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# Pyrimido[1,2-*a*]benzimidazolocyanines

**A. N. Frolov**

*St. Petersburg State Institute of Technology, St. Petersburg, Russia*

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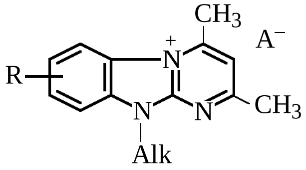
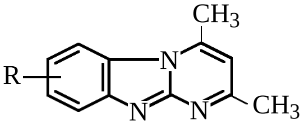
**Abstract**—Cyanine dyes containing a pyrimido[1,2-*a*]benzimidazole chromophore are described.

It is known that quaternary salts of methyl-substituted heterocycles react with various reagents in the presence of bases to give condensation products [1]. The present work estabilshes the reactivity of methyl groups in pyrimido[1,2-*a*]benzimidazolium salts **Ia**–**Id** as exemplified by the condensation of the latter with orthoformic ester.



**Ia–Id**

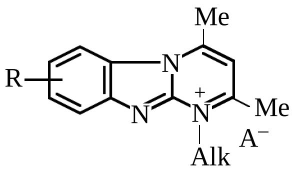


**IIa–IId**

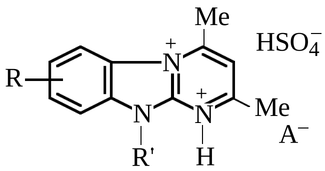
**I, II**, R = H (**a**), 7-Cl (**b**), 8-$SO_2CH_3$ (**c**), 7,8-$Cl_2$ (**d**); Alk = Et (**a, c, d**), Me (**b**); $A^-$ = $ClO_4^-$ (**a**), $I^-$ (**b**–**d**).

Quaternary salts **I** were prepared by alkylation of the corresponding bases **II** with alkyl iodides (salts **Ib**–**Id**) or by photocyclization by the nitrogen atom of 2-(*N*-ethyl-2-chloroanilino)-4,6-dimethylpyrimidine (**III**) (salt **Ia**) [2].

Pyrimido[1,2-*a*]benzimidazoles **II** can be quaternized by $N^4$ and $N^5$. Comparison of the electronic absorption and emission spectra of salts **I** obtained by photocyclization of amine **III** and quaternization of azoles **II** (see table) shows that the salts are alkylated by $N^5$.



**IV**



**Va–Vc**

**V**, R = H, R' = Et, A = Cl (**a**); R = 7-Cl, R' = Me, $A^-$ = $I^-$ (**b**); R = 7-Cl, R' = H, $A^-$ = $HSO_4^-$ (**c**).

The $^1H$ NMR spectra, too, reveal no isomer like **IV** in the alkylation products of azinoazole **IIa**.

Quaternary salts **Ia, Ib** are not alkylated by $N^4$. Indirect evidence for this conclusion comes from the effect of the acidity of the medium on the electronic spectra of the alkylation products of salts **Ia, Ib** and base **IIb**: Absorption and emission of dications like **V** that model the corresponding quaternary salts are observed in the acidity function range. Among the alkylation products of bases **II** no compounds with similar spectra were found (see table).

Heating of quaternary salts **Ia**–**Id** in the presence of triethyl formate in base medium gives rise to cyanines **VIa**–**VId**. They were isolated as perchlorates (the groups are the same as in compounds **I, II**).

These deeply colored compounds are soluble in acetonitrile and DMF and poorly soluble in water. The

Electronic absorption and fluorescence spectra of monocations **Ia, Ib** (50% aqueous EtOH), dications **Va, Vb, Vc** (95% $H_2SO_4$), and cyanine perchlorates **VIa**–**VId** (MeCN)

| Comp. no. | $\nu^{max} \times 10^3$, $cm^{-1}$ ($\varepsilon \times 10^3$, $l\ mol^{-1}\ cm^{-1}$) | $\nu_{fl}^{max} \times 10^3$, $cm^{-1}$ |
|---|---|---|
| **Ia** | 42.5 (17), 33.9 (6.4), 29.4 sh (2.1) | 21.4 |
| **Ib**[a] | 42.0 (42.0), 33.5 (12.4), 30.5 sh (5.4) | 23.3 |
| **Va** | 37.0, 31.0 | 27.7 |
| **Vb** | 38.5, 30.0 | 27.4 |
| **Vc** | 38.9, 33.3 | – |
| **VIa** | 16.0 (14.0)[b] | 15.5 |
| **VIb** | 33.0 (8.0), 15.9 (23.0)[c] | 15.4 |
| **VIc** | 40.0 (38.6), 31.0 (14.6), 15.7 (38.0)[d] | 15.4 |
| **VId**[f] | 40.6 (37.0), 31.0 (14.0), 15.6 (63.5)[e] | 15.3 |

[a] Electronic spectrum of a monoprotonated form like **Ib** (Alk = H), $\nu \times 10^3$, $cm^{-1}$: 42.2, 33.3, 31.2 sh; acetate buffer, pH 3.6. Concentrations (MeCN), M: [b] $3.3 \times 10^{-5}$, [c] $5.7 \times 10^{-5}$, [d] $5.02 \times 10^{-5}$, [e] $2 \times 10^{-4}$. [f] $^1H$ NMR spectrum ($CD_3CN$), δ, ppm: 1.42 s ($CH_3$), 2.73 br.s ($CH_3$), 4.3 br.s ($NCH_2$), 6.2 d (α,α'-H, 2H, 12 Hz), 7.07 s (2H, ArH), 7.78–7.90 (β-CH + 2H, ArH), 7.95 s (2H, ArH).

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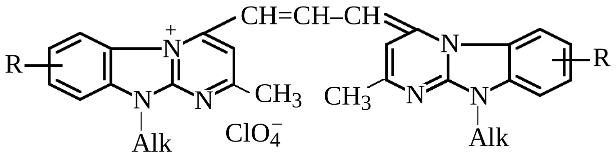
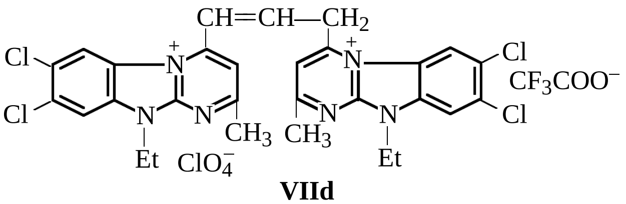


**VIa–VId**

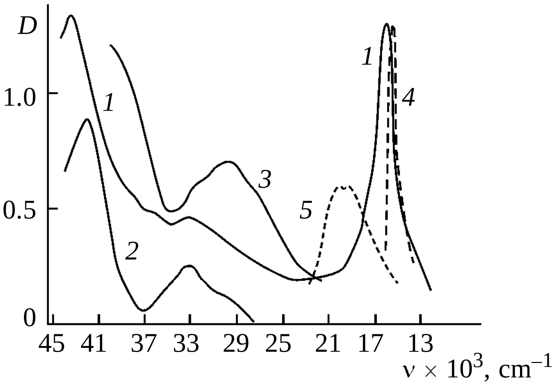


**VIId**

electronic absorption spectra of dyes **VIa**–**VId** show fragments of the spectrum of the starting quaternary salt, while in the low-frequency region there is a narrow absorption band, which implies a symmetrical electron density distribution in molecules **VI** (see figure). In acid medium, the low-frequency band suffers a hypsochromic shift, probably, due to the formation of a dication like **VIId** whose absorption spectrum is similar to that of the parent quaternary salt (see figure).

Compounds **VI** do not adhere the Bouguer–Lambert–Beer law; thus for dye **VIb** we obtained the following ε values:

| | | | | |
|---|---|---|---|---|
| $c \times 10^{-5}$, M | 2.1 | 5.78 | 21 | 65.6 |
| $\varepsilon \times 10^4$ (MeCN), l mol$^{-1}$ cm$^{-1}$ | 2.0 | 2.4 | 2.9 | 3.3 |



Electronic absorption spectra of (*1*) cyanine **VIb**, (*2*) 7-chloro-1,3,5-trimethylpyrimido[1,2-*a*]benzimidazolium iodide (**Ib**), and (*3*) the protonated form of cyanine **VIId**. The fluorescence spectra of (*4*) cyanine **VIb** and (*5*) the protonated form of cyanine **VIId**. Solvent: (*1*, *2*, *4*) acetonitrile and (*3*, *5*) 15% of trifluoroacetic acid in acetonitrile.

Apparently, the chromaticity of these dyes in acetonitrile is much dependent on association, which is characteristic of polymethine dyes [3].

Substituents in the 7 and 8 positions of the starting salt **I** exert bithochromic and hypsochromic effects on the absorption spectra of compounds **VI** (see table). Dyes **VIa**–**VId** show fluorescence whose maximum is independent of excitation wavelength and tends to bathofloric shifting in the presence of substituents (see table). In acid medium, the fluorescence maxima are shifted hypsoflorically (see figure) by formation of a dication like **VIId**. The observed emission spectrum of dication **VIId** in energy and Stoke's shift resembles the corresponding absorption spectra of quaternary salts **I**. The low-frequency band in the electronic absorption spectrum of dication **VIIb** is ill-resolved and, therefore, as well as because of the lack of data on its fluorescence excitation spectrum, we could not exactly determine its Stoke's shift, but the estimated value of ~8000 cm$^{-1}$ is close to respective values for quaternary salts **Ia, Ib**: 7000–8000 cm$^{-1}$. For dyes **VIa**–**VId** this parameter is no higher than 300–500 cm$^{-1}$ (see table).

The $^1$H NMR spectra of dyes **VIb, VIc**, except for **VId**, are ill-resolved. Nevertheless, apart from N–Me and N–Et signals, the spectra contain signals of methyl substituents in the pyrimidine ring (~2.7 ppm) and of the SO$_2$Me group for compound **VIc** (3.14 ppm). The spectrum of cyanine **VId** contains aromatic proton singals shifted upfied compared with salt **Id**, N–Et, pyrimidine Me (~2.7 ppm), and α-metine proton signals (~6.2 ppm). The β-methine proton signal (7.8–7.9 ppm) overlaps with the aromatic proton signals.

It should be noted that the pyrimidine Me signals of bases **II** and their quaternary salts **I** are nonequivalent. Thus, the Me protons of 2-(*N*-ethyl-2-chloroanilino)-4,6-dimethylpyrimidine give a single signal at ~2.2 ppm [2]. The 1-Me signals of the cyclization product of this amine, base **IIa**, are at $\delta_1$ 3.25 ppm and those of 3-Me, at $\delta_3$ 2.92 ppm [4], for bases **IIc**, $\delta_1$ is 3.27 ppm and $\delta_3$ is 2.64 ppm [2]. The nonequivalence of the 1-Me and 3-Me groups of pyrimido-[1,2-*a*]benzimidazoles correlates with the difference in the chemical shifts of H$^1$ and H$^3$ in the isoelectronic pyrido[1,2-*a*]benzimidazoles [5, 6] and dipyrido[1,2-*a*:3',2'-*d*]imidazole [7], therewith, the former absorbs in a weaker field. In latter gave us grounds to assign the weaker field signal to 1-Me, and the stronger field one, to 3-Me. The nonequivalence of the 1- and 3-Me groups is still preserved in the quaternary salts: **Ia**: $\delta_1$ 3.2 ppm and $\delta_3$ 2.8 ppm [2]; **Id**: $\delta_1$ 3.2 ppm and $\delta_3$ 2.7 ppm.

In the $^1$H NMR spectra of dyes **VIb**–**VId**, protons of the Me groups of the condensed pyrimidine nucleus absorb near ~2.7 ppm. From a comparison of the pyrimidine Me signals of quaternary salts **Ia, Id** and cyanines **VIb, VIc, VId** it follows that the condensation involves the 1-Me group of the parent quaternary salt **I**.

## EXPERIMENTAL

The IR spectra were measured in KBr on a UR-20 spectrophotometer. The UV spectra were obtained on Specord M-40 and SF-20 spectrophotometers. The $^1$H NMR spectra were measured on an AC-200 spectrometer (200 MHz) (Institute of Antibiotics and Medical Preparations). The luminescence spectra were obtained on an instrument described in [8].

The synthesis of bases **IIa**–**IId** is described in [2, 4]. Quaternary salt **Ia** was prepared photochemically from 2-(*N*-ethyl-2-chloroanilino)-4,6-dimethylpyrimidine as described in [2]. To convert salt **Ia** into perchlorate, after photolysis *tert*-butyl alcohol was distilled off, dried to glassy, mixed with equimolar amount of sodium perchlorate in acetonitrile, the solvent was exaporated, and the dry residue was dried to glassy, recrystallized from 2-PrOH to obtain a light brown powder. Its $^1$H NMR spectrum is given in [2], and the electronic spectra, in the table. IR spectrum, ν, cm$^{-1}$: 3400 ($H_2O$), 3000, 2940 (CH), 1650 s, 1570, 1490, 1460, 1400, 1380, 1360, 1300, 1100 v.s ($ClO_4$), 950, 760, 740.

Quaternary salts **Ib**–**Id** were obtained by alkylation with methyl iodide (salt **Ib**) or ethyl iodide (salts **Ic, Id**) of corresponding bases: 0.1 g of base and 3 ml of alkyl iodide were heated under reflux for 2–3 h in 15 ml of acetonitrile, following the reaction progress by TLC (Silufol UV-254, eluent ether). The solvent was distilled off, and the residue was washed with ether.

**7-Chloro-1,3,5-trimethylpyrimido[1,2-*a*]benzimidazolium iodide (Ib)** was dried to glassy (dark powder). The electronic spectra are listed in the table. IR spectrum, ν, cm$^{-1}$: 1650 s, 1600, 1570, 1450, 1430, 1370, 1300, 1280, 1250, 1150, 1090, 1030, 850, 800, 750.

Salt **Ic** was isolated, washed with ether, and used, without analysis, in the condensation reaction.

**7,8-Dichloro-1,3,5-trimethylpyrimido[1,2-*a*]benzimidazolium (Ig)** is a crystalline crimson substance. $^1$H NMR spectrum ($CD_3CN$), δ, ppm: 1.4 s ($CH_3$), 2.7 s ($CH_3$), 3.2 s ($CH_3$), 4.3 br.s ($NCH_2$), 7.7 s (1H, ArH), 8.05 s (1H, ArH), 8.3 s (1H, ArH).

Dications **Va**–**Vc** were obtained by dissolution of quaternary salt **Ia, Ib** or base **IIb** in conc. $H_2SO_4$.

***N*-Alkyl-1-{3-(*N*-alkyl-3-methylpyrimido[1,2-*a*]benzimidazol-1-ylidene)-1-propenyl}-3-methylpyrimido[1,2-*a*]benzimidazolium perchlorates VIa–VId** *(general procedure).* Quaternary salt **Ia**–**Id** (~0.1 g) and ethyl orthoformate (~0.1 ml) in pyridine (~1 ml) with a drop of acetic anhydride was heated under reflux for 40–50 min. After cooling, the resulting dye was precipitated with ether, the precipitate was filtered off, washed with ether, dissolved in a minimum of acetonitrile, and a saturated solution of sodium (or lithium) perchlorate in 2-propanol was added. The precipitate that formed was filtered off and washed with ether.

Dyes **VIa**–**VId** are bluish dark powders with ill-defined melting points. Decompose when heated in the solid state to give compounds whose spectral characteristics are similar to those of the starting salts **I**. Yield 30–40%.

The IR spectra of the cyanines contain a strong absorption band at 1100–1150 cm$^{-1}$ ($ClO_4^-$). The electronic spectra are listed in the table.

## ACKNOWLEDGMENTS

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