolinium nucleus, was carried out.*

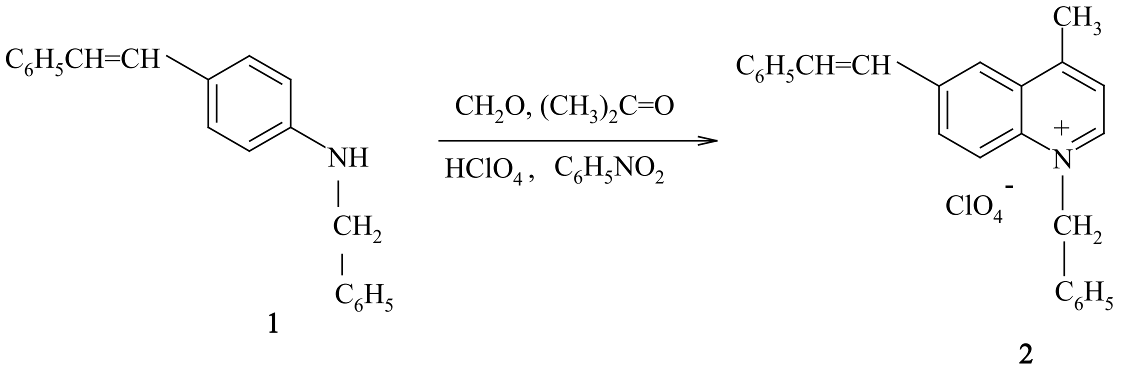
Key words: *quaternary salts, condensation, cyanine dyes, absorption spectra.*

Introduction.

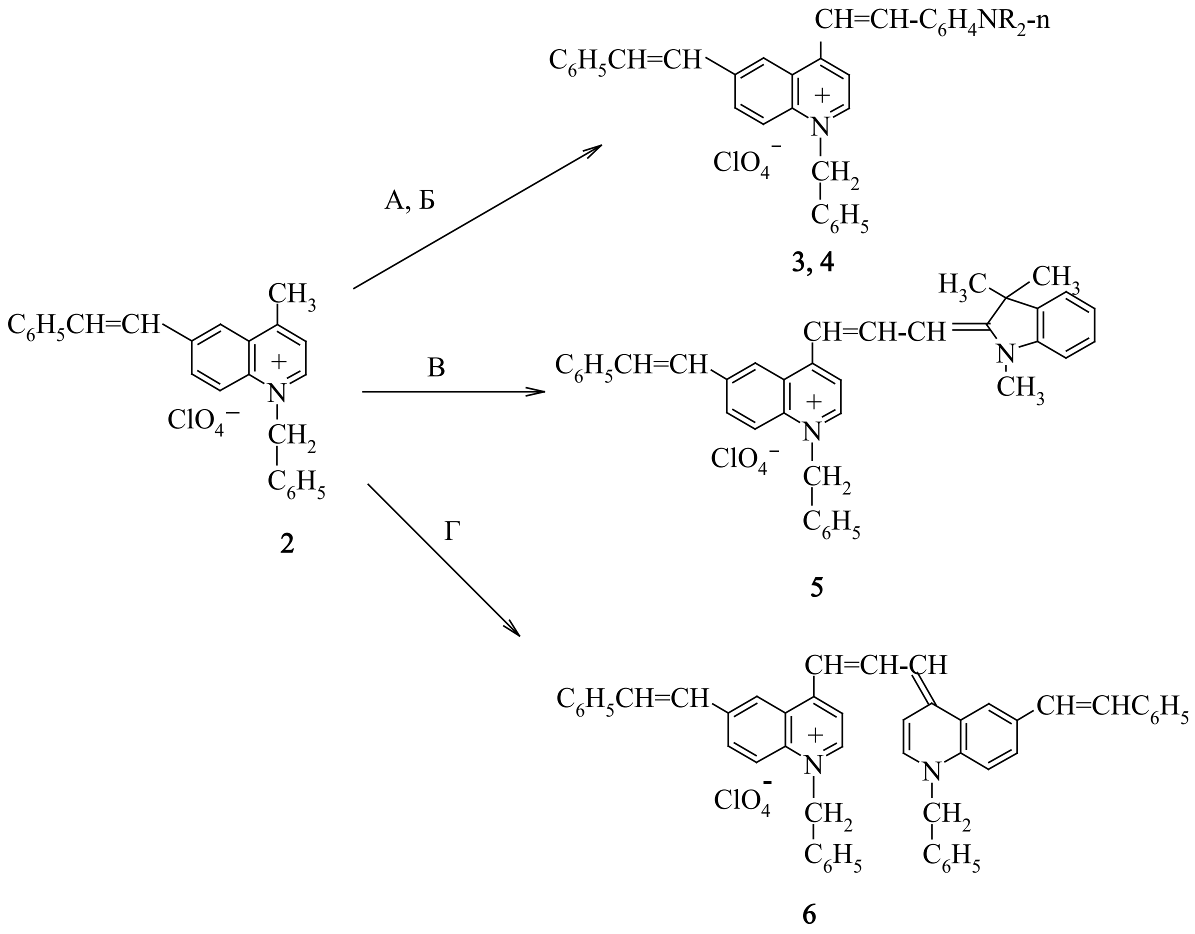
It is known that cyanine dyes are convenient models for studying the influence of the structure of dye molecules on the nature and magnitude of their absorption band maxima. The study of the properties of cyanine dyes, the symmetry of which is broken by the introduction of substituents, showed that this leads to a shift in the maxima of their absorption bands, which is due to changes in the coplanarity of the dye molecules, as well as their polar effect [1].

It is interesting to develop a method for the synthesis of cyanines based on quaternary salts that contain a styryl fragment in the sixth position of the quinolinium nucleus. The study of this type of dyes makes it possible to compare the effect of the fragment on the maxima of the absorption bands of similar cyanine dyes, which contain substituents of different electronic structure. Before the beginning of our research, polycarbocyanines with styryl substituents in the benzothiazole nuclei were described in the literature [2]. It was established that *cis*-styrylcarbocyanines absorb light in a shorter wavelength range (for the 5,5'-derivative – 574 nm, and for the 6,6'-derivative – 579 nm) than the corresponding *trans*-isomers (for the 5,5'-derivative – λ_{max} 578 nm, and for 6,6' – 595 nm). The hypsochromic shift of the maxima of the absorption bands in *cis*-styrylcarbocyanines is explained by the violation of conjugation of styryl fragments with the main polymethine chromophore. In addition, the synthesis of 6-styryl-thiadimethinemerocyanines and rhodacyanines was carried out in [3]. It is shown that the presence of a styryl fragment in the benzothiazole residue of merocyanines and complex trinuclear dyes – rhodacyanines also leads to a deepening of the color. Works [4-7] show that the optical properties of 6-substituted quinocyanines depend to a large extent on electron-donating and electron-accepting substituents.

Continuing research in the field of quinocyanine dyes obtained on the basis of N-benzyl-2-methyl-6-styrylquinolinium perchlorate [8], we carried out a synthesis based on the quaternary salt of N-benzyl-4-methyl-6-styrylquinolinium perchlorate (**2**), obtained cyclization of 4-aminobenzylstilbene (**1**) with acetone and formaldehyde under Bayer reaction conditions [9] (Scheme 1).



Scheme 1



R = CH_3 (3), C_2H_5 (4)

Scheme 2

Synthesized N-benzyl-4-methyl-6-styrylquinolinium perchlorate (**2**) easily undergoes condensation on the active methyl group with *p*-dimethylaminobenzaldehyde (**A**), *p*-diethylaminobenzaldehyde (**Б**), 1,3,3-trimethyl-2-formylmethyleneindoline (**B**) and formic acid orthoester (**Г**), as a result of which cyanine dyes (**3-6**) were obtained (Scheme 2). Yields, constants, elemental analysis data and visible absorption spectra of cyanine dyes (**3-6**) are given in table 1.

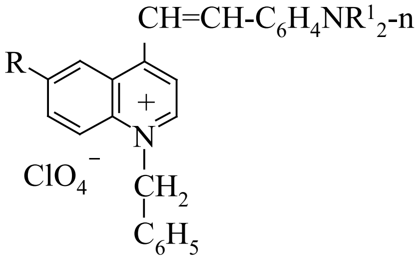
It can be seen from the table that the absorption spectra of quinocyanines are characterized by one absorption maximum in the region of 578-746 nm.

Table 1 - Physico-chemical characteristics of cyanins (3-6)

Compound	Yield, %	$T_{melt.}$, °C (decomposition)	$\lambda_{max.}$, nm (in ethanol)	lgε	Found, %		Formula	Calculated, %	
					Cl	N		Cl	N
3	77	250	578	4,65	6,12	4,83	$C_{34}H_{31}ClN_2O_4$	6,25	4,94
4	88	220	590	4,82	5,80	4,59	$C_{36}H_{35}ClN_2O_4$	5,95	4,71
5	86	218	630	5,02	5,51	4,34	$C_{38}H_{35}ClN_2O_4$	5,72	4,52
6	60	> 300	746	5,20	4,38	3,40	$C_{51}H_{41}ClN_2O_4$	4,54	3,58

To study the degree of electron-accepting action of the styryl fragment in the dye system, we selected similar dyes containing hydrogen and a sulfamide group. Analysis of absorption spectra shows that the presence of an electron-accepting styryl substituent in the sixth position of the quinolinium nucleus in cyanine molecules (**3**, **4**), compared to similar unsubstituted dyes, causes a bathochromic shift of the absorption band by 14 and 4 nm, respectively (Table 2).

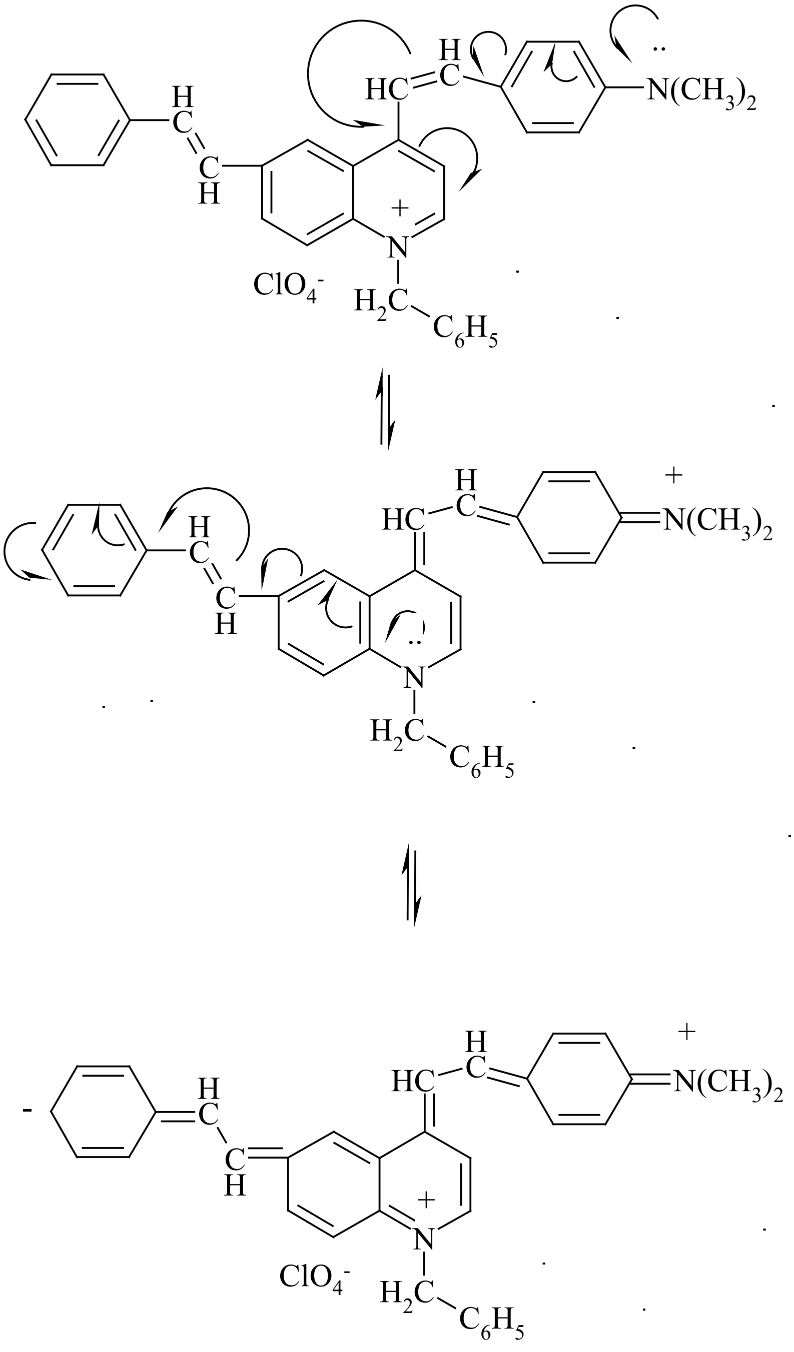
Table 2 - Dependence of the maxima of the absorption bands of styryl dyes on the nature of the substituents



3, 4

Compound	R	R^1	λ_{max}, nm (in ethanol)	The amount of displacement λ_{max}, nm
3	$C_6H_5CH{=}CH$-	CH_3	578	—
4	$C_6H_5CH{=}CH$-	C_2H_5	590	—
—	H	CH_3	564 [7]	14
—	H	C_2H_5	586 [7]	4
—	H_2NSO_2-	CH_3	604 [7]	-26
—	H_2NSO_2-	C_2H_5	624 [7]	-34

This can be explained by the fact that the introduction of the styryl fragment leads to a decrease in the basicity of the quinoline core and an increase in the equivalence of the boundary structures (Scheme 3).



Scheme 3

The formation of a resonance structure with an elongated chromophore system leads to the ease of delocalization of π-electrons, and as a result, the shift of the absorption band of the dye to the long-wavelength region. This is possible only in the case when the chromoform system of the dye is in the same plane, that is, by placing styryl fragments in the *trans*-configuration.

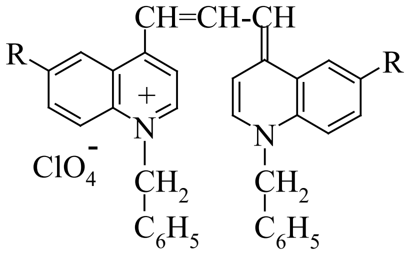
If the dyes (**3-6**) contained *cis*-styryl fragments, this would lead both to a violation of the conjugation with the chromoform system of the dye and to a shift of their absorption bands to the short-wavelength region. In the case of finding styryl fragments in the *trans* form, there is no spatial interaction in the conjugation chain.

A comparison of quinocyanines (**3, 4**) with similar dyes containing a sulfamide group shows that there is a hypsochromic shift of the absorption band in the dyes at 26 and 34 nm, respectively (Table 2).

This indicates a lower degree of electronic influence of the styryl fragment compared to the sulfamide group, since the presence of this group leads to a greater decrease in the basicity of the core and the dye becomes less asymmetric.

A comparison of the absorption spectra of carbocyanine dye (**6**) with similar dyes containing hydrogen and a sulfamide group shows that the presence of styryl fragments in the carbocyanine molecule causes a bathochromic shift of the absorption bands by 30 and 13 nm, respectively (Table 3).

Table 3 - Dependence of the maxima of the absorption bands of bistrimethine dyes on the nature of the substituents



6

Compound	R	λ_{max}, nm (in ethanol)	The amount of displacement λ_{max}, nm
6	$C_6H_5CH=CH-$	746	–
—	H	716 [7]	30
—	H_2NSO_2-	733 [7]	13

This is explained by the fact that the presence of styryl fragments in the dye molecule leads to the elongation of the chromoform system, which causes absorption in a longer wavelength region.

Experimental part

Electronic absorption spectra of dyes were recorded on a SF-46 spectrophotometer at concentrations of $1\cdot10^{-4} - 1\cdot10^{-5}$ mol/l. Melting points were determined using a Boetius apparatus.

4-Benzylaminostilbene (1). A mixture of 19.5 g (0.1 mol) of 4-aminostilbene [9], 12.6 ml (0.1 mol) of benzyl chloride and 4 g (0.1 mol) of sodium hydroxide in 25 ml of ethanol was boiled in a sealed ampoule in a water bath for 18-25 hours. Unreacted substances were driven off with steam from the reaction mixture acidified with hydrochloric acid. The remaining solution was separated from the resinous products and the secondary amine (**1**) was precipitated with a 10% alkali solution. The formed precipitate was filtered, washed with water and dried. Yield 14.3 g (50%). Crystallized from isopropyl alcohol. $T_{melt.}$ 116-118 °C. Found, %: C 88.21; H 6.50; N 4.86. Calculated, %: C 88.38; H 6.71; N 4.91.

N-Benzyl-4-methyl-6-styrylquinolinium perchlorate (2). In a three-necked flask containing a mechanical stirrer, a reflux condenser and a dropping funnel 24.5 g (0.86 mol) of 4-benzylaminostilbene, 50 ml of water, 35 ml of perchloric acid (30%), 18.75 ml (0.26 mol) of acetone, and 10 ml of nitrobenzene were added. The reaction mixture was heated in a boiling water bath for 30 minutes. While stirring, 12.5 ml of formalin (30%) was added in small portions for 30 minutes. After adding all the formalin, the reaction mixture was continued to be heated with stirring for 7 hours. The brown resinous product formed at the bottom of the flask was treated six times with small portions of boiling water. Water extracts were combined and boiled with activated charcoal. After filtering, the solution was evaporated in a porcelain cup in a water bath until the crystallization of the quaternary salt began. After 12 hours, the precipitate that fell out was crystallized twice from ethanol. Yield 7.1 g (19 %). $T_{melt.}$ 140-142 °C. Found, %: Cl 7.92; N 3.08. $C_{25}H_{22}ClNO_4$. Calculated, %: Cl 8.13; N 3.21.

N-Benzyl-4-(*p*-dimethylaminostyryl)-6-styrylquinolinium perchlorate (3). A mixture of 0.11 g (0.00025 mole) of quaternary salt (**2**) and 0.037 g (0.00025 mol) of *p*-dimethylaminobenzaldehyde in 5 ml of acetic anhydride was boiled for 45 minutes. After cooling, the reaction mixture was treated with diethyl ether. The formed precipitate was filtered and crystallized from ethanol (Table 1).

N-Benzyl-4-(*p*-diethylaminostyryl)-6-styrylquinolinium perchlorate (4). A mixture of 0.11 g (0.00025 mole) of quaternary salt (**2**) and 0.044 g (0.00025 mole) of *p*-diethylaminobenzaldehyde in 5 ml of acetic anhydride was boiled for 50 minutes. The resulting precipitate was filtered off and crystallized from ethanol.

N-Benzyl-6-styryl-(4-quinolyl)(1,3,3-trimethyl-2-indolinylidene)-trimethinecyanine perchlorate (5). A mixture of 0.11 g (0.00025 mole) of quaternary salt (**2**) and 0.048 g (0.00025 mole) of 1,3,3-trimethyl-2-formylmethyleneindoline in 3 ml of acetic anhydride was boiled for 50 minutes. After cooling, the reaction mixture was treated with diethyl ether. The formed precipitate was filtered and crystallized from ethanol.

Bis-(N-benzyl-6-styryl-4-quinolyl)trimethyncyanine perchlorate (6). A mixture of 0.11 g (0.00025 mole) of quaternary salt (**2**) and 0.040 g (0.00025 mole) of formic acid orthoester in 3 ml of pyridine was boiled for 50 minutes. After cooling, the precipitate was filtered, washed with ethanol and diethyl ether. Crystallized from aqueous ethanol (Table 1).

Conclusion A method of synthesis of the quaternary salt of N-benzyl-4-methyl-6-styrylquinolinium, based on which styryl and carbocyanine dyes were obtained, was developed.

The degree of electronic influence of the styryl fragment in the system of the obtained dyes was studied.

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