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# New Biscyanine Dye Based On 1-{2-Oxo-2-[4-(2-oxo-2*H*-chromen-3-yl)phenyl]ethyl}-4-methylpyridinium Bromide. Electron Transitions and Electronic Spectra

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**Abstract**—New biscyanine dye, 4-{2-[4-(dimethylamino)phenyl]ethenyl}-1-{2-[4-(dimethylamino)phenyl]-1-[4-(2-oxo-2*H*-chromen-3-yl)benzoyl]ethenyl}pyridinium bromide, has been prepared via condensation of 4-dimethylaminobenzaldehyde with 4-methyl-1-{2-oxo-2-[4-(2-oxo-2*H*-chromen-3-yl)phenyl]ethyl}pyridinium bromide. The latter has been synthesized via the Meerwein reaction of coumarin with 4-acetylphenyldiazonium chloride with subsequent bromination and quaternization of the formed α-bromoketone under the action of 4-methylpyridine. Electronic spectra are analyzed, and quantum-chemical simulation of possible isomers of the biscyanine dye has been performed.

**Keywords:** cyanine dye, coumarin derivative, arylation, quantum-chemical simulation, pyridinium salt

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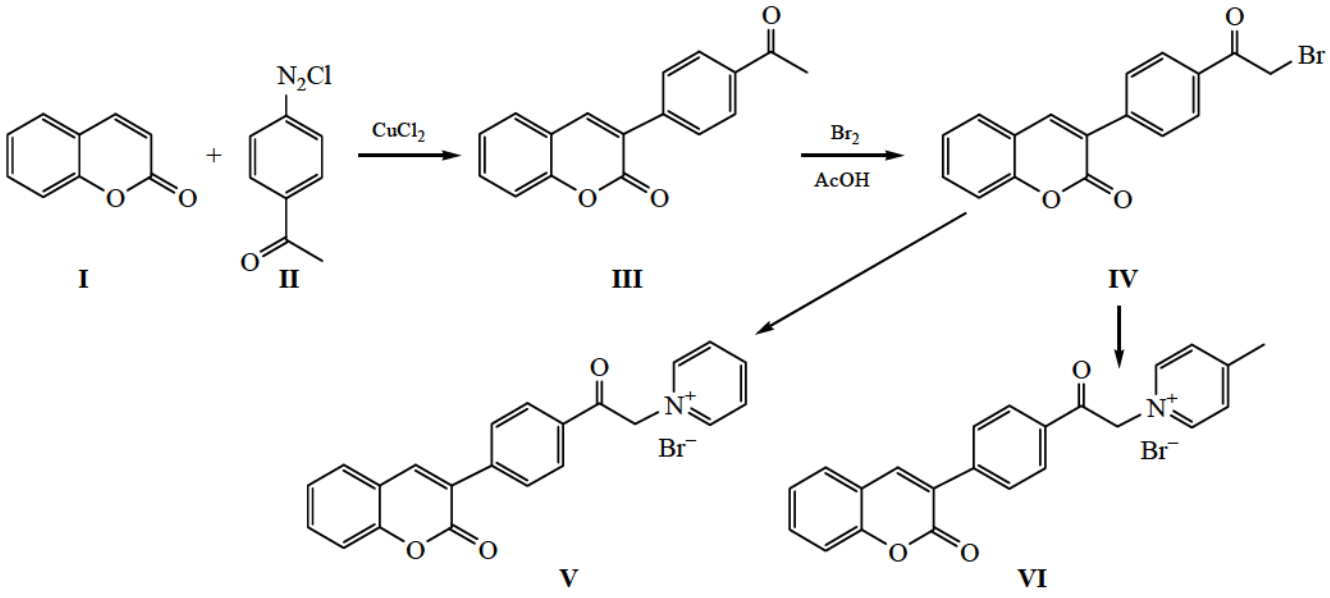
Quaternary salts of methyl-substituted pyridine and quinoline are intermediates in the synthesis of cyanine dyes. The presence of two chromophore systems in the molecules of cyanine dyes results in nonlinear effects reflected in their electronic spectra. Due to interaction of the chromophores, the spectrum is not a linear superposition of the spectra of the separate chromophores; instead, the absorption bands are moving apart, and their intensity is changed [1, 2]. This effect has been discovered in the case of cyanines by Kiprianov and Mushkalo [3, 4], and later its quantum-chemical explanation has been given [5, 6].

Earlier, cyanine dyes with two conjugated chromophores based on 1-[2-oxo-2-(coumarin-3-yl)ethyl]-4-methylpyridinium bromide were prepared, and their spectral properties were studied [7]. Spatial arrangement of the chromophores in biscyanine dyes was analyzed on the basis of their electronic spectra, and quantum-chemical simulation of geometry and electronic transitions parameters was performed for the similar salt of 4-methylquinolinium [8, 9].

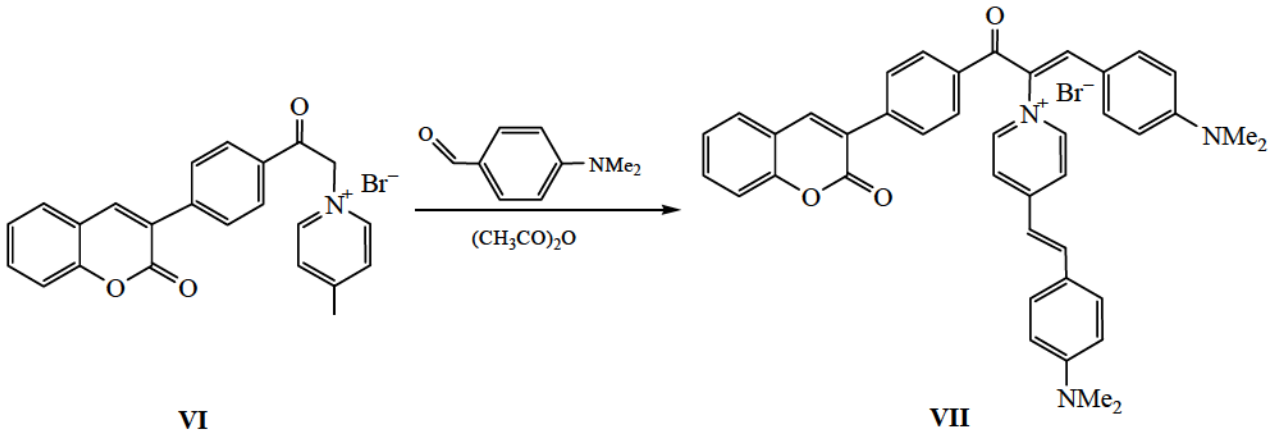
Extending our studies of biscyanine dyes, we first prepared biscyanine **VII** based on quaternary salt **VI** containing, apart from the carbonylmethyl group, the benzene ring between the coumarin and the pyridine rings. The quaternary salt was prepared via sequential transformations **III** → **IV** → **VI**. The Meerwein reaction of coumarin **I** with 4-acetylphenyldiazonium chloride **II** gave the substituted coumarin **III**. Its bromination in acetic acid led to bromoketone **IV**, its heating with pyridine or 4-methylpyridine in toluene afforded quaternary salts **V** and **VI** (Scheme 1).

The C=O absorption band in the IR spectra of salts **V** and **VI** appeared at 1660–1680 $cm^{-1}$, and the carbonyl group of the pyrone ring was assigned to the band at 1715–1725 $cm^{-1}$ [10]. The presence of N–$CH_2$

**Scheme 1.**




**Scheme 2.**



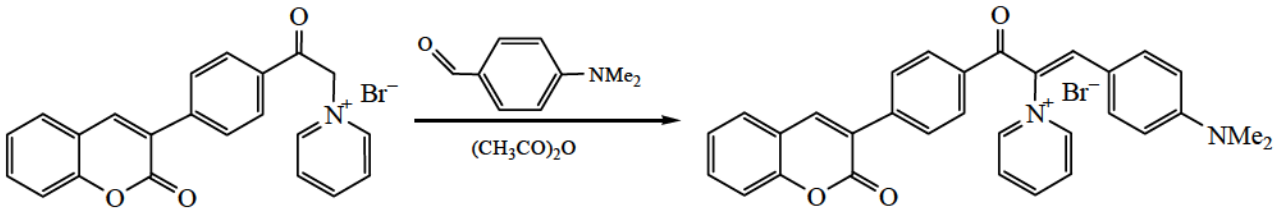

group was indicated by the absorption band at 3400 $cm^{-1}$ [11].

Salt **VI** in acetic anhydride entered the cyanine condensation with 4-dimethylaminobenzaldehyde both at the methyl and the methylene groups to form biscyanine dye **VII**. Reactivity of the methylene group in quaternary salt **VI** was due to the presence of two electron-accepting centers in the molecule: quaternary nitrogen atom and carbonyl group (Scheme 2).

Electronic absorption spectrum of biscyanine **VII** contained two bands: a stronger short-wavelength band at 432 nm (log ε 4.40) and a weaker long-wavelength band at 510 nm (log ε 4.19). The earlier prepared similar biscyanine having no benzene ring between the carbonyl group and the coumarin moiety [7] was characterized by two absorption bands at 442 (log ε 4.60) and 524 nm (log ε 4.46). Therefore, the maxima of the absorption bands of biscyanine **V** were shifted to shorter wavelength by 10 and 14 nm, respectively. The observed shift was apparently caused by steric interactions between the benzene ring and the chromophore at the pyridine nitrogen atom, leading to distortion of the normal geometry of the biscyanine molecule (violation of coplanarity of the chromophore groups).

In order to check whether the appearance of two bands in the electronic spectra of the biscyanine was due to interaction of the spatially isolated chromophores, it was necessary to prepare two "parent" monocyanines based on the pyridinium salts containing only the methyl or the methylene active group. Using salt **V**

**Scheme 3.**




**V** **VIII**

in condensation with 4-dimethylbenzaldehyde allowed preparation of the first type of monocyanine **VIII** with the spectrum containing an absorption maximum at 436 nm (Scheme 3).

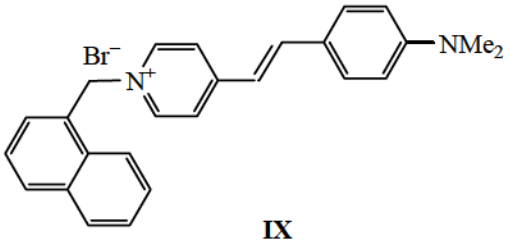
In our previous work [7] the "parent" monocyanine **IX** was obtained, based on the quaternary salt prepared via reaction of 1-chloromethylnaphthaline with 4-methylpyridine. Its spectrum revealed an absorption maximum at 492 nm (Scheme 4).

We have chosen this salt as the "parent" monocyanine of the second type because of the following reasons. Synthesis of the analogous coumarin-containing salt requires a hardly accessible 3-(4-bromomethylphenyl)coumarin. On the other hand, taking into account partial isolating effect for transfer of electronic effects via the methylene group [12], one can assume that the absorption maxima of the styryl dyes containing the naphthalene and coumarin fragments will be close.

Absorption maxima of dye **VII** revealed, respectively, blue shift by 4 nm and red shift by 18 nm with respect to the bands of the "parent" dyes **VIII** and **IX** containing a single chromophore each.

A larger shift of the long-wavelength band as compared to that of the short-wavelength band is explained by the difference in degree of delocalization of π-electrons in polymethine chromophores of the "parent" dyes. Longer polymethine chain leads to more prominent electrons delocalization and to stronger interaction with the second chromophore [6].

**Scheme 4.**




**IX**

The physical origin of the interaction of the chromophore systems in the dye molecule and, hence, of the bands shift can be considered in the frame of perturbation theory applied to the electronic spectra [6, 13]. If the cyanine molecule contains two conjugated chromophores (similar to those in each of the "parent" dyes) that absorb different quanta of energy, such chromophores only slightly affect each other. However, if the conjugated chromophores absorb quanta close in energy, they affect one another in such a way that the frequency of absorption of one of them is increased, absorption of another one is shifted to lower frequency (that is, the distance between the bands increases).

To elucidate the spatial structure of the biscyanine, we simulated the angle between the planes of the chromophores using the previously developed method [5]. The angle was of 80°. The degree of interaction of the chromophores was expressed as $\Delta_2 - \Delta_1$ [6] ($\Delta_2$ is the difference of the maxima of the two absorption bands of the biscyanine dye, and $\Delta_1$ is the difference of the maxima of its two "parent" dyes), it was of 22 nm.

We have previously shown [9] that for the model dye **VIIa** (containing a hydrogen atom instead of the carbonyl-coumarin group in **VII**) four structures are possible, differing in arrangement of the styryl fragments. For molecule **VII**, due to substantial steric hindrance, even more isomers are possible. We performed quantum-chemical simulation of the equilibrium geometry and of the electronic structure of the isomers. Geometry optimization was performed at the DFT/6-31G(d,p) level, the parameters of electronic transitions were calculated using the TD DFT method with the same basis set (GAUSS 03 software package [14]).

According to the simulation, the most stable isomer was that shown in Fig. 1. Theoretical electronic absorption spectrum of that isomer was most close to

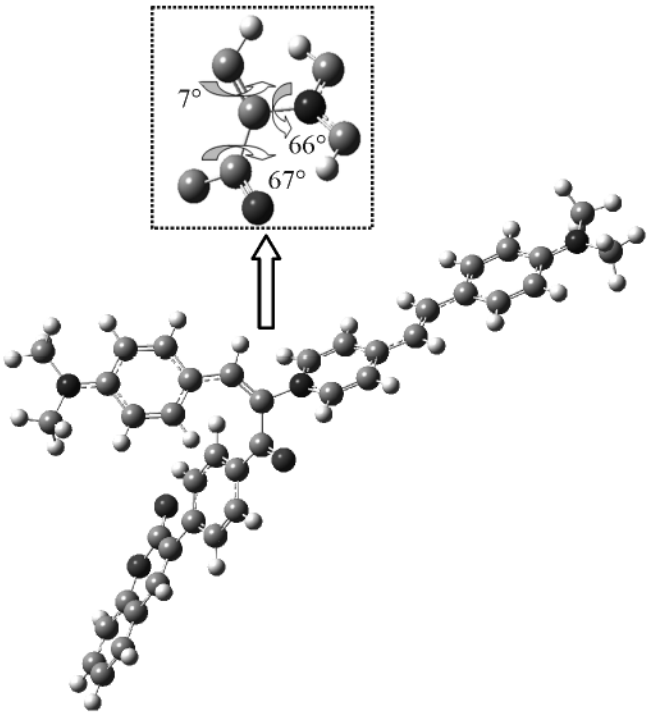



**Fig. 1.** Optimized spatial structure of compound **VII**.

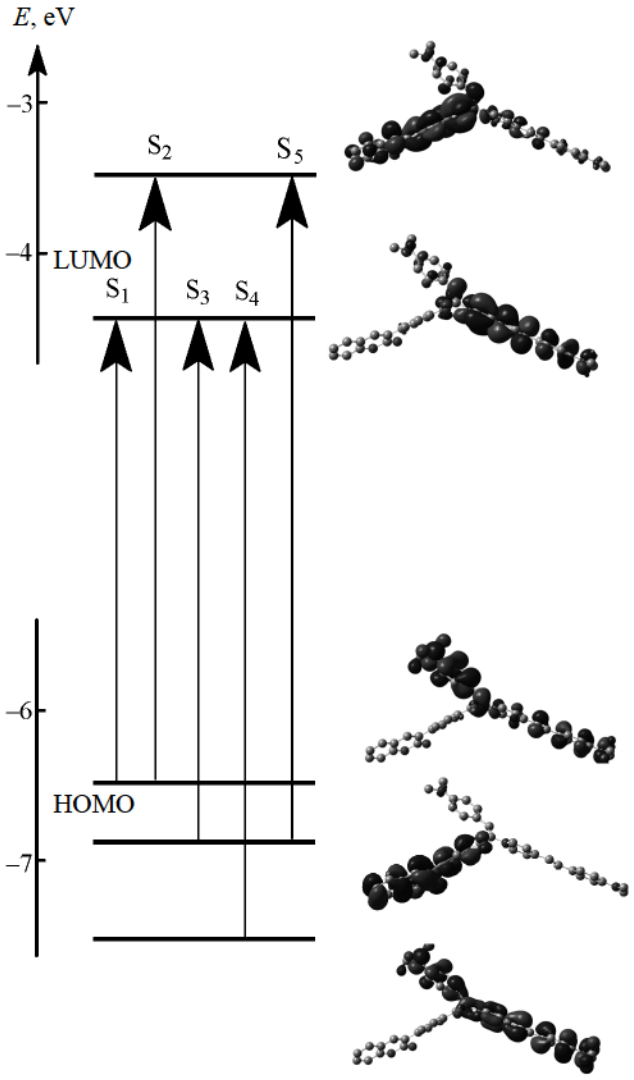



**Fig. 2.** Electronic transitions in the molecule of dye **VII**.

the experimental absorption spectrum. As can be seen from Fig. 1, the molecule contained three planar fragments twisted with respect to each other by substantial angle. Nevertheless, the simulation showed the existence of notable interaction between the fragments, allowing assumption of existing of the common π-system in the molecule.

The nonplanar structure resulted in different degree of delocalization of the boundary (and close to them) molecular orbitals. In Fig. 2, the shape of the orbitals participating in the lowest electronic transitions observed in the UV–visible absorption spectra is presented. Due to branching of the common chromophore of dye **VII** into three fragments, the pattern of the electronic transitions was more complicated than that in the simple classical scheme of chromophores interaction [5, 6], the latter suggesting uniform delocalization of orbitals over the whole molecule of the biscyanine. In the table, the parameters of transitions computed in the ZINDO approximation are presented along with the contribution of most important configuration $\Phi_{i\to j}$; the contribution was quantitatively estimated from the coefficient $T_{p,i\to j}$ in the expansion of the function of the p excited state $\Psi_p$ in the method of configuration interaction: $\Psi_p = \Sigma T_{p,i\to j}\Phi_{i\to j}$, summation being done over all configurations, and indices *i* and *j*-referring to the orbitals participating in the transition [15]. The most important configurations for all the given transitions are also depicted in the Scheme in Fig. 2. Analysis of data in the Table showed that two following transitions should be the strongest: $S_0 \rightarrow S_1$ transition with the oscillator strength $f_1$ = 0.632 with participation of the HOMO and the LUMO, and the $S_0 \rightarrow S_3$ transition ($f_3$ = 0.990) from the next occupied MO to the LUMO. The ratio of the oscillator strengths of these transitions, $f_1$ and $f_3$, was close to the ratio of intensities of the observed long-wavelength and short-wavelength bands in the spectrum. Hence, we assumed that those transitions, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$, were manifested in the spectrum by maxima at 510 and 432 nm, respectively.

Calculated wavelengths ($\lambda_{max}$) and oscillator strengths ($f$) of electronic transitions in compound **VII**

| Transition | $\lambda_{max}$, nm | $f$ | Configuration, $T_{p,i\rightarrow j}$ [a] |
|---|---|---|---|
| $S_0 \rightarrow S_1$ | 591 | 0.632 | $\|S_1 \geq 0.96\|$ HOMO→LUMO> |
| $S_0 \rightarrow S_2$ | 508 | 0.107 | $\|S_2 \geq 0.98\|$ HOMO→LUMO + 1> |
| $S_0 \rightarrow S_3$ | 480 | 0.990 | $\|S_3 \geq 0.83\|$ HOMO-1→LUMO > |
| $S_0 \rightarrow S_4$ | 451 | 0.006 | $\|S_4 \geq 0.97\|$ HOMO-2→LUMO > |
| $S_0 \rightarrow S_5$ | 434 | 0.394 | $\|S_5 \geq 0.90\|$ HOMO-1→LUMO + 1> |

[a] S is contribution of configuration corresponding to electron transition from the $i$ to the $j$ orbital.

Besides those strong transitions, the simulation predicted two more transitions, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_4$, in the same spectral region, they were not observed in the spectrum due to low intensity and overlap with the stronger bands. According to the simulation, the next transition should be stronger, but higher transitions should appear in the same region, and their identification is complicated.

To conclude, a set of experimental and simulation data confirmed that the observed spectrum corresponded to the isomer shown in Fig. 1. Weaker absorption bands may appear in between the two strong absorption bands typical of bis-dyes spectra, the former bands being assigned to transfer of the electron density between the molecule fragments due to different localization of the border and the close orbitals.

## EXPERIMENTAL

IR spectra were recorded with a Specord IR–75 spectrometer (KBr). Electronic absorption spectra of $2 \times 10^{-5}$ mol/L solutions in ethanol were registered with a SF-46 spectrophotometer. $^1$H NMR spectra were registered using a Varian Mercury 400 (400 MHz) spectrometer in DMSO-$d_6$ with TMS as internal reference. Melting point was determined with a Boethius apparatus.

**4-Acetylphenyldiazonium chloride (II)**. A mixture of 7.6 g (0.056 mol) of 4-aminoacetophenone, 36 mL of conc. HCl, and 10 mL of water was heated to boiling, the solution was cooled to 0–5°C and a solution of 4.8 g (0.07 mol) of $NaNO_2$ in 15 mL of water was added dropwise upon stirring and cooling to the formed suspension of 4-aminoacetophenone hydrochloride. After 15–20 min, the obtained diazonium salt solution was filtered, and the filtrate was neutralized with saturated aqueous sodium acetate to pH 6.

**3-(4-Acetylphenyl)chromen-2-one (III).** The reaction was performed in a flask equipped with thermometer, the evolving gas bubbles counter, and dropping funnel. A cooled solution of salt **II** was added to a mixture of 8.2 g (0.056 mol) of coumarin **I**, 0.7 g (4 mmol) of $CuCl_2 \cdot 2H_2O$ and 70 mL of acetone The solution of salt **II** was added dropwise upon stirring in such a manner that nitrogen was evolving at a moderate rate. After the gas evolution ceased, the formed precipitate was filtered off, washed with water, dried, and crystallized from the ethanol–DMF mixture. Yield 6.2 g (42%), mp 225–227°C. $^1$H NMR spectrum, δ, ppm: 2.61 s (3H, $CH_3$), 7.34–7.47 m (2H, coumarin), 7.63 t (1H, coumarin, $J$ 8.0 Hz), 7.80 d (1H, coumarin, $J$ 7.6 Hz), 7.86 d (2H, $C_6H_4$, $J$ 8.2 Hz), 8.03 d (2H, $C_6H_4$, $J$ 8.2 Hz), 8.36 s (1H, coumarin). Found, %: C 77.08; H 4.31. $C_{17}H_{12}O_3$. Calculated, %: C 77.26; H 4.58.

**3-[4-(2-Bromacetyl)phenyl]chromen-2-one (IV)**. 0.52 mL (10 mmol) of bromine was added dropwise at 85–90°C to a solution of 2.64 g (10 mmol) of ketone **III** in 120 mL of acetic acid; the mixture was cooled; the formed precipitate was filtered off, washed with water, dried, and crystallized from aqueous DMF. Yield 2.44 g (71%), mp 175–177°C. $^1$H NMR spectrum, δ, ppm: 5.60 s (2H, $CH_2$), 7.37 t (1H, coumarin, $J$ 7.4 Hz), 7.42 d (1H, coumarin, $J$ 8.2 Hz), 7.63 t (1H, coumarin, $J$ 7.4 Hz), 7.76 d (1H, coumarin, $J$ 7.4 Hz), 7.94 d (2H, $C_6H_4$, $J$ 8.6 Hz), 8.02 d (2H, $C_6H_4$, $J$ 8.6 Hz), 8.38 s (1H, coumarin). Found, %: C 59.63; H 3.38; Br 23.05. $C_{17}H_{11}BrO_3$. Calculated, %: C 59.50; H 3.23; Br 23.28.

**Pyridinium salts (V, VI)**. The mixture of 0.26 g (1 mmol) of compound **IV** and 0.08 g (1 mmol) of pyridine or 0.09 g (1 mmol) of 4-methylpyridine was refluxed in 15 mL of dry toluene during 1 h. The formed precipitates of salts **V** and **VI** were filtered off and washed with ether.

**1-(2-Oxo-2-[4-(2-oxo-2*H*-chromen-3-yl)phenyl]-ethyl)pyridinium bromide (V)**. Yield 0.38 g (90%), mp > 260°C ($CH_3COOH$). $^1$H NMR spectrum, δ, ppm: 6.59 s (2H, $CH_2$), 7.45 t (1H, coumarin, $J$ 7.4 Hz), 7.51 d (1H, coumarin, $J$ 8.2 Hz), 7.70 t (1H, coumarin, $J$ 7.4 Hz), 7.87 d (1H, coumarin, $J$ 7.2 Hz), 8.07 d (2H, $C_6H_4$, $J$ 8.2 Hz), 8.18 d (2H, $C_6H_4$, $J$ 8.2 Hz), 8.32 t (2H, pyridine, $J$ 6.8 Hz), 8.53 s (1H, coumarin), 8.79 t

(1H, pyridine, *J* 7.2 Hz), 9.08 d (2H, pyridine, *J* 6.1 Hz). Found, %: C 62.69; H 3.67; N 3.21. $C_{22}H_{16}BrNO_3$. Calculated, %: C 62.58; H 3.82; N 3.32.

**4-Methyl-1-(2-oxo-2-[4-(2-oxo-2*H*-chromen-3-yl)-phenyl]ethyl)pyridinium bromide (VI)**. Yield 0.40 g (92%), mp 260–262°C (toluene–EtOH). $^1$H NMR spectrum, δ, ppm: 2.65 s (3H, $CH_3$), 6.55 s (2H, $CH_2$), 7.40 t (1H, coumarin, *J* 7.4 Hz), 7.44 d (1H, coumarin, *J* 8.2 Hz), 7.64 t (1H, coumarin, *J* 7.4 Hz), 7.84 d (1H, coumarin, *J* 7.8 Hz), 8.00 d (2H, $C_6H_4$, *J* 8.2 Hz), 8.10–8.21 m (4H), 8.48 s (1H, coumarin), 8.92 d (2H, pyridine, *J* 6.1 Hz). Found, %: C 63.46; H 4.28; N 3.47. $C_{23}H_{18}BrNO_3$. Calculated, %: C 63.32; H 4.16; N 3.21.

**4-{2-[4-(Dimethylamino)phenyl]ethenyl}-1-{2-[4-(dimethylamino)phenyl]-1-[4-(2-oxo-2*H*-chromen-3-yl)benzoyl]ethenyl}pyridinium bromide (VII).** A mixture of 0.22 g (0.5 mmol) of salt **VI** and 0.15 g (1 mmol) of 4-dimethylbenzaldehyde in 7 mL of acetic anhydride was refluxed during 70 min, the reaction mixture was cooled and treated with ether. The precipitated dye was filtered off and crystallized from ethanol. Yield 0.2 g (57%). mp 193°C (decomp.). $^1$H NMR spectrum, δ, ppm: 2.98 s (6H, $CH_3$), 3.06 s (6H, $CH_3$), 6.65–6.85 m (8H, $C_6H_4NMe_2$), 7.44 t (1H, coumarin, *J* 7.4 Hz), 7.50 d (1H, coumarin, *J* 8.2 Hz), 7.69–7.88 m (4H), 7.96–8.08 m (6H), 8.31 s (1H), 8.47 s (1H, coumarin), 8.89 d (1H, pyridine, *J* 5.8 Hz), 9.15 d (1H, pyridine, *J* 5.8 Hz). Found, %: C 70.62; H 5.36; N 6.23. $C_{41}H_{36}BrN_3O_3$. Calculated, %: C 70.49; H 5.19; N 6.01.

**1-{2-[4-(Dimethylamino)phenyl]-1-[4-(2-oxo-2*H*-chromen-3-yl)benzoyl]ethenyl}-pyridinium bromide (VIII).** A mixture of 0.11 g (0.26 mmol) of salt **V** and 0.04 g (0.26 mmol) of 4-dimethylaminobenzaldehyde in 5 mL of acetic anhydride was refluxed during 1 h, cooled, and treated with ether. The precipitated dye was filtered off and crystallized from ethanol. Yield 0.11 g (79%). mp 201°C (decomp.). $^1$H NMR spectrum, δ, ppm: 2.99 s (6H, $CH_3$), 6.64 d (2H, $C_6H_4NMe_2$, *J* 9.0 Hz), 6.68 d (2H, $C_6H_4NMe_2$, *J* 9.0 Hz), 7.44 t (1H, coumarin, *J* 7.8 Hz), 7.50 d (1H, coumarin, *J* 8.2 Hz), 7.70 t (1H, coumarin, *J* 7.8 Hz), 7.84–7.89 m (2H), 7.98 d (2H, $C_6H_4$, *J* 9.0 Hz), 8.03 d (2H, $C_6H_4$, *J* 9.0 Hz), 8.47–8.51 m (3H), 8.97 t (1H, pyridine, *J* 7.4 Hz), 9.33 d (2H, pyridine, *J* 5.6 Hz). Found, %: C 67.42; H 4.68; N 5.17. $C_{31}H_{25}BrN_2O_3$. Calculated, %: C 67.28; H 4.55; N 5.06.

## REFERENCES


1. Kiprianov, A.I., *Tsvet i stroenie tsianinovykh krasitelei* (The Color and Structure of Cyanine Dyes), Kiev: Naukova Dumka, 1979.
2. Kachkovskii, A.D., *Stroenie i tsvet polimetinovykh krasitelei* (Structure and Color of Polymethine Dyes), Kiev: Naukova Dumka, 1989.
3. Kiprianov, A.I. and Mushkalo, I.L., *Zh. Org. Khim.*, 1965, vol. 1, no. 4, p. 744.
4. Kiprianov A.I. and Mushkalo, I.L., *Zh. Org. Khim.*, 1965, vol. 1, no. 4, p. 750.
5. Kiprianov, A.I. and Dyadyusha, G.G., *Ukr. Khim. Zh.*, 1969, vol. 35, no. 6, p. 608.
6. Kiprianov, A.I., *Russ. Chem. Rev.*, 1971, vol. 40, no. 7, p. 594.
7. Yagodinets, P.I., *Russ. J. Gen. Chem.*, 1998, vol. 68, no. 8, p. 1252.
8. Yagodinets, P.I., *Russ. J. Gen. Chem.*, 1997, vol. 67, no. 9, p. 1482.
9. Yagodinets, P.I., Kachkovskii, O.D., and Skripskaya, O.V., *Zh. Org. Farm. Khim.*, 2005, vol. 3, no. 2, p. 55.
10. Prey, V., Kerres, B., and Berbalk, H., *Monatsh. Chem.*, 1960, vol. 91, N 5, p. 774.
11. Brahmbhatt, D.I. and Hirani, B.R., *Ind. J. Chem. B*, 1994, vol. 33, no. 11, p.1072.
12. Pridan, V.E., Chernyuk, I.N., Rogovik, L.I., and Bukachuk, O.M., *Zh. Org. Khim.*, 1980, vol. 16, no. 9, p. 1973.
13. *Chemical Applications of Spectroscopy*, West, W., Ed., Wiley Interscience, 1956.
14. Frisch, M.J., Trucks, G.W., and Schlegel, H.B., et al., *Gaussian 03*, Revision B.03, Gaussian: Pittsburgh, 2003.
15. Hedwig, P., *Applied Quantum Chemistry*, Moscow: Mir, 1977.