

solutions of sydnones. The energy of the T^*_1 state of 3-methylsydnone (~ 0.5 eV) determined from the spectrum is in good agreement with the calculated value (Table 1).

Data on the luminescence of liquid or solid dilute solutions of sydnones and sydnone-imines are not available in the literature. We have found that weak pale-blue luminescence corresponds to dilute ($c \sim 10^{-3}$ M) solutions of 3-methylsydnone, 3-phenylsydnone, and 3-methylsydnonimine hydrochloride in water during irradiation with an SVD-120A mercury-quartz lamp with a UFS-3 light filter (ISP-51 apparatus with a photoelectric adapter) (Fig. 2). The strong bathochromic shift of the luminescence bands with respect to the corresponding absorption bands may be due, on the one hand, to a change in the geometry of the molecules in equilibrium states S^*_1 , and, on the other hand, to disruption of the Boltzmann distribution of the unit cells that include the molecules of the investigated compounds and the solvent with respect to the energies of interaction of the molecules in these cells [12].

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POLYMETHINE DYES — 4-SUBSTITUTED FURO[2,3-b]- AND

SELENOPHENO[2,3-b]PYRIDINE DERIVATIVES

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Polymethine dyes that are 4-substituted furo[2,3-b]pyridine and selenopheno[2,3-b]pyridine derivatives were synthesized. It was shown that replacement of the vinylene group in the benzene ring of a 4-quinoline heteroresidue in the cyanine dyes by an oxygen or selenium atom causes a greater hypsochromic shift in their absorption maxima than replacement by a sulfur atom.

Polymethine dyes that are 4-substituted thienopyridine derivatives (I) were previously studied [1-2]. It was shown that replacement of the vinylene group by a sulfur atom in the benzene ring of a 4-quinoline heteroresidue in the cyanine dyes leads to a sharp hypsochromic shift of their absorption maxima. In this connection, it seemed of interest to synthesize polymethine dyes of the cyanine and merocyanine series, as well as p-dimethyl-

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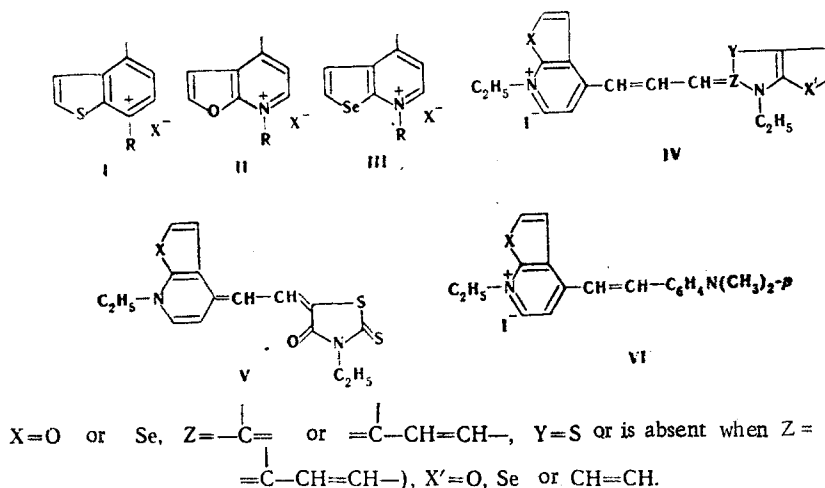
TABLE 1. Absorption Maxima and Hypsochromic Shifts of the Carbocyanines

Compound	In formula IV				λ_{max} , nm*	lg ϵ	Hypsochromic shift, [†] nm
	X	Z	Y	X'			
VII	CH=CH	C-CH=CH	—	CH=CH	711 ⁴	5,22	—
VIII	S	C-CH=CH	—	S	640 ¹⁻²	5,12	—
VIII	O	C-CH=CH	—	O	616	5,26	—
IX	Se	C-CH=CH	—	Se	624	5,08	—
X	CH=CH	C	S	CH=CH	630 ⁴	5,18	4,5
	S	C	S	CH=CH	583 ²	5,14	16,0
XI	Se	C	S	CH=CH	571	5,09	20,0
	O	C	S	CH=CH	569	5,16	18,0
XII	S	C-CH=CH	—	CH=CH	674	5,24	1,0
XIII	O	C-CH=CH	—	CH=CH	663	5,28	0,5
XIV	Se	C-CH=CH	—	CH=CH	661	5,11	6,5

*The λ_{max} value of the symmetrical thiocarbocyanine is 558 nm (in ethanol [4]).

[†]These are the hypsochromic deviations of the λ_{max} values from the arithmetic mean values calculated from the λ_{max} values of the corresponding symmetrical dyes (see [5]).

aminostyryl derivatives of 4-substituted furo[2, 3-b]pyridines (II) [3] and selenopheno[2, 3-b]pyridines (III) with structures IV, V, and VI:



The dyes were obtained by known methods for the synthesis of similar compounds (see [4]). It should be noted that symmetrical carbocyanines with 4-substituted furo- or selenophenyl-[2, 3-b]pyridine residues could not be obtained under various conditions by condensation of quaternary salts of 4-methylfuro- and 4-methylselenopheno[2, 3-b]pyridines with ethyl orthoformates. These dyes were synthesized by condensation of the ethiodides of these bases with the quaternary salts of their 4- β -acetanilidovinyl derivatives in acetic anhydride by heating in the presence of triethylamine.

The positions of the absorption maxima (in ethanol) of symmetrical and unsymmetrical carbocyanines with 4-substituted furo [2, 3-b]- and selenopheno[2, 3-b]pyridine residues and, for comparison, the corresponding 4-quinolyl and 4-substituted thieno[2, 3-b]pyridine derivatives, as well as the hypsochromic shifts for the unsymmetrical dyes, are presented in Table 1.

The data in Table 1 show that replacement of the vinylene groups by an oxygen or selenium atom in the benzene ring of a 4-quinolyl residue in the cyanines causes a greater hypsochromic shift of the absorption maxima of the dye as compared with replacement of it by a sulfur atom, and the 4-substituted furo [2, 3-b]pyridine derivative dye is more highly colored than the 4-substituted selenophenopyridocarbocyanine.

TABLE 2. Absorption Maxima of the Merocyanines and Styryl Dyes

Compound	X in formulas V or VI	λ_{max} , nm	$\lg \epsilon$	Hypsochromic shift,* nm
XV XVI	B In formula V	614 ⁴	—	12,5
	CH=CH	581 ²	5,04	10
	S	571	5,10	8,0
	O	578	5,03	5,0
	Se	—	—	—
XVII XVIII XIX	B In formula VI	550 ⁴	—	110,5
	CH=CH	508	5,08	117
	S	500	5,12	113,0
	O	496	4,96	121,0
	Se	—	—	—

*These are the deviations of the λ_{max} values from the arithmetic mean values from the λ_{max} values of the corresponding symmetrical dyes (see [5, 6]).

TABLE 3. Excitation Energies of the Cyanines

Compound	E_{th} , β unite	E_{th} , eV	E_{exp} , eV	λ_{max}^{exp} , nm
1,1'-Diethylquino-4,4'-carbocyanine	0,477 ⁸	1,710	1,744	711 ⁴
VII	0,530	1,897	1,937	640
IX	0,551	1,972	1,987	624
VIII	0,564	2,020	2,013	616

*It was assumed that $|\beta| = 3.58$ eV [8].

The positions of the absorption maxima (in ethanol) of the dimethylidinerocyanines (V) and the styryl derivatives (VI) with 4-substituted furo[2, 3-b]- and selenopheno[2, 3-b]-pyridine residues and, for comparison, 4-substituted thieno[2, 3-b]pyridine and 4-quinolyl derivatives, as well as the hypsochromic shifts calculated for them, are presented in Table 2.

It is apparent from Table 2 that the 4-substituted furo[2, 3-b]pyridine dimethylidynemerocyanine and the carbocyanine are more highly colored than the corresponding dyes with both thienopyridine and selenophenopyridine residues.

A comparison of the hypsochromic shifts shows that the basicities of the 4-substituted furo- and selenopheno[2, 3-b]pyridine and thienopyridine residues [7] exceed the basicity of the 4-quinoline residue, and that the basicities of the 4-substituted thieno- and furopyridine residues are close to one another.

The excitation energies (E_{th}) calculated by the MO method within the Hückel approximation and from the formula $E_{exp} = \frac{hc}{\lambda_{max}^{exp}}$, where λ_{max}^{exp} is the absorption maximum of an alcohol solution of the dye and E_{exp} is the excitation energy corresponding to λ_{max}^{exp} , are presented in Table 3.

A comparison of the data presented in Table 3 shows that an appreciably greater energy is necessary in the case of carbocyanine VII for excitation of transition of an electron from the upper occupied energy level of the ground state to the lower vacant level of the excited state than for realization of the same transition in the case of the quino-4,4'-carbocyanine, and this is the reason for the higher color of dye VII — the 4-substituted thieno[2, 3-b]pyridine derivative. The data in Table 3 show that dyes with 4-substituted selenopheno[2, 3-b]pyridine and, particularly, 4-substituted furo[2, 3-b]pyridine residues (IX and VIII, respectively) should be more highly colored than the 4-substituted thieno[2,

TABLE 4. Cyanine Dyes

Com- pound	mp, °C (dec.)	Empirical formula	Found, %			Calc. %			Yield, %
			C	H	I	C	H	I	
VIII	>200 ^a	C ₂₁ H ₂₁ IN ₂ O ₂	54.7	4.4	27.3	54.8	4.56	27.5	12
IX	>200 ^a	C ₂₁ H ₂₁ IN ₂ Se ₂	43.0	3.4	—	43.1	3.6	—	11
X	222—223 ^b	C ₂₁ H ₂₁ IN ₂ SSe	—	5.1 ^f	23.4	—	5.2 ^f	23.6	31
XI	219—221 ^b	C ₂₁ H ₂₁ IN ₂ OS	56.6	4.5	28.4	56.7	4.7	28.6	36
XII	204—206 ^c	C ₂₃ H ₂₃ ClN ₂ O ₄ S	—	—	6.0 ^f	—	—	6.1 ^f	24
XIII	246—247 ^d	C ₂₃ H ₂₃ IN ₂ O	58.3	4.7	26.8	58.5	4.9	27.0	29
XIV	231—233 ^e	C ₂₃ H ₂₃ IN ₂ Se	—	5.2 ^f	23.7	—	5.3	23.9	26
XV	210—211 ^b	C ₁₆ H ₁₆ N ₂ O ₂ S ₂	57.4	4.6	—	57.6	4.8	—	37
XVI	205—207 ^b	C ₁₆ H ₁₆ N ₂ OS ₂ Se	48.6	3.8	—	48.7	4.0	—	31
XVII	214—216 ^b	C ₁₉ H ₂₁ IN ₂ S	52.2	4.6	6.2 ^f	52.3	4.8	6.4 ^f	56
XVIII	234—235 ^b	C ₁₉ H ₂₁ IN ₂ O	54.1	4.8	30.1	54.3	5.0	30.2	24
XIX	224—225 ^b	C ₁₉ H ₂₁ IN ₂ Se	—	5.6 ^e	26.1	—	5.8 ^f	26.3	23

^aDark-blue prisms; ^bdark-violet prisms; ^cdark-blue plates;
^dgreen plates; ^egreen prisms; ^fnitrogen content in %.

3-b]pyridine derivative, and this is agreement with the experimental results.

EXPERIMENTAL

4-Methylselenopheno[2, 3-b]pyridine (XX). This compound was synthesized by condensation of 12.5 g (0.02 mole) of the double tin salt of 2-aminoselenophene hydrochloride [obtained in 50% yield by reduction of 17.5 g (0.1 mole) of 2-nitroselenophene with 90 g of stannous chloride in 230 ml of concentrated hydrochloric acid at 43–45° for 3 h] with 2.1 g (0.03 mole) of methyl vinyl ketone in anhydrous ethanol in the presence of ferric chloride and zinc chloride via the method we previously described in [9]. Workup of the reaction mixture gave 0.65 g (16.5%) of a light-yellow oil with bp 122–125° (7 mm). Found: C 49.0; H 3.6; N 6.9%. C₈H₇NSe. Calculated: C 49.0; H 3.6; N 7.0%. The ethiodide was obtained as grayish prisms (from anhydrous ethanol) with mp 164–165°. Found: I 36.0%. C₁₀H₁₂INSe. Calculated: I 36.1%.

Polymethine Dyes (Table 4).

4-β-Acetanilidovinylfuro[2, 3-b]pyridine Ethiodide (XXI). This compound was obtained by condensation of 0.001 mole of 4-methylfuro[2, 3-b]pyridine ethiodide (XXII) [3] with 0.001 mole of diphenylformamidine in 5 ml of acetic anhydride at 120–125° for 20 min in the presence of 0.001 mole of triethylamine. The product was isolated by dilution of the cooled reaction mixture with ether, dissolving of the resinous precipitate by heating in 3 ml of ethanol, and addition of 10% potassium iodide solution to the resulting solution. The yield of light-brown prisms (from ethanol) with mp 206–207° was 0.21 g (49%). Found: C 52.5; H 4.2; N 6.3%. C₁₉H₁₉IN₂O₂. Calculated: C 52.6; H 4.4; N 6.4%.

4-β-Acetanilidovinylselenopheno[2, 3-b]pyridine Ethiodide (XXIII). The method used to prepare XXI was used to obtain this compound in 43% yield from 0.001 mole of the ethiodide of XX. The light-brown prisms (from ethanol) had mp 213–214°. Found: C 45.8; H 3.7%. C₁₉H₁₉IN₂OSe. Calculated: C 46.0; H 3.8%.

Symmetrical Carbocyanines (VIII and IX). These compounds were synthesized by condensation of 0.001 mole of XXII or the ethiodide of XX, respectively, with 0.001 mole of XXI or XXIII in 4–6 ml of acetic anhydride at 100–105° for 5–10 min in the presence of 0.001 mole of triethylamine.

Unsymmetrical Carbocyanines (X–XIV). These compounds were obtained by condensation of 0.001 mole of the ethiodide of XX or XXII with 0.001 mole of 2-β-acetanilidovinylbenzothiazole ethiodide or 4-β-acetanilidovinylquinoline ethiodide in 5–6 ml of acetic anhydride at 125–130° for 20 min in the presence of 0.001 mole of triethylamine.

p-Dimethylaminostyryl Dyes (XVIII and XIX). These dyes were obtained by condensation of 0.002 mole of XXII or the ethiodide of XX with 0.002 mole of p-dimethylaminobenzaldehyde in 5 ml of pyridine in the presence of piperidine by heating on a boiling-water bath for 1 h.

The isolation of iodides VIII-XIV and XVIII and XIX was accomplished as follows. The mixture was cooled and treated with ether, and the resulting precipitate or resinous mass was dissolved by heating in ethanol. An equal volume of 10% potassium iodide solution was added to the resulting solution and the mixture was cooled. The isolated dyes were purified by recrystallization from ethanol.

Dimethylidynemerocyanines (XV and XVI). These dyes were obtained by condensation of 0.001 mole of the ethiodide of XX or XXII with 0.001 mole of 3-ethyl-5-acetanilidomethylene-rhodanine in 4-6 ml of anhydrous ethanol in the course of 1 h while refluxing in the presence of 0.001 mole of triethylamine. The mixture was cooled, and the dye was removed by filtration and purified by recrystallization from ethanol.

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SYNTHESES IN THE BENZO-2, 1,3-THIADIAZOLE SERIES.

II.* DERIVATIVES OF 1,2,5-THIADIAZOLO[3,4-h]QUINOLINE AND

BENZO-2, 1, 3-THIADIAZOLO[4, 5-h]-1,6-NAPHTHYRIDINE

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Derivatives of 1,2,5-thiadiazolo[3,4-h]quinoline and benzo- 2,1,3-thiadiazolo-[4, 5-h]-1, 6-naphthyridine were synthesized from 4-aminobenzo-2, 1, 3-thiadiazole.

We have accomplished the synthesis of 1,2,5-thiadiazole[3,4-h]quinoline derivatives [2, 3] (Table 1), their conversion to potential antiparasitic compounds (IIg and IIh), and the transition to a new heterocyclic system - benzo-2,1,3-thiadiazolo[4,5-h]-1,6-naphthyridine.

*See [1] for communication I.

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