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Photosynthesis and Properties of Halomethyl Derivatives of Azinobenzimidazoles

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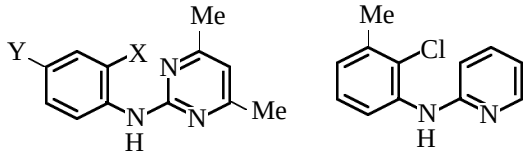
Abstract — Photocyclization of 2-(pentafluoroanilino)-, 2-(4-chloro-2-iodoanilino)-, and 2-(2-chloro-4-iodoanilino)-4,6-dimethylpyrimidines, as well as 2-(2-chloro-3-methylanilino)pyridine was used to prepare condensed azinobenzimidazoles, including previously unknown 8-chloro-1,3-dimethylpyrimido[1,2-*a*]benzimidazole and 9-methylpyrido[1,2-*a*]benzimidazole. With isomeric chloroiodoanilinopyrimidines as example it was shown that the iodine atom affects photocyclization direction. Quaternization of 6,7,8,9-tetrafluoro-1,3-dimethylpyrimido[1,2-*a*]benzimidazole, 8-chloro-1,3-dimethylpyrimido[1,2-*a*]benzimidazole, and 9-methylpyrido[1,2-*a*]benzimidazole with alkylating agents and C–H activity of alkyl groups in the quaternary salts in reactions with orthoformic ester were studied.

It is known that *ortho*- and *para*-halo derivatives of the aromatic and heterocyclic series are susceptible to intermolecular photosubstitution on irradiation in the presence of electron-donor reagents [1, 2]. Arylheterylamines having halogen *ortho* to the amino group were found to undergo regioselective photocyclization by the heteroring nitrogen atom (see, for example, [3]). This process exemplifies intramolecular photocyclization involving aromatic ring heteroatom. Indirect evidence in favor of the similarity of intra- and intermolecular photosubstitution reactions is provided by the fact that the photocyclization of fluoroanilines into fluoroazinazoles is sensitized by 2,6-disulfoanthraquinone, implying a radical-ion reaction [4]. Alkylsulfonyl derivatives of arenes with electron-donor substituents in the ring, too, undergo intermolecular photosubstitution [5, 6] and photocyclization [7]. The intramolecular photosubstitution reactions with sulfonyl and halo derivatives exhibit different regioselectivities: In the former, *ortho*, *meta*, and *para* isomers are all reactive [6]. Sulfonyl derivatives photocyclize less selectively than halo derivatives, and the reactions can result in either C–N or C–C bond formation, depending on substrate structure [7].

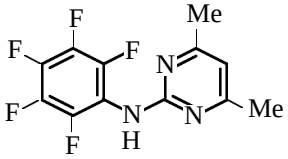
The reasons for the above differences are unclear. Apparently, they are associated with different pathways of transformation of radical cations of these classes of compounds.

As shown earlier (see, for example, [8]), the regioselectivity of intramolecular photosubstitution of halogen in haloanilines depends on halogen nature. Similar data on photocyclization of *ortho*-haloarylheterylamines are lacking. In this work we studied the effect of halogen nature on the composition of photocyclization products on an example of isomeric chloroiodoanilinoazines and the reactivity of previously unknown condensed azinazoles in quaternization reaction and in condensation with orthoformic ester.



Ia, Ib

II



Ic

X = Cl, Y = I (**Ia**); X = I, Y = Cl (**Ib**).

As objects for study we took haloanilinodimethylpyrimidines **Ia**–**Ic** and 2-(2-chloro-3-methylanilino)-pyridine (**II**).

It was found that irradiation promotes heterocyclization of isomeric chloroiodoanilinoazines **Ia** and **Ib**. However, instead of the expected 8-iodo-1,3-dimethylpyrimido[1,2-*a*]benzimidazole, the reaction with compound **Ia** gave 1,3-dimethylpyrimido[1,2-*a*]-benzimidazole (**IIIa**) (preparative yield 6%). Along with this product, the postreaction mixture contained,

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according to TLC, the starting amine **Ia**, 2-anilino-1,3-dimethylpyrimidine, and an unidentified compound whose absorption spectrum gave no evidence for a condensed azinazole like **III**.

Photoheterocyclization of amine **Ib** occurs more successfully and yields 8-chloro-1,3-dimethylpyrimido-[1,2-*a*]benzimidazole (**IIIb**), yield 15%.

Thus, comparing the behavior of halogen in different molecules one can note that iodine substituent in the aromatic nucleus reduces the yield of heterocyclization of chloroiodoanilinopyrimidines compared with the corresponding chloroanilinodimethylpyrimidines (cf. [9]). On the other hand, estimating the behavior of halogen in different positions of one molecule in terms of the preparative yields of cyclizations of amines **Ia** and **Ib** we can see that iodine is a more efficient nucleofuge than chlorine. These qualitative trends are both consistent with the effect of halogen atoms in intermolecular photosubstitutions of halogen by nucleophiles, established in our previous works [8].

With fluorine and chlorine as nucleofuges, cyclization occurs regioselectively and in quantitative or nearly quantitative yields of condensed imidazoles, specifically 6,7,8,9-tetrafluoro-1,3-dimethylpyrimido-[1,2-*a*]benzimidazole (**IIIc**) and 9-methylpyrido[1,2-*a*]-benzimidazole (**IV**).

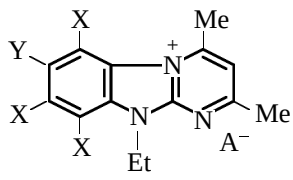
The structures of the photoheterocyclization products were proved by spectral methods, elemental analysis, and comparison with known analogs (Tables 1–3).

From a comparison of the IR spectra of the starting amines **Ia**–**Ic** and **II** and their heterocyclization products **IIIa**–**IIIc** and **IV** it follows that the formation of the azinobenzimidazole chromophore results in disappearance of the NH stretching and bending absorption bands at 3400–3100 and 1570–1600 cm^{-1}. A band at 1640–1650 cm^{-1} (C=N) appears, and a slight low-frequency shift (growth of the relative intensity) of the C=C bands at 1440–1510 cm^{-1}, associated with the fact that azinazoles have a longer conjugation chain than the parent amines. Thus, for instance, in the IR spectrum of tetrafluoropyrimidobenzimidazole **IIIc** formed from amine **Ic** we observe splitting of the overlapping C=C, C=H, and NH absorption bands of the latter to bands at 1640 cm^{-1} (C=N) and 1560 cm^{-1} (C=C). The band of amine **Ic** at 1510–1530 cm^{-1} transforms into a C=C absorption band of azinazole **IIIc** at 1500 cm^{-1}.

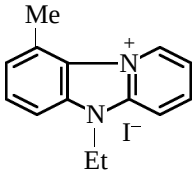
On the formation of methylpyridobenzimidazole **IV** from amine **II** the C=C absorption band of the latter (1550 cm^{-1}) shifts to 1510 cm^{-1} in azinazole **IV**.

Similar tendencies can be observed in the IR spectra of chloroiodoanilinopyridines **Ia** and **Ib** and dimethylpyrimidobenzimidazole **IIIa**, and its 8-chloro derivative **IIIb** (Table 1).

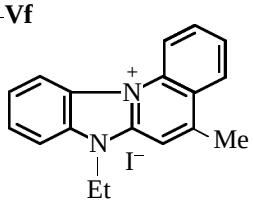
The electronic absorption spectra of azinazoles **IIIa**–**IIIc** and **IV** are shifted bathochromically relative to those of the parent amines **Ia**–**Ic** and **II** (Table 1). In the number of bands, transition energies, and extinctions the spectra of **IIIa**, **IIIb**, and **IV** are similar to the spectra pyrido- and pyrimidobenzimidazoles, described in [9, 10]. The singlet transition energy of compound **IV** (3.24 eV), estimated from the absorption and emission spectra, corresponds to the respective parameter of pyrido[1,2-*a*]benzimidazole [10].



Va–**Vf**



VI



VII

X = H, Y = Cl, A^- = ClO_4^- (**Va**); X = Y = F, A^- = p-$CH_3C_6H_4SO_3^-$ (**Vb**), ClO_4^- (**Vc**), BPh_4^- (**Vd**), $OC_6H_2(NO_2)_3^-$ (**Ve**), I^- (**Vf**).

Alkylation of bases **IIIb**, **IIIc**, and **IV**, as well as of 5-methylquino[1,2-*a*]benzimidazole with ethyl iodide gives quaternary salts **V**–**VII**. Pyrido- and quinobenzimidazole iodides **VI** and **VII** are high-melting crystalline substances. The quaternary salts of dimethylpyridobenzimidazole and especially of its tetrafluoro derivative (compounds **Va**–**Vf**) contain crystallization water.

The strongest bands in the IR spectra of alkylated azinazoles **V**–**VII** (Table 2) are at 1650–1500 (C=C and C=N bonds), 1100 [perchlorate ion (salt **Va**)], 1100–1000 [perchlorate ion and C–F bond (salt **Vc**)], and 1040 and 1100–1200 cm^{-1} [C–F bond and tosylate ion (salt **Vb**)]. The IR spectrum of picrate **Ve** at 1600– 1500 cm^{-1} shows overlapping bands of C=C vibrations and of asymmetric (1510, 1560 cm^{-1}) and symmetric (1380, 1350 cm^{-1}) of NO_2 vibrations. The IR spectra of tetraphenylborate **Vd** displays a characteristic BPh_4^- absorption in the region of C–H bending

Table 1. UV and IR spectra of starting amines **Ia**–**Ic** and **II** and photocyclization products **IIIa**–**IIIc** and **IV**

Comp. no.	UV spectrum		IR spectrum, ν, cm^{-1}
	solvent	$\nu \times 10^3$, cm^{-1} ($\varepsilon \times 10^4$, l mol^{-1} cm^{-1})	
Ia	2-PrOH	36.36 (3.21)	3420, 3390, 3120, 2930; (1610, 1580, 1530) v.s; (1480, 1450) s; (1380, 1350) s; 1310, 1040, 1010, 860, 810 s, 790, 750
Ib	2-PrOH	36.23 (2.81)	3390, 3120, 3080, 2930; (1610, 1570, 1540) v.s; (1495, 1470) s; (1380, 1350) s; 1290, 1250, 1040 w, 830 s
Ic	EtOH	38.70 (1.50), 34.0 sh	3200, 3150, 2980, 2920; (1610, 1600, 1580, 1530, 1510) v.s; 1450 s, (1370, 1340) s; 1090, 1070; (1040, 1020, 1000) v.s (C–F); 850, 810, 790, 760, 740
II	BuOH	36.40 (1.90), 32.20 sh (0.87)	3230, 3180 sh, 3110 (NH), 3040, 2980, 2930 (CH); (1600, 1590) v.s; 1550, (1460, 1440) v.s; 1320 v.s, 1160, 1050, 1000, 800, 780, 770 v.s, 730
IIIa	2-PrOH	40.40 sh, 39.80 (4.03), 37.45 (1.10), 34.48 (0.5), 33.30 (0.53), 32.00 (0.55), 28.50 (0.28)	3060, 2930 (CH), 1650 s, 1610, 1540 v.s, 1470, 1450 s, 1380, 1310 s, 1270, 1200, 1140; (1050, 1040, 1030); 880, 780 s, 740 s
IIIb	2-PrOH	40.82 sh, 39.68 (5.0), 36.36 sh, 34.48 (0.45), 33.30 (0.54), 32.05 (0.54), 28.40 (0.32)	3070 (CH), 2940, 1650 s, 1540 s, 1460 s, 1440; (1380, 1360, 1300) w; (1290, 1200) w; 810 s, 770
IIIc	EtOH	40.50 (3.40), 33.50 (0.31), 32.20 (0.29), 29.30 (0.28)	3060, 2940, 1640 s; (1560, 1500) v.s; 1470; (1390, 1340) s; (1260, 1210) s; (1100, 1080, 1010) v.s (C–F); 860 s, 820, 770
IV[a]	50% MeCN	40.80 (3.90), 33.00 (0.37), 29.40 (0.34), 28.60 sh (0.31)	3030, 2940, 1650, 1600; 1510 v.s; 1470, 1450, 1420; (1370, 1340) s; 1290 s, 1260, 1220, 1150, 1090, 1000, 970; (790, 760, 750) v.s

[a] Fluorescence spectrum (fluorescence yield) (2-PrOH), ν, cm^{-1}: 25000 sh, 24000, 22900 (max), 21500, 20500 sh (0.37).

Table 2. UV and IR spectra of quaternary salts **Va**–**Vf, VI**, and **VII** and cyanines **VIII**

Comp. no.	UV spectrum		IR spectrum[a], ν, cm^{-1}
	solvent	$\nu \times 10^3$, cm^{-1} ($\varepsilon \times 10^4$, l mol^{-1} cm^{-1})	
Va	2-PrOH	41.15 (2.80), 33.78 (0.69), 29.67 (0.42)	2940, 2870, 1650 s, 1570, 1490, 1470, 1200, 1100 v.s (ClO_4); 1050, 1020, 820, 750
Vb	2-PrOH	41.67 (1.8), 35.70 (0.60), 30.30 (0.38)	2940, 1660 s; (1560, 1510) v.s; 1490, 1390, (1230*, 1180*, 1120) v.s; (1040, 1020*) s; 850, 820* s, 690* s
Vc	2-PrOH	41.67 (2.0), 35.70 (0.50), 30.77 (0.31)	2930, 1640 s; (1560, 1510) s; 1460, 1390, 1220, 1180; (1100, 1040, 1010) v.s; 880, 850, 820, 770, 690
	$CHCl_3$	33.90, 30.70	
Vd	2-PrOH	41.67 (3.95), 34.48 (0.80), 30.30 (0.54)[a]	3070, 2940 (CH); (1640, 1560, 1510) s; 1390, 1270* w, 1080, 1070, 850*; (730, 710*) s
Ve	2-PrOH	41.67 (3.40), 33.90 (0.65), 27.77 (1.62), 25.00 (0.85) sh	3050, 2900, 1650 s; (1560, 1510*) s; 1440, (1390, 1380*, 1350*, 1330) s; 1270* s, 1170 s, 1080, 1070, 1050, 1020, 910*, 890*, 880, 840, 790*, 750*, 690*
Vf	2-PrOH	41.67 (1.85), 34.48 (0.73), 29.00 (0.35)[a]	3000, 2930 (CH); (1680, 1640) v.s; (1550, 1510) v.s; 1460, 1390, 1360; 1080, 1070; 870, 860; 810, 760
	$CHCl_3$	33.90 (0.68), 27.77 (0.33)[a]	

Table 2. (Contd.)

Comp. no.	UV spectrum		IR spectrum[a], ν, cm^{-1}
	solvent	$\nu \times 10^3$, cm^{-1} ($\varepsilon \times 10^4$, $l\ mol^{-1}\ cm^{-1}$)	
VI[b]	H_2O	35.00 sh, 33.70 (0.59), 30.00 (0.62)	2980, 2930, 1650 s, 1610, 1540 s, 1505, 1480, 1460, 1390, 1330, 1250 w, 1160 s, 1030; (780, 770, 760) s
	2-PrOH	38.46 (0.77), 34.5 sh 33.80 (0.62), 29.50 (0.62)	
VII	BuOH	41.70 (3.60), 32.30 (1.12), 30.80 (1.54), 29.40 (1.39)	3030, 2940, 1640 v.s, 1620 s, 1570 s, 1480 s, 1420, 1350, 1210 w, 1160 w, 1000 w, 830 s, 770 v.s
VIIIa[c]	MeCN–2-PrOH, 1 : 1	41.67 (4.4), 34.48 (2.5), 17.2 sh, 15.87 (1.7)	3000, 2940; (1650, 1550, 1500) br.s; (1460, 1420, 1390, 1370, 1300) w; (1220, 1180) s; 1070, 1050, 1020, 820, 690
VIIIb[c]		41.67 (2.8), 34.48 (1.7), 17.2 sh, 15.87 (2.7)	3000, 2950; (1650, 1550, 1500) br, v.s; (1460, 1410, 1390, 1370, 1300, 1270) w; 1170 br.s, 1100 br.s, 1020, 820, 690 w
VIIIc[c]		41.67 (3.2), 32.25 (1.6), 15.75 (2.4)	2940, 1640 br.s, 1550 sh, 1490 s; 1400 br; 1300 br; (1180, 1140, 1130, 1090) br, s; 1000, 940, 810 br, 750

[a] Elemental composition was not determined, and extinctions were calculated without account for water contents. [b] Fluorescence spectrum (2-PrOH), ν, cm^{-1} (quantum yield): 24400 (0.52). [c] Concentration, M: 0.85×10^{-4}, 1.69×10^{-4} (**VIIIa**), 1.38×10^{-4} (**VIIIb**), and 1.87×10^{-4} (**VIIIc**).

Table 3. Melting points and elemental analyses of **Ia, Ib**, and **II**, condensed imidazoles **IIIb** and **IV**, quaternary salts **Va**, **Vb**–**VII**, and trimethylcyanines **VIIIb, VIIIc**

Comp. no.	mp, °C (solvent for crystallization)	Found, %			Formula	Calculated, %		
		C	H	N		C	H	N
Ia[a]	165–166 (hexane)	40.4	3.3	11.1	$C_{12}H_{11}ClIN_3$	39.8	3.04	11.6
Ib[a]	146–147 (hexane)	40.6	3.4	11.4	$C_{12}H_{11}ClIN_3$	39.8	3.04	11.6
II	72–73 (50% 2-PrOH)	65.8	4.9	12.9	$C_{12}H_{11}ClN_2$	65.9	5.03	12.8
IIIb	258–260 (decomp.) (MeCN)	61.9	4.3	18.2	$C_{12}H_{10}ClN_3$	62.2	4.3	18.1
IV	123–125 (60% 2-PrOH)	77.9	6.3	14.3	$C_{12}H_{10}N_2$	79.1	5.5	15.3
Va	215–217 (decomp.) (2-PrOH)	44.3	3.1	11.2	$C_{14}H_{15}Cl_2N_3O_4 \cdot H_2O$	44.4	4.4	11.1
Vb	~365	50.5	3.8	8.03	$C_{21}H_{19}F_4N_3SO_3 \cdot 2H_2O$	49.9	4.5	8.3
VI	231–233 (decomp.) (2-PrOH)	50.1	4.3	8.2	$C_{14}H_{15}IN_2$	49.7	4.4	8.2
VII	>300 (2-PrOH)	55.1	4.2	6.9	$C_{18}H_{17}IN_2$	55.6	4.4	7.2
VIIIb	$\gtrsim$ 200 (decomp.)	49.3	3.1	11.7	$C_{29}H_{21}ClF_8N_6O_4$	49.4	3.0	11.9
VIIIc	$\gtrsim$ 200 (decomp.) (MeCN–2-PrOH)	54.9	3.9	13.1	$C_{29}H_{27}Cl_3N_6O_4$	55.2	4.2	13.3

[a] Molecular weight: found 359 (**Ia**), 353 (**Ib**). Calculated *M* 359.

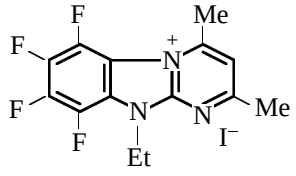
vibrations (710–850 cm^{-1}) (Table 2). In Table 2 in the IR spectra of quaternary salts **Vb**, **Vd**, and **Ve** stars mark bands common for salts **V** and sadium salts of the correposponding anions.

The UV spectra of alkyl derivatives of pyrido- and quino[1,2-*a*]benzimidazoles **VI** and **VII** contain two groups of bands in the range 35000–26000 cm^{-1} and two overlapping high-frequency bands (≥39000 cm^{-1}). The spectra of pyrimidobenzimidazolium **V** show three bands in the range 29000–42000 cm^{-1}. The spectral bands of quaternary salts **V**–**VII** are shifted hypsochromically compared with azinazoles **III** and **IV**. The similarity of the absorption spectra of quaternary derivatives of pyrido- and quinobenzimidazoles **VI** and **VII** and pyrimidobenzimidazoles **V** are evi-

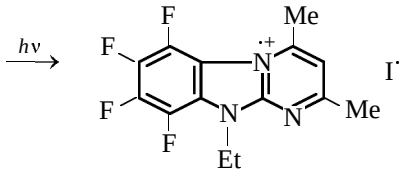
dence showing that pyrimido[1,2-*a*]benzimidazoles **IIIa**–**IIIc** have been alkylated by the heteroring N^5 atom.

With tetrafluorodimethylpyrimidobenzimidazolium salts **V**, we studied the effect of the counter ion on their spectral characteristics. It is known that the absorption of an organic cation with a counter ion (picrate, tosylate, or perchlorate) is additive. Thus, the extinctions of perchlorate **Vc** and tosylate **Vb** at the frequency 41670 cm^{-1} are close to each other (Table 2), i.e. the extinctions of these salts are determined by the organic cation, since the tosylate ion at this transition energy has ε 300 l mol cm^{-1}.

The difference in the extinctions of picrate **Ve** and perchlorate **Vc** at 41670 and 34480 cm^{-1} is equal to the extinction of the picrate anion (1.4×10^4 l mol cm^{-1}, 2.3×10^3); sodium picrate has ε 1.2×10^4 l mol cm^{-1} at 41670 cm^{-1} and ε 2.3×10^3 l mol cm^{-1} at 34480 cm^{-1}. With tetraphenylborate **Vd**, the additivity rule is not obeyed, presumably because of the contribution of the charge-transfer state from the BPh_4^- anion to the organic cation. The iodide ion strongly affects the absorptivity of the tetrafluoropyrimidobenzimidazolium cation: Compared with perchlorate **Vc**, the low-frequency band in the spectrum of iodide **Vf** is shifted bathochromically by 1770 cm^{-1} in 2-propanol and by ~2900 cm^{-1} in chloroform (Table 2). Therewith, iodide **Vf** exhibits a negative solvatochromism: In chloroform, compared to 2-propanol, its low-frequency band is shifted bathochromically by ~1230 cm^{-1}. These data are supportive of the proposed charge transfer from the iodide anion to the fluorobenzimidazolium cation in quaternary salt **Vf**. Similar properties are characteristic of pyrimidinium cations (see, for instance, [11]).

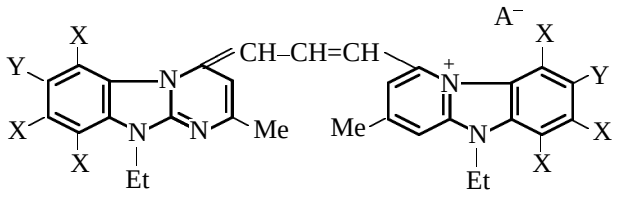


Vf



To assess the effect of the condensed nucleus on the C–H activity of the methyl groups in quaternized azinazoles **V**–**VII**, we studied reaction of the latter with triethyl orthoformate.

By heating quaternary salts **Va** and **Vb** in the presence of ethyl orthoformate in basic medium we obtained cyanines **VIIIa** and **VIIIb** as tosylates or perchlorates.



VIIIa–**VIIIc**

X = Y = F, A^- = *n*-$CH_3C_6H_4SO_3^-$ (**a**), ClO_4^- (**b**); X = H, Y = Cl, A^- = ClO_4^- (**c**).

The condensation with quaternary salt **Vf** gave two dyes **VIIIb** and **VIIId** isolated as perchlorates. These compounds have close transition energies in the electronic absorption spectra but different chromatographic mobilities on alumina. The structure of dye **VIIId** [ν_{max} 34480 (ε 15×10^3) and 15620 cm^{-1} (ε 12×10^3)] was not established. In view of the fact that increased reaction time and temperature reduce the yield of perchlorate **VIIIb** and increase the yield of compound **VIIId**, we can explain the different behavior of these compounds by elimination of one or two fluorine atoms from the heterocyclic nucleus in the course of formation of the latter compound.

As judjed from the ^1H NMR spectrum of the model compound, *N*-ethylpyrido[1,2-*a*]benzimidazolium perchlorate [12] and the chemical shifts of H^1 (9.10 ppm), H^3 (8.22 ppm), and H^9 (8.33 ppm), the 3-or 9-Me groups in this cation or its close analog should be less reactive that the 1-Me group. This assumption is consistent with experimental data: We failed to obtain cyanines from 5-ethyl-9-methylpyrido[1,2-*a*]benzimidazolium iodide (**VI**) and 7-ethyl-5-methylquino-[1,2-*a*]benzimidazolium iodide (**VII**).

Our present results agree with the conclusion in [13] that the Me group in the 1 position of the azinazole nucleus in quaternary salts like **V** is more active than in other positions.

The structure of compounds **VIIIa**–**VIIIc** is proved by their spectra (Table 2). The IR spectra of compounds **VIII** are ill-resolved and show broadened signals. The strongest bands are at 1640–1650 (C=N) and 1490–1550 cm^{-1} (C=C). The spectrum of tosylate **VIIIa** shows strong absorption at 1220–1100 cm^{-1} (overlapping tosyl C=O and stretching C–F bands). The spectra of perchlorates **VIIIb** and **VIIIc** show strong absorption at 1150–1020 (overlapping C–F and ClO_4 bands) and 1180–1100 cm^{-1} (ClO_4) (**VIIIc**).

The electronic spectra of cyanines **VIII** (Table 2)

in the UV and visible ranges contain two strong bands with transition energies and extinctions close to those of cyanines with the pyridobenzimidazole chromophore [13].

EXPERIMENTAL

The UV spectra were measured on an SF-20 spectrophotometer. The IR spectra were obtained on a UR-20 spectrophotometer in KBr pellets. Elemental analysis was performed on a Perkin–Elmer-240 microanalyzer.

The molecular weights of compounds **Ia** and **Ib** were determined by back ebullioscopy in chloroform on a VPO-302B osmometer.

The fluorescence spectra of compounds **IV** and **VI** were measured on the apparatus described in [14], reference quinine bisulfate. The ^{1}H and ^{19}F NMR spectra of compound **Vc** were obtained on a Bruker AM-500 spectrometer. The ^{19}F spectrum was measured at 470.59 MHz.

Freshly distilled solvents were used. Since salts **Va**–**Vf** are sparingly soluble in absolute chloroform, the solvent was not specially dried. The melting points were determined in a capillary and were not corrected.

2-Fluoro-4,6-dimethylanilinopyrimidine (**Ic**) [4] and 5-methylquino[1,2-a]benzimidazole [12] were described earlier.

The spectral characteristics of the compounds obtained are listed in Tables 1 and 2, and their melting points and elemental analyses, in Table 3.

2-(2-Chloro-4-iodoanilino)-4,6-dimethylpyrimidine (Ia) and 2-(4-chloro-2-iodoanilino)-4,6-dimethylpyrimidine (Ib). A mixture of 0.01 mol of 2-chloro-4-iodoanoline (or 4-chloro-2-iodoaniline) and 0.011 mol of 2-chloro-4,6-dimethylpyrimidine was heated at 120–130°C for 6 h and then treated with water and made alkaline with sodium carbonate. The precipitate was filtered off, dried, and subjected to column chromatography on Al_2O_3 in ether. Yield 55 (**Ia**) or 70% (**Ib**).

2-(2-Chloro-3-methylanilino)pyridine (II). A mixture of 0.014 mol of 2-chloro-3-methylaniline and 0.0168 mol of 2-bromopyridine was heated for 10 h at 150–160°C and then treated as described above. Yield 60%.

1,3-Dimethylpyrimido[1,2-*a*]benzimidazole (IIIa). 2-(2-Chloro-4-iodoanilino)-4,6-dimethylpyrimidine (**Ia**), 0.6 g, in 300 ml of *tert*-butanol in the presence of phosphate buffer (0.7 g of KH_2PO_4 and 0.06 g of NaOH in 150 ml of water) was irradiated with a DRL-400 mercury lamp (400 W) through a submerged quartz condenser with stirring with an argon stream for 5 h. After photolysis, the reaction solution was treated with aqueous sodium thiosulfate (3 g in 50 ml of H_2O), the *tert*-butanol was distilled off, the residue was extracted with ethyl acetate. The extract was dried, the ethyl acetate was distilled off, and the residue was subjected to column chromatography on Al_2O_3, eluents benzene–acetonitrile (1 : 1) and acetonitrile, to isolate 0.4 g of a mixture of the starting compound Ia, an unidentified compound, and 2-anilino-4,6-dimethylpyrimidine (identification by TLC on Silufol and Al_2O_3 plates using reference compounds), and 0.02 g (6% per taken substrate) of azinazole **IIIa** (identification by TLC on Silufol and Al_2O_3 plates using reference sample, by UV and IR spectroscopy, and the lack of melting point depression of the mixed sample with an authentic 2-(2-chloroanilino)-4,6-dimethylpyrimidine obtained by photocyclization [9].

8-Chloro-1,3-dimethylpyrimido[1,2-*a*]benzimidazole (IIIb). 2-(4-Chloro-2-iodoanilino)-4,6-dimethylpyrimidine (**Ib**), 0.7 g, in 400 ml of 80% *tert*-butanol in the presence of phosphate buffer was irradiated with a DRL-400 mercury lamp for 4 h as described above. After photolysis, the reaction solution was treated with sodium thiosulfate, the *tert*-butanol was distilled off, and the precipitate was filtered off to obtain 0.05 g of compound **IIIb**. The filtrate was extracted with ethyl acetate, the extract was dried, the ethyl acetate was distilled off, and the residue was subjected to chromatography on Al_2O_3, eluents acetonitrile–benzene (1 : 1) and acetonitrile to isolate 0.2 g of the starting amine **Ib** and 0.02 g of compound **IIIb**. The total yield of chlorodimethylpyrimidobenzimidazole **IIIb** was 0.07 g (15% per taken substrate).

6,7,8,9-Tetrafluoro-1,3-dimethylpyrimido[1,2-*a*]benzimidazole (IIIc) was prepared by irradiation of 0.7 g of 4,6-dimethyl-2-(pentafluoroanilino)pyrimidine (**Ic**) under the above conditions. The light yellow precipitate of compound **IIIc**, remaining after removal of *tert*-butanol, was filtered off, and dried. Yield 0.6 g (92%). Mixed sample with an authentic compound **IIIc** [4] showed no melting point depression.

9-Methylpyrido[1,2-*a*]benzimidazole (IV). 2-(2-Chloro-3-methylanilino)pyridine (**II**), 0.7 g, in 300 ml of 80% aqueous *tert*-butanol in the presence of phosphate buffer was irradiated with a DRL-400 mercury lamp for 5 h under the above conditions. After irradiation, the solvent was removed, the aqueous residue was extracted with ethyl acetate, and the solvent was removed. The residue was subjected to column chro-

matography on Al_2O_3, eluents benzene (7 : 3) and benzene–acetonitrile (1 : 1). Yield of 9-methylpyrido-[1,2-*a*]benzimidazole (**IV**) 0.35 g (60%).

8-Chloro-5-ethyl-1,3-dimethylpyrimido[1,2-*a*]-benzimidazolium perchlorate (Va). 8-Chloro-1,3-dimethylpyrimido[1,2-*a*]benzimidazole (**IIIb**), 0.195 g, and 0.17 g ethyl tosylate were heated for 5 h at 120–125°C. The mixture was cooled, washed with ether, treated with 2-propanol, and filtered. The filtrate was evaporated, the dry residue was dissolved in 15 ml of acetonitrile, treated with 0.122 g of $Co(ClO_4)_2 \cdot 2H_2O$ in 10 ml of 2-propanol, and left to stand for 0.5 h. After cooling with ice, the cobalt tosylate precipitate was filtered off and washed with chloroform. The filtrate was evaporated, and the residue was recrystallized from 2-propanol.

6,7,8,9-Tetrafluoro-1,3-dimethylpyrimido[1,2-*a*]-benzimidazolium tosylate (Vb). Tetrafluoroazinazole **IIIc**, 1 g, and 0.75 g of ethyl tosylate were heated at 120°C for 6 h. The reaction progress was followed by the consumption of base **IIIc** by TLC on Silufol plates, eluent acetonitrile–benzene, 1 : 1. After the reaction was complete, the reaction mixture was cooled and washed with ether, dissolved with heating in 2-propanol, filtered, the filtrate was evaporated, and the residue was dried. Yield 95%. The light brown glassy material was powdered.

6,7,8,9-Tetrafluoro-1,3-dimethylpyrimido[1,2-*a*]-benzimidazolium perchlorate (Vc). Tosylate **Vb**, 0.2 g, in 20 ml of chloroform was added to a solution of 0.063 g of $Co(ClO_4)_2 \cdot 2H_2O$ in acetonitrile, and the mixture was left to stand for 0.5 h, and cooled. The cobalt tosylate precipitate was filtered off and washed with chloroform. The filtrate was evaporated and dried. Yield 80%. The light orange glassy material was powdered, mp 70–75°C (deliquesces), 155–158°S (decomp.). ^{1}H NMR spectrum (Me_2CO-d_6), δ, ppm (*J*, Hz): 1.62 t (Me), 2.64 s (Me), 3.26 s (Me), 4.93 q (CH_2, 3), 7.93 s (H^2). ^{19}F NMR spectrum (Me_2SO-d_6, relative to C_6F_6), δ_F, ppm (*J*, Hz): –135.1 m (1F, 4, 10), –152.7 t.d (1F, 4, 21), –158.4 d.d (1F, 21), –159.6 t (21).

6,7,8,9-Tetrafluoro-5-ethyl-1,3-dimethylpyrimido[1,2-*a*]benzimidazolium tetraphenylborate (Vd). A solution of 0.073 g of $NaBPh_4$ in 10 ml of acetonitrile was added to a solution of 0.1 g of tosylate **Vb** in 15 ml of chloroform. The mixture was left to stand for 0.5 h and then cooled. The sodium tosylate was filtered off, washed with chloroform, and the filtrate was evaporated. The residue was dissolved in chloroform, the solution was filtered, the filtrate was evaporated, and the dry residue was crystallized from 2-propanol. Yield 20%, mp 172–173°C, dark gray powder.

6,7,8,9-Tetrafluoro-1,3-dimethylpyrimido[1,2-*a*]-benzimidazolium perchlorate (Ve). Sodium picrate, 0.055 g, in 10 ml of acetonitrile was added to a solution of 0.1 g of tosylate **Vb** in 10 ml of chloroform, and the mixture was left to stand for 0.5 h. After cooling, the sodium tosylate precipitate was filtered off, the filtrate was evaporated, the residue was dissolved in chloroform, the solution was filtered, the filtrate was evaporated, and the residue was dried to obtain a dark orange powder, mp 52–55°C.

6,7,8,9-Tetrafluoro-1,3-dimethylpyrimido[1,2-*a*]-benzimidazolium iodide (Vf). *a*. A mixture of tetrafluoroazinazole **IIIc**, 0.1 g, ethyl iodide, 10 ml, and 15 ml of acetonitrile was refluxed for 10 h. The reaction progress was followed by TLC on Silufol plates (UV-Vis, acetonitrile). The solvent was distilled off, the residue was washed with ether, and dried; chromatographically and spectrally the product was identical to iodide **Vf** obtained by method *b*.

b. A solution of 0.035 g of KI in 10 ml of acetonitrile was added to a solution of 0.1 g of tosylate **Vb** in 10 ml of chloroform. The mixture was left to stand for 0.5 h, after which the precipitate was filtered off and washed with chloroform. The filtrate was evaporate, the dry residue was dissolved in chloroform, the solution, if necessary, was filtered, the solvent was distilled off, and the residue was dried to obtain a light yellow material, mp 45–50°C. According to IR data, it contained a potassium tosylate admixture. Chromatographically and spectrally the product was identical to iodide **Vf** obtained by method *a*.

5-Ethyl-9-methylpyrido[1,2-*a*]benzimidazolium iodide (VI) and 7-ethyl-5-methylquino[1,2-*a*]-benzimidazolium iodide (VII) were obtained by alkylation of 9-methylpyrido[1,2-*a*]benzimidazole (**IV**) and 5-methylquino[1,2-*a*]benzimidazole (0.1 g), respectively, with ethyl iodide (10 ml) in acetonitrile (15 ml), refluxing for 3–4 h. The reaction progress was followed by the consumption of the starting base by TLC on Silufol plates (UV-Vis, eluent acetonitrile). The solvent was removed, the precipitate was washed with ether, suspended in ether, and filtered off.

6,7,8,9-Tetrafluoro-1-{3-(6,7,8,9-tetrafluoro-5-ethyl-3-methylpyrimido[1,2-*a*]benzimidazol-1-ylidene)-1-propenyl}-5-ethyl-3-methylpyrimido-[1,2-*a*]benzimidazolium tosylate (VIIIa). Triethyl orthoformate, 0.25 g, and one drop of acetic anhydride were added to a solution of 0.2 g of 6,7,8,9-tetrafluoro-5-ethyl-1,3-dimethylpyrimido[1,2-*a*]benzimidazolium tosylate (**Vb**) in 2 ml of pyridine. The mixture was

heated for 40 min at 100–105°C. The dye was precipitated with diethyl ether and filtered off. Yield 0.11 g (67%). Tosylate **VIIIa** was reprecipitated from acetonitrile with water, filtered off, and dried. The product has no defined melting point and decomposed on fast heating.

6,7,8,9-Tetrafluoro-1-{3-(6,7,8,9-tetrafluoro-5-ethyl-3-methylpyrimido[1,2-*a*]benzimidazol-1-ylidene)-1-propenyl}-5-ethyl-3-methylpyrimido-[1,2-*a*]benzimidazolium perchlorate (VIIIb). Ethyl orthoformate, 0.25 g, and one drop of acetic anhydride were added to a solution of 0.2 g tetrafluroethyldimethylpyrimidobenzimidazolium perchlorate (**Vc**) in 2 ml of pyridine. The mixture was heated for 40 min at 100°C. The dye was precipitated with ether, dissolved in a little 1:1 2-propanol–acetonitrile mixture, reprecipitated with water, filtered off, and dried. Yield 0.1 g (55%). The product had no defined melting point and decomposed with flash on fast heating.

The reaction with iodide **Vf** was perfomed like those with tosylate **Vb** and perchlorate **Vc**. Iodide was converted to perchlorate by means of lithium perchlorate. Chromatography was performed on Al_2O_3 (activity grade II), eluent acetonitrile. All other operations were the same as with tosylate and perchlorate.

8-Chloro-1-{3-(8-chloro-5-ethyl-3-methylpyrimido[1,2-*a*]benzimidazol-1-ylidene)-1-propenyl}-5-ethyl-3-methylpyrimido[1,2-*a*]benzimidazolium perchlorate (VIIIc). Ethyl orthoformate, 0.25 g, and one drop of acetic anhydride were added to 0.2 g of perchlorate **Va** in 2 ml of pyridine. The mixture was heated for 40 min at 100°C. The reaction product was precipitated with ether, dissolved in a little acetonitrile, reprecipitated with 2-propanol, filtered off, and dried. Yield 0.06 g (34%). The product had no defined melting point.

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REFERENCES

1. Cornelisse, J., Lodder, G., and Havinga, E., *Rev. Chem. Intermed.*, 1979, vol. 2, p. 231.
2. Frolov, A.N., *Zh. Org. Khim.*, 1993, vol. 29, no. 8, p. 1645.
3. Frolov, A.N., *Zh. Org. Khim.*, 1994, vol. 30, no. 7, p. 1059.
4. Frolov, A.N., *Zh. Org. Khim.*, 1998, vol. 34, no. 7, p. 1098.
5. Frolov, A.N., Smirnov, E.V., and El'tsov, A.V., *Zh. Vses. Khim. O–va*, 1975, vol. 20, no. 2, p. 237.
6. El'tsov, A.V., Kul'bitskaya, O.V., Smirnov, E.V., and Frolov, A.N., *Zh. Org. Khim.*, 1973, vol. 9, no. 12, p. 2521.
7. Frolov, A.N., *Zh. Obshch. Khim.*, 1999, vol. 69, no. 8, p. 1303.
8. Frolov, A.N., Yunnikov, V.V., Kul'bitskaya, O.V., and El'tsov, A.V., *Zh. Org. Khim.*, 1977, vol. 13, no. 3, p. 603.
9. Frolov, A.N. and Rtishchev, N.I., *Zh. Org. Khim.*, 1993, vol. 29, no. 10, p. 2035.
10. Frolov, A.N., Rtishchev, N.I., and Baklanov, M.V., *Zh. Obshch. Khim.*, 1992, vol. 62, no. 8, p. 1903.
11. Mackay, R.A., Landolph, J.R., and Poziomek, E.A., *J. Am. Chem. Soc.*, 1971, vol. 93, p. 5026.
12. Rtishchev, N.I. and Frolov, A.N., *Zh. Org. Khim.*, 1991, vol. 27, no. 3, p. 638.
13. Frolov, A.N., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 4, p. 596.
14. Rtishchev, N.I., El'tsov, A.V., Kvitko, I.Ya., and Alam, L.V., *Zh. Obshch. Khim.*, 1980, vol. 50, no. 9, p. 2070.