POLYMETHINE DYES – BENZOFURO[2,3-b]PYRIDINE AND SELENONAPHTHENO[2,3-b]PYRIDINE DERIVATIVES

P. I. Abramenko and V. G. Zhiryakov

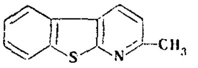
UDC 668.8:547.836.3'728.821'739.
821'789.3:543.422.6

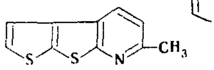
Polymethine dyes – benzofuro[2,3-b]pyridine and selenonaphtheno[2,3-b]pyridine derivatives – were synthesized, and their spectral properties are discussed. Replacement of a vinylene group by an oxygen or selenium atom in one benzene ring of the 2-benzo[h]quinoline residue in the cyanines causes a large bathochromic shift of the absorption maxima of the dyes as compared with replacement by a sulfur atom. The dyes derived from benzofuro[2,3-b]pyridine derivatives are more deeply colored than the derivatives of both thionaphtheno[2,3-b]pyridine and selenonaphtheno[2,3-b]pyridine.

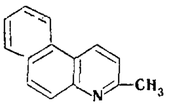
Polymethine dyes derived from thionaphtheno[2,3-b]pyridine (I) derivatives have been previously studied [1,2]. It was shown that replacement of vinylene groups by a sulfur atom in one or two benzene rings of benzo[h]quinoline (III) [3] in cyanine dyes leads to a bathochromic shift in their absorption maxima. In this connection, it seemed of interest to synthesize polymethine dyes of the cyanine and merocyanine series, as well as p-dimethylaminostyryl dyes, derived from benzofuro[2,3-b]pyridine (IV) and selenonaphtheno[2,3-b]pyridine (V) derivatives, of the general structure VI-VIII.

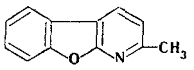
The dyes were obtained by known methods for the synthesis of such compounds [4].

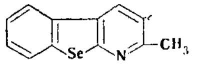
The positions of the absorption maxima (in ethanol) of symmetrical and unsymmetrical carbocyanines, derivatives of the synthesized bases, and, for comparison, of the corresponding benzo[h]quinoline and thionaphtheno[2,3-b]pyridine derivatives, are presented in Table 1 along with the hypsochromic shifts for the unsymmetrical dyes. The data in Table 1 demonstrate that replacement of the vinylene groups by an oxygen or selenium atom in one of the benzene rings of the benzo[h]quinoline residue in the cyanines causes a greater bathochromic shift of the absorption maxima of the dyes than when it is replaced by a sulfur atom.

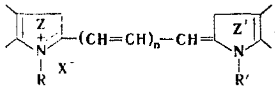

I

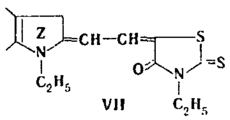

II

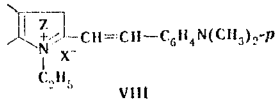

III


IV


V


VI


VII


VIII

Z is a benzofuro[2,3-b]pyridine or selenonaphtheno[2,3-b]pyridine residue, Z' is a benzofuro[2,3-b]pyridine, selenonaphtheno[2,3-b]-pyridine, benzothiazole, benzoxazole benzoselenazole, or quinoline residue, R and R' are alkyl groups, n = 0 or 1, and X is an acid residue.

All-Union State Scientific-Research and Design Institute of the Photographic-Chemical Industry, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp.1611-1614, December, 1972. Original article submitted October 19, 1971.

TABLE 1. Absorption Maxima of Carbocyanines and Hypsochromic Shifts

Compound	Z in formula VI ($R = C_2H_5$, $n = 1$)	Z' in formula VI	λ max, nm	Hypsochromic shift,* nm
	Benzo[h]quinoline	Benzo[h]quinoline	653 [3]	
	Thionaphtheno[2,3-b]pyridine	Thionaphtheno[2,3-b]pyridine	648 [1]	
IX	Benzofuro[2,3-b]pyridine	Benzofuro[2,3-b]-pyridine	653	
X	Selenonaphtheno[2,3-b]pyridine	Selenonaphtheno-[2,3-b]pyridine	650	
	Benzo[h]quinoline	Benzoxazole	556	4.0
XI	Benzofuro[2,3-b]pyridine	Benzoxazole	559	10.0
XII	Selenonaphtheno[2,3-b]pyridine	Benzoxazole	555	12.5
	Benzo[h]quinoline	2-Quinoline	616	5.0
XIII	Benzofuro[2,3-b]pyridine	2-Quinoline	631	1.0
XIV	Selenonaphtheno[2,3-b]pyridine	2-Quinoline	625	3.5
XV	Selenonaphtheno[2,3-b]pyridine	Benzoselenazole	590	21
	Benzo[h]quinoline	4-Quinoline	671	2.0
XVI	Selenonaphtheno[2,3-b]pyridine	4-Quinoline	680	0.5
XVII	Benzofuro[2,3-b]pyridine	4-Quinoline	684	2.0

---

* The hypsochromic shifts are the deviations of the absorption maxima of the unsymmetrical carbocyanines from the arithmetic mean values calculated from the absorption maxima of the corresponding symmetrical dyes. The λ_{max} values for the symmetrical carbocyanines – benzoxazole, benzothiazole, benzoselenazole, 2-quinoline, and 4-quinoline derivatives – are, respectively, 485, 558, 572, 607, and 711 nm (in ethanol) [3].

TABLE 2. Absorption Maxima of Dimethylidynemerocyanines and Hypsochromic Shifts

Comp.	Z in formula VII	λ_{max}, nm (in ethanol)	Hypsochromic shift,* nm
	Benzo[h]quinoline	584	4,5
	Thionaphtheno[2,3-b]pyridine	586[1]	9,0
XVIII	Benzofuro[2,3-b]pyridine	591	6,5
XIX	Selenonaphtheno[2,3-b]pyridine	587	9,0

---

*The hypsochromic shifts are the deviations of the absorption maxima of the dimethylidynemerocyanines from the arithmetic mean values calculated from the absorption maxima of the corresponding symmetrical carbocyanines and monomethylidyneoxanine – a 3-ethylrhodanine derivative; λ_{max} 542 nm (in ethanol) for the latter [5].

TABLE 3. Absorption Maxima of p-Dimethylaminostyryl Dyes and Hypsochromic Shifts

Comp.	Z in formula VIII	λ_{max}, nm (in ethanol)	Hypsochromic shift,* nm
	Benzo[h]quinoline	528	94,5
	Thionaphtheno[2,3-b]pyridine	518	111
XX	Benzofuro[2,3-b]pyridine	506	125,5
XXI	Selenonaphtheno[2,3-b]pyridine	476	154

---

*Absorption maximum of Michler's blue hydrol at 610 nm (in nitromethane).

The dyes derived from benzofuro[2,3-b]pyridine derivatives are more deeply colored than both the thionaphtheno[2,3-b]pyridine and selenonaphtheno[2,3-b]pyridine derivatives.

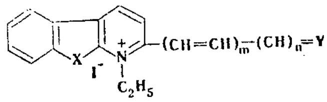
A comparison of the hypsochromic shifts presented in Table 1 shows that the basicities of the benzofuro[2,3-b]pyridine and selenonaphtheno[2,3-b]pyridine residues are close to the basicity of the 4-quinoline residue; the basicity of the selenonaphtheno[2,3-b]pyridine residue somewhat exceeds that of the benzofuro[2,3-b]pyridine residue.

The positions of the absorption maxima (in ethanol) of merocyanine dyes, derivatives of the new bases, and,for comparison, thionaphtheno[2,3-b]pyridine and benzo[h]quinoline derivatives are presented in Table 2 along with the hypsochromic shifts calculated for them.

It is seen from Table 2 that dimethylidynecyanines derived from benzofuro[2,3-b]pyridine and selenonaphtheno[2,3-b]pyridine derivatives are, like the carbocyanines, more deeply colored than the thionaphtheno[2,3-b]pyridine derivative. A comparison of the hypsochromic shifts presented in Table 2 demonstrates that the basicities of the benzofuro[2,3-b]-, thionaphtheno[2,3-b]-, and selenonaphtheno[2,3-b]-pyridine residues are of about the same order.

The positions of the absorption maxima (in ethanol) of p-dimethylaminostyryl dyes and the hypsochromic shifts calculated for them are presented in Table 3. It is apparent from a comparison of the hypsochrom-

TABLE 4. Cyanine Dyes



Comp.	X	*m*	*n*	Y	mp, °C	λ_{max}, nm (in ethanol)
IX	O	1	1	1-Ethylbenzofuro[2,3-b]dihydropyridylidene	247—248 [a]	653
X	Se	1	1	1-Ethylselenonaphtheno-[2,3-b]dihydropyridylidene	253—254 [a]	650
XXII[b]	O	0	1	3-Ethylbenzothiazolinylidene	232—234 [b]	486
XI	O	1	1	3-Ethylbenzoxazolinylidene	229—230 [c]	559
	Se	1	1	3-Ethyl-4,5-diphenylthiazolinylidene	130—131 [d]	593
XII	Se	1	1	3-Ethylbenzoxazolinylidene	186—187 [c]	555
XIII	O	1	1	1-Ethyldihydro-2-quinolylidene	253—254 [a]	631
XIV	Se	1	1	1-Ethyldihydro-2-quinolylidene	228—229 [a]	625
XV	Se	1	1	3-Ethylbenzoselenazolinylidene	195—196 [c]	590
XVI	Se	1	1	1-Ethyldihydro-4-quinolylidene	247—248 [a]	680
XVII	O	1	1	1-Ethyldihydro-4-quinolylidene	254—255 [a]	684

Comp.	Empirical formula	Found, %			Calc., %			Yield, %
		C	H	I	C	H	I	
IX	$C_{29}H_{25}IN_2O_2$	62,0	4,4	22,5	62,1	4,5	22,6	16
X	$C_{25}H_{25}I_3N_2Se_2$	50,7	3,5	18,4	50,7	3,6	18,5	19
XXII[b]	$C_{23}H_{21}IN_2OS$	55,0	4,1	25,3	55,2	4,2	25,4	34
XI	$C_{25}H_{23}IN_2O_2$	58,6	4,4	24,8	58,8	4,5	24,9	27
	$C_{33}H_{29}IN_2SSe$	—	4,1	18,2	—	4,2	18,3	36
XII	$C_{25}H_{23}IN_2OSe$	52,2	4,0	22,2	52,4	4,0	22,1	29
XIII	$C_{27}H_{25}IN_2O$	62,2	4,7	24,3	62,3	4,8	24,4	43
XIV	$C_{27}H_{25}IN_2Se$	55,5	4,1	21,6	55,6	4,2	21,7	41
XV	$C_{25}H_{23}IN_2Se_2$	47,2	3,5	19,8	47,2	3,6	19,9	38
XVI	$C_{27}H_{25}IN_2Se$	55,6	4,1	21,8	55,6	4,2	21,7	34
XVII	$C_{27}H_{25}IN_2O$	62,2	4,1	24,3	62,3	4,2	24,4	31

---

[a] Dark blue prisms. [b] Obtained by condensation of 0.34 g (1 mmole) of the ethiodide of IV with 0.35 g (1 mmole) of 2-ethylmercaptobenzothiazole ethiodide in 5 ml of pyridine in the presence of piperidine at 100-105°; dark brown prisms. [c] Violet prisms. [d] Dark violet prisms.

ic shifts presented in Table 3 that, as in the case of thionaphtheno[2,3-b]pyridine, the basicities of the benzofuro[2,3-b]pyridine and selenonaphtheno[2,3-b]pyridine residues are higher than the basicity of the benzo[h]quinoline residue. The basicity of the selenonaphtheno[2,3-b]pyridine residue somewhat exceeds that of both the thionaphtheno[2,3-b]pyridine and benzofuro[2,3-b]pyridine residues.

EXPERIMENTAL

Cyanine Dyes (Table 4). Symmetrical Carbocyanines (IX, X). These dyes were synthesized by condensation of, respectively, 0.34 g (1 mmole) of the ethiodide of IV or 0.40g (1 mmole) of the ethiodide of V with an equimolar amount of the 2-β-acetanilidovinyl derivative of the same base in 5 ml of acetic anhydride at 120-125° (20-30 min) in the presence of triethylamine.

Unsymmetrical Carbocyanines (XI-XVII). These dyes were obtained by the condensation of 0.34 g (1 mmole) of the ethiodide of IV or 0.40 g (1 mmole) of the ethiodide of V with an equimolar amount of the ethiodide of the 2-β-acetanilidovinyl derivative of benzothiazole, benzoxazole, or quinoline in 3-6 ml of acetic anhydride at 125-130° (20-30 min) in the presence of triethylamine. The symmetrical and unsymmetrical carbocyanines were purified by chromatography on aluminum oxide and were recrystallized from ethanol.

2-Thiono-3-ethyl-5-[2-(1-ethylbenzofuro[2,3-b]dihydro-2-pyridylidene)ethylidene]-4-thiazolidinone (XVIII). This compound was obtained in 26% yield by condensation of 0.34 g (1 mmole) of the ethiodide of base IV with 0.30 g (1 mmole) of 2-thiono-3-ethyl-5-acetanilidomethylene-4-thiazolidinone in 5 ml of anhydrous ethanol in the presence of triethylamine by heating on a boiling-water bath for 60 min. The dye was purified by the method used for the carbocyanines. The violet needles (from ethanol) had mp 292-293°. Found,%: C 62.6; H 4.6; S 16.7. $C_{20}H_{18}N_2O_2S_2$. Calculated,%: C 62.8; H 4.7; S 16.7.

2-Thiono-3-ethyl-5-[2-(1-ethylselenonaphtheno[2,3-b]dihydro-2-pyridylidene)ethylidene]-4-thiazolidinone (XIX). This compound was similarly obtained in 28% yield from 0.40 g (1 mmole) of the ethiodide of V. The violet needles (from ethanol) had mp 237-238°. Found,%: C 53.8; H 4.0; S 14.3. $C_{20}H_{18}N_2OS_2Se$. Calculated,%: C 53.9; H 4.0; S 14.4.

2-(p-Dimethylaminostyryl)benzofuro[2,3-b]pyridine Ethiodide (XX). This compound was synthesized in 21% yield by condensation of 0.34 g (1 mmole) of the ethiodide of IV with 0.17 g (1.1 mmole) of p-dimethylaminobenzaldehyde in 5 ml of pyridine in the presence of piperidine by heating on a boiling-water bath for 30 min. The dark violet prisms (from ethanol) had mp 214-215°. Found,%: C 58.7; H 4.9; I 26.9. $C_{23}H_{23}IN_2O$. Calculated,%: C 58.7; H 5.0; I 27.0.

2-(p-Dimethylaminostyryl)selenonaphtheno[2,3-b]pyridine Ethiodide (XXI). This dye was similarly obtained in 23% yield from 0.40 g (1 mmole) of the ethiodide of V. The dark violet prisms (from ethanol) had mp 211-212°. Found,%: C 51.7; H 4.2; I 23.8. $C_{23}H_{23}IN_2Se$. Calculated,%: C 51.8; H 4.3; I 23.8.

LITERATURE CITED

1. V. G. Zhiryakov and P. I. Abramenko, Khim. Geterotsikl. Soedin., 491 (1969).
2. V. G. Zhiryakov and P. I. Abramenko, Trudy Gosniikhimfotoproekt, No. 1, 26 (1968).
3. N. I. Fisher and F. M. Hamer, Proc. Roy. Soc. (London), 154A, 703 (1936).
4. F. M. Hamer, The Cyanine Dyes and Related Compounds, New York — London (1964).
5. M. V. Deichmeister, I. I. Levkoev, and É. B. Lifshits, Zh. Obshch. Khim., 23, 1529 (1953).