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ABSORPTION SPECTRA AND NATURE OF ELECTRONIC TRANSITIONS OF BISCYANINE DYES BASED ON QUINOLON-CONTAINING QUATERNARY SALT OF 4-METHYLPYRIDINIUM

Jagodinetz P.*Yuriy Fedkovych Chernivtsi National University,
Chernivtsi, st. Kotsyubinsky 2, 58012 Ukraine***Skrypska O.***c.ch.s., as.prof.*

ORCID: 0000-0001-7212-2929

*Yuriy Fedkovych Chernivtsi National University,
Chernivtsi, st. Kotsyubinsky 2, 58012 Ukraine***Hotynchan A.**

ORCID: 0000-0002-1569-8590

*Yuriy Fedkovych Chernivtsi National University,
Chernivtsi, st. Kotsyubinsky 2, 58012 Ukraine***Barus M.***c.ch.s., as.prof.*

ORCID: 0000-0001-9447-6170

*Bukovinian State Medical University,
Chernivtsi, sq. Teatralna 2, 58000 Ukraine***Olga HORYNYK***Grozynetsky Lyceum of the Toporiv village council of the Chernivtsi district
of the Chernivt region, st. Druzhyby, 1-A, 60020 Ukraine*

Abstract. *Biscyanine dyes were synthesized by the interaction of quinolone-containing quaternary salts of 4-methylpyridinium with p-diethylaminobenzaldehyde and 1,3,3-trimethyl-2-formylmethyleneindoline. Two absorption bands due to the interaction of chromophores were found in the spectra of the dyes. The angle between the chromophores and the degree of their interaction were calculated. Electronic spectra of biscyanine dyes were analyzed.*

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

Introduction.

Quaternary salts of methyl derivatives of pyridine and quinoline are intermediate products for obtaining cyanine dyes. The existence of two chromophore systems in the molecules of cyanine dyes leads to nonlinear phenomena in their absorption spectra. As a result of the interaction of chromophores, instead of the additive superimposition of the absorption spectra of individual chromophore-components, there is a repulsion of the absorption bands and a change in their intensities [1, 2]. The phenomenon of mutual influence of chromophores in biscyanine molecules was discovered by Kyprianov and Mushkalo [3, 4], and a quantum-chemical interpretation was proposed by Dyadyusha and Kyprianov [5, 6].

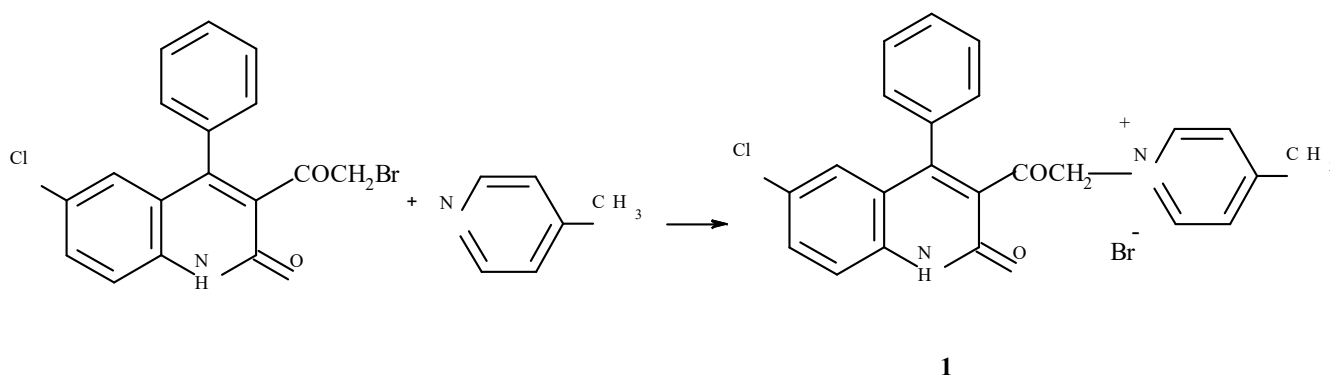
Biquaternary salts are used to obtain cyanines with two chromophores.

Previously, we obtained and studied dyes with two conjugated chromophores based on 1-[2-oxo-2-(coumarin-3-yl)ethyl]-4-methylpyridinium bromide [7]. Cyanine dyes using quaternary 4-methylquinolinium salts containing phenyl-, naphthyl-, and coumarinylcarbomethylene fragments near the nitrogen heteroatom were also investigated. It was established that they are capable of simultaneously entering into



condensation on both methyl and methylene groups, the activity of which is due to the presence of two electron-accepting centers in the molecules: a quaternary nitrogen atom and a carbonyl group [8-10]. The choice of such salts made it possible to investigate the influence of phenyl, naphthyl and coumarinyl radicals on the absorption spectra of biscyanine dyes and to study their spatial interaction. Optical spectra showed that the interaction of chromophores takes place in the dyes. A bischinocyanine dye based on the quaternary salt of 2-quinolone was studied, the synthesis of which was carried out by quaternization of 4-methylquinoline with the previously described 3-(ω -bromoacetyl)-4-phenyl-6-chloro-2-quinolone [11, 12]. Two absorption bands at 445 and 630 nm were found in the spectrum of the dye, which indicates the interaction of chromophores.

Continuing research in the field of quinolone-containing cyanine dyes, we used, as the starting compound, the quaternary salt **1**, which was obtained by the interaction of 4-methylpyridine with 3-(ω -bromoacetyl)-4-phenyl-6-chloro-2-quinolone (Scheme 1).



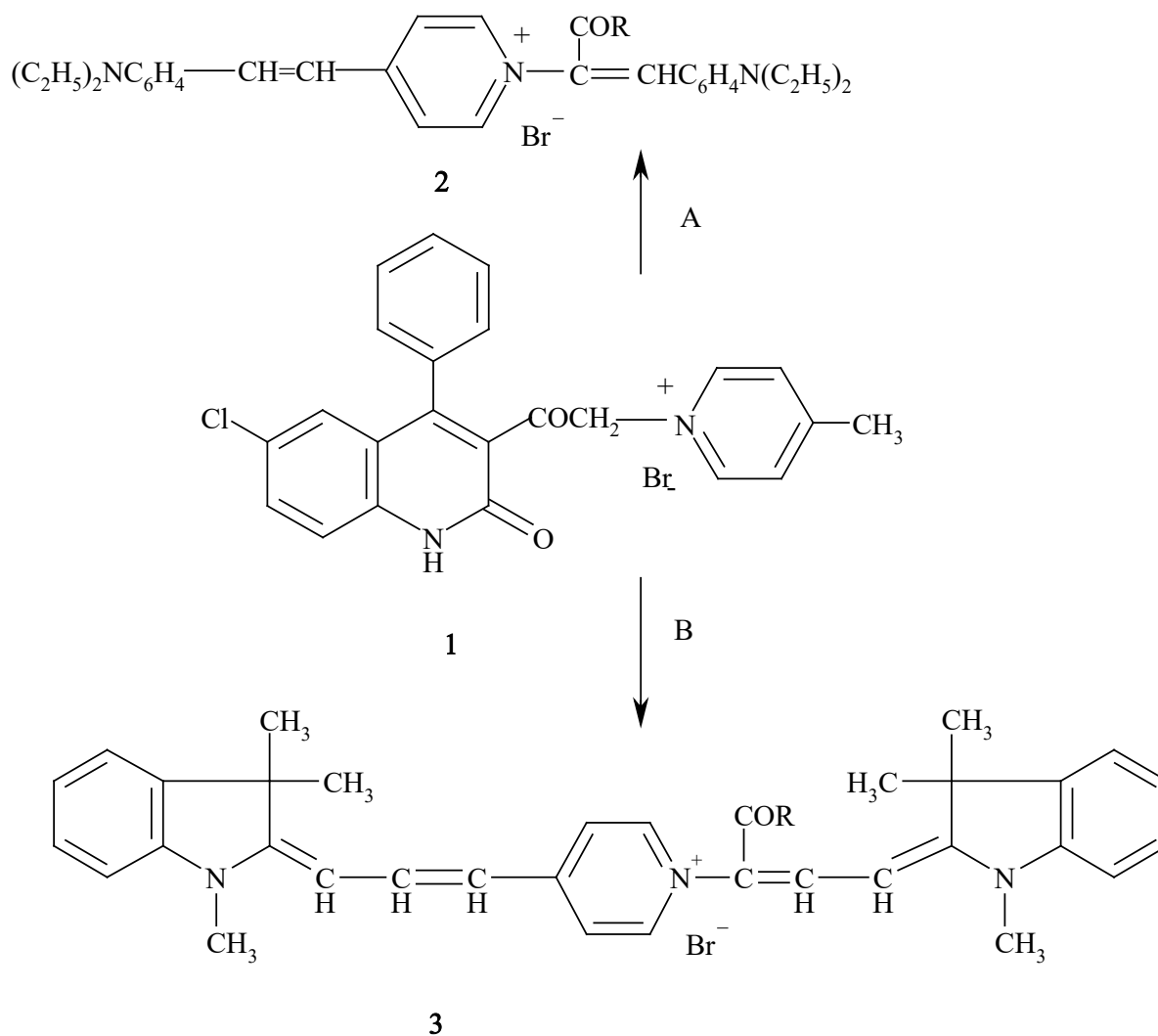
Scheme 1

Salt **1** in acetic anhydride undergoes cyanine condensation with *p*-diethylaminobenzaldehyde (**A**) and 1,3,3-trimethyl-2-formylmethyleneindoline (**B**) both on the methyl and methylene groups, forming biscyanines **2** and **3** (Scheme 2).

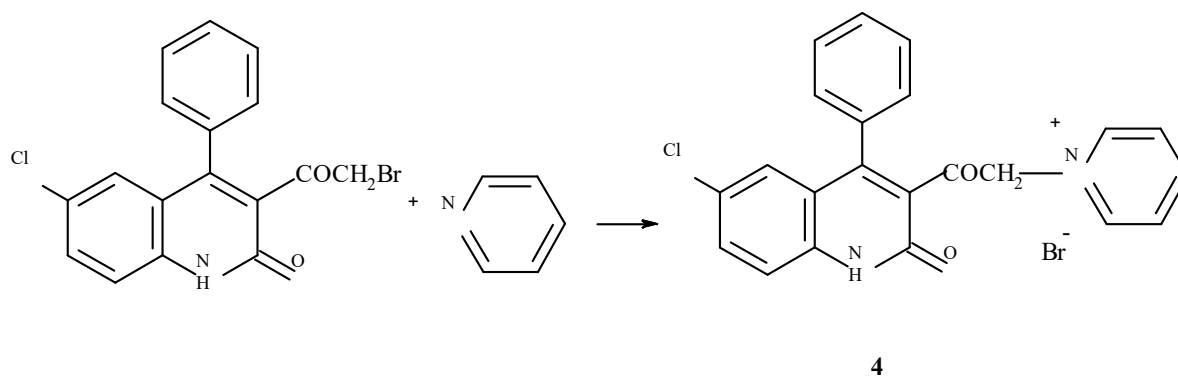
The absorption spectra of alcoholic solutions of biscyanines **2**, **3** have two bands: the first, short-wave, in the region of 450-456 nm and the second, long-wave, in the region of 535-568 nm (Table 1).

To confirm that the appearance of two absorption bands in the spectrum of biscyanine is due to the interaction of chromophores, we synthesized the "mother" cyanines **5**, **6** on the basis of the quaternary pyridinium salt **4**, which contains only one reaction center – a methylene group. Quaternization of pyridine with 3-(ω -bromoacetyl)-4-phenyl-6-chloro-2-quinolone was used for its synthesis (Scheme 3).

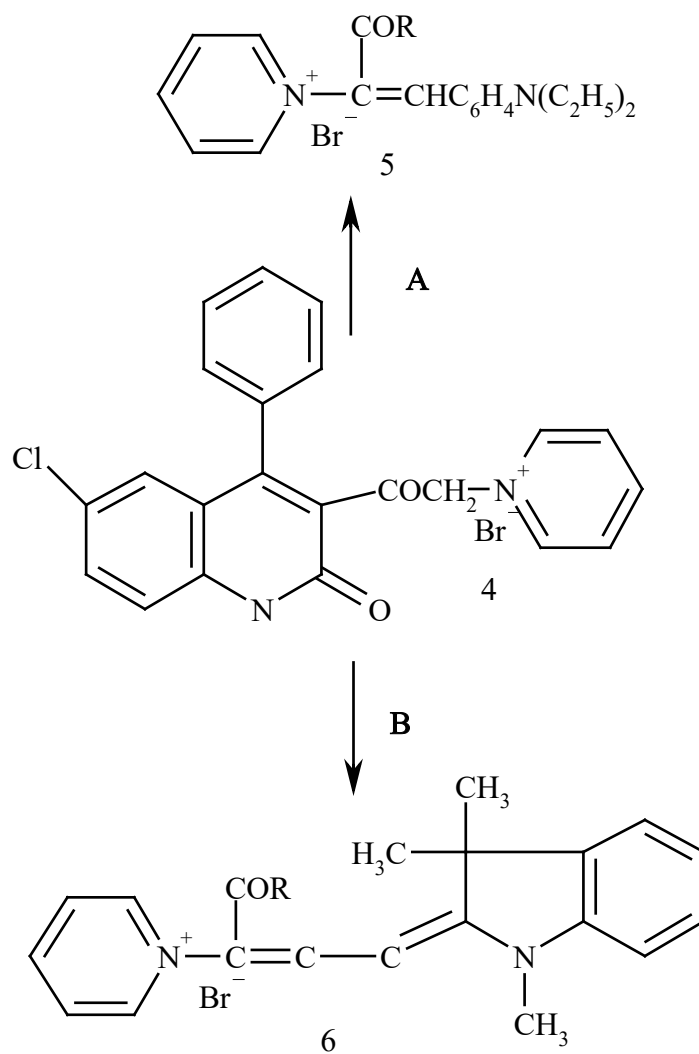
Monocyanines **5**, **6** were synthesized by condensation of the obtained salt **4** with the above-mentioned aldehydes **A** and **B** (Scheme 4), the physical and chemical characteristics of which are given in Table 2.



Scheme 2
 where R = 3-(4-phenyl-6-chloro-2-quinolonyl)



Scheme 3



Scheme 4



Table 1 - Yields, melting points, and data from elemental analysis and visible spectra absorption of biscyanine dyes 2, 3

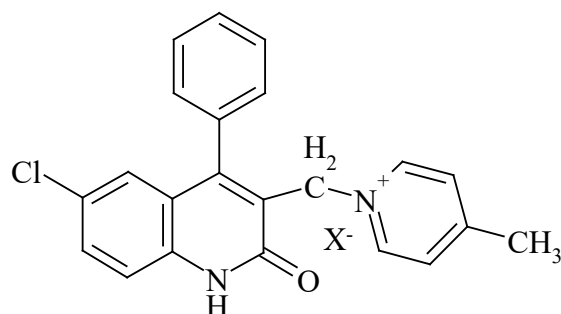
Compound	Yield, %	T.melt.°C (decomposition)	λ_{\max} , nm (in ethanol) (lg ϵ)	θ°	Δ , nm	Found, %		Formula	Calculated, %	
						Br	N		Br	N
2	58	235	450 (4,65) 535 (4,52)	88	37	9,84	6,82	C ₄₅ H ₄₄ BrClN ₄ O ₂	10,13	7,11
3	72	265	456 (4,42) 568 (4,48)	103	34	9,38	6,54	C ₄₉ H ₄₄ BrClN ₄ O ₂	9,55	6,69

Table 2. - Yields, melting points, and data from elemental analysis and visible spectra absorption of monocyanine dyes 5, 6

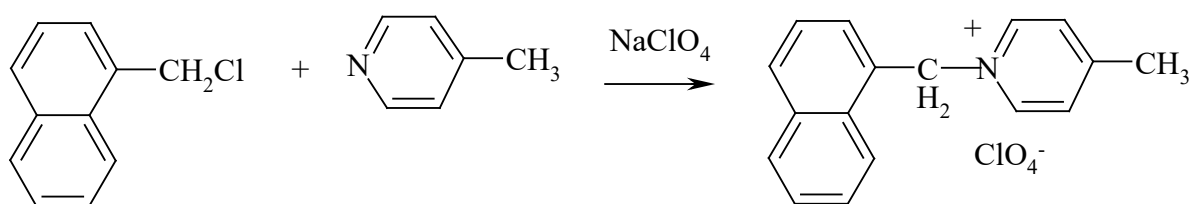
Compound	Yield, %	T.melt.°C (decomposition)	λ_{\max} , nm (in ethanol) (lg ϵ)	Found, %		Formula	Calculated, %	
				Br	N		Br	N
5	45	270	458	12,69	6,64	C ₃₃ H ₂₉ BrClN ₃ O ₂	12,99	6,83
6	42	282	460	12,31	6,42	C ₃₅ H ₂₉ BrClN ₃ O ₂	12,50	6,57



A quaternary pyridinium quinolone-containing salt containing only an active methyl group is not described in the literature.



Therefore, to obtain "mother" dyes based on a quaternary salt containing only an active methyl group, we used N-(1-naphthylmethyl)-4-methylpyridinium perchlorate **7** as a starting material, which was synthesized by the interaction of 1-chloromethylnaphthalene with 4-methylpyridine [7].



Taking into account the partial insulating effect of the methylene group during the transmission of electronic effects [13], it can be assumed that the maxima of the absorption bands in the spectra of styryl dyes containing naphthalene or quinolone fragments will not differ significantly.

As a result of the condensation of aldehydes **A**, **B** on the active methyl group of salt **7**, monocyanines with absorption maxima of 506 and 538 nm were obtained, respectively [7].

A comparison of the maxima of the absorption bands of biscyanines **2**, **3** with the maxima of the absorption bands of their "mother" dyes shows that the short-wave band in biscyanines is shifted to the violet, and the long-wave band to the red region of the spectrum, compared to the absorption bands of the component dyes.

Therefore, the absorption bands corresponding to the chromophores of the two "mother" dyes, as a result of the interaction of these chromophores in the biscyanine molecule, shifted. The greater shift of the maximum of the long-wave band compared to the short-wave band is explained by the different degree of delocalization of π -electrons in the polymethine chromophores of the "mother" dyes. The longer the polymethine chain, the more delocalized π -electrons, the stronger its interaction with the second chromophore [6].

Based on the perturbation theory and its application to electronic spectra [14, 3], it can be seen that in dyes with two conjugated chromophores, the mutual influence of chromophores depends on the absorption energy of each of the chromophores separately. If the absorbed light quanta differ greatly in energy, then there is no interaction of chromophores. If the absorbed quanta differ little, then the chromophores interact, and in such a way that the wavelength of absorption by one chromophore increases, and the wavelength of absorption by the other chromophore decreases, and the absorption bands are shifted.



In order to clarify the features of the spatial structure of biscyanines **2**, **3**, the angles θ between the directions of the chromophores in space were calculated according to the method developed earlier [5]. As can be seen from the table. 1, the transition from biscyanine **2** to **3** is accompanied by a change in the angle from acute to obtuse, which is caused by an increase in spatial constraints on the part of the chromophore chains. As the angle increases, the degree of chromophore interaction decreases, which determines the value $\Delta_2 - \Delta_1$, where Δ_2 is the difference between the maxima of the absorption bands of the biscyanine dye, and Δ_1 is the difference between the absorption maxima of its two "parent" dyes [6] (Table 1).

Therefore, based on the calculations, the interaction of chromophores in biscyanine dyes obtained on the basis of quinolone-containing quaternary salt of 4-methylpyridinium was confirmed.

Experimental part

The electronic absorption spectra of dyes were recorded on a SF-46 spectrophotometer in an ethanol solution at concentrations of $1 \cdot 10^{-4}$ - $1 \cdot 10^{-5}$ mole/l.

4-Phenyl-6-chloro-3-[carbomethyl-(4'-methylpyridiniumbromide)]-2-quinolone (1).

A mixture of 0.94 g (0.0025 mol) of 3-(ω -bromoacetyl)-4-phenyl-6-chloro-2-quinolone and 0.23 g (0.0025 mol) of 4-methylpyridine in 15 ml of toluene was boiled for 1 hour and left for 12 hours at room temperature. The formed precipitate was filtered off, washed with diethyl ether. Yield 0,9 g (77%). T melting >300 °C. Found, %: Br 16,75, N 5,73. $C_{23}H_{18}BrClN_2O_2$. Calculated, %: Br 17,00, N 5,96.

1-(3-(6-Chloro-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)-1-(4-(diethylamino)phenyl)-3-oxoprop-1-en-2-yl)-4-(4-(diethylamino)styryl)pyridinium bromide (2), 1-(1-(6-chloro-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)-1-oxo-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-2-yl)-4-(3-(1,3,3-trimethylindolin-2-ylidene)prop-1-enyl)pyridinium bromide (3).

A mixture of 0.0003 mol of salt **1** and 0.0003 mol of the corresponding aldehyde: *p*-diethylaminobenzaldehyde, 1,3,3-trimethyl-2-formylmethyleneindoline in 5 ml of acetic anhydride was boiled for 1-1.5 hours. After cooling, the reaction mixture was treated with diethyl ether. The resulting dyes were filtered and crystallized from ethanol (Table 1).

4-Phenyl-6-chloro-3-(carbomethylpyridiniumbromide)-2-quinolone (4).

A mixture of 0.94 g (0.0025 mol) of 3-(ω -bromoacetyl)-4-phenyl-6-chloro-2-quinolone and 0.2 g (0.0025 mol) of pyridine in 15 ml of toluene was boiled for 1.5 hours and left for 12 hours at room temperature. The formed salt precipitate was filtered, washed with diethyl ether. Yield 0.6 g (53%). T melting >230 °C. Found, %: Br 17.18, N 5.73. $C_{22}H_{16}BrClN_2O_2$. Calculated, %: Br 17.53, N 6.14.

1-{3-[6-Chloro-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)-1-(4-(diethylamino)phenyl)-3-oxoprop-1-en-2-yl]}pyridiniumbromide (5), 1-{1-[6-chloro-2-oxo-4-phenyl-1,2-dihydroquinolin-3-yl)-1-oxo-4-(1,3,3-trimethylindolin-2-ylidene)but-2-en-2-yl]}pyridiniumbromide (6).

A mixture of 0.0003 mol of salt **4** and 0.0003 mol of the corresponding aldehyde: *p*-diethylaminobenzaldehyde, 1,3,3-trimethyl-2-formylmethyleneindoline in 5 ml of acetic anhydride was boiled for 1-1.5 hours. After cooling, the reaction mixture was treated with diethyl ether. The resulting dyes were filtered and crystallized from



ethanol (Table 2).

Conclusion

1. By the interaction of 4-phenyl-6-chloro-3-[carbomethyl-(4'-methylpyridiniumbromide)]-2-quinolone with *p*-diethylaminobenzaldehyde and 1,3,3-trimethyl-2-formylmethyleneindoline, biscyanines were synthesized dyes.

2. A shift of the absorption bands of biscyanines compared to the absorption maxima of the "parent" monocyanines was revealed. The angles between the directions of chromophores in space and the degree of their interaction were calculated.

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