X-Arylsulfonylchlorophenoxazines (VIa-d, Table 1). A 5-mmole sample of sodium methoxide and 5 mmole of III were dissolved in 30 ml of methanol, after which the solvent was removed by vacuum distillation, 50 ml of DMF was added to the residue, and the mixture was refluxed for 7 h. It was then cooled and poured into water. The resulting precipitate (where necessary, NaCl was added for coagulation) was removed by filtration, dried, washed with benzene, and crystallized from nitromethane.

10-Arylsulfonylphenoxazines (VIIa-c, Table 1). A solution of 0.01 mole of phenoxazine and 0.015 mole of arenesulfonyl chloride in 2 ml of pyridine was allowed to stand for 4 h, after which the resulting precipitate was washed with isopropyl alcohol, removed by filtration, dried, and crystallized from isopropyl alcohol.

X-Arylsulfonylphenoxazines (IXa-c, Table 1). A solution of 0.01 mole of VII in DMF was refluxed for 20 h, after which it was cooled and poured into 2% NaCl. The resulting precipitate was removed by filtration, dried, washed with benzene, and crystallized from nitromethane. An additional amount of the reaction product was isolated by evaporation of the benzene washes.

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POLYMETHINE DYES — FURO[3,2-e]INDOLENINE DERIVATIVES

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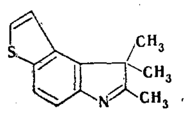
UDC 668.8: 547.722'754

7,8,8'-Trimethylfuro[3,2-e]indolenine and polymethine dyes of various types that are derivatives of this base were synthesized. It is shown that incorporation of a furo[3,2] group in the 4 and 5 positions of the indolenine residue in the cyanines leads to a smaller bathochromic shift of the absorption maxima than does the introduction of thieno and benzo groups in the same position.

On passing from dyes with a 3,3-dimethylindolenine residue to the corresponding 4,5-thieno[3,2]derivatives (I) one observes a smaller bathochromic shift of the absorption maximum than on passing to 4,5-benzoindolenine derivatives (II). The basicity of the thieno[3,2-e]indolenine residue is appreciably higher than that of the 3,3-dimethylindolenine residue [1].



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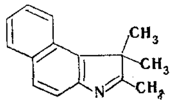
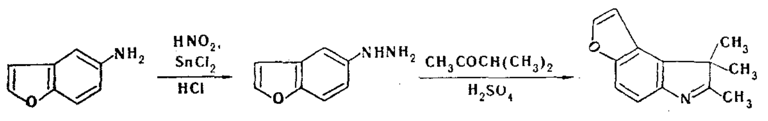


II

We have synthesized a new analogous heterocyclic base — 7,8,8'-trimethylfuro[3,2-e]indolenine (III) — from 5-aminobenzofuran (IV) (see [2]):



IV V III

All-Union State Scientific-Research and Design Institute of the Photographic-Chemical Industry, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1599-1602, December, 1975. Original article submitted December 16, 1974.

TABLE 1. Absorption Maxima of the Carbocyanines

Compound	In formula VI			λ_{max}, nm	log ε	Hypsochromic shift,* nm
	B	X	B′			
	H	$C(CH_3)_2$	H	548[5]		
	Benzo [3, 2]	$C(CH_3)_2$	Benzo †	587[6]		
	Thieno [3, 2]	$C(CH_3)_2$	Thieno [3, 2]	578[1]	5,13	
IX	Furo [3, 2]	$C(CH_3)_2$	Furo [3, 2]	564	5,06	
	Thieno [3, 2]	S		564	5,16	4,0
X	Furo [3, 2]	S		556	5,02	5,0
XI	Furo [3, 2]	CH=CH		576	5,21	9,5

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* These are the hypsochromic deviations of λ_{max} from the arithmetic mean values calculated from the λ_{max} values of the corresponding symmetrical dyes (see [7]).

† N,N′-Dimethiodide.

TABLE 2. Absorption Maxima of Dimethylidynemerocyanines and Styryl Dyes

Compound	B	λ_{max}, nm	log ε	Hypsochromic shift,* nm
	In formula VII			
	H	503[8]		42,0
	Thieno [3, 2]	520	4,98	40,0
XII	Furo [3, 2]	520	5,10	33,0
	In formula VIII			
	H	545 †[9]		34,0
	Thieno [3, 2]	559	4,76	35,0
XIII	Furo [3, 2]	548	4,83	39,0

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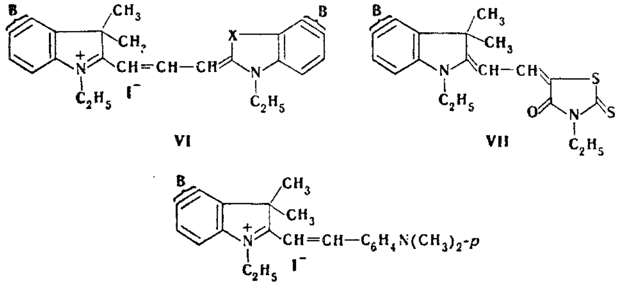
* These are the hypsochromic deviations of the λ_{max} values of the dyes from the arithmetic mean values calculated from the λ_{max} values of the corresponding symmetrical dyes (see [7]).

† This is the λ_{max} value in methanol.

It was found that the condensation of 5-hydrazinobenzofuran (V) with methyl isopropyl ketones proceeds with ring closing in the 4 position (see [3]). This is confirmed by the PMR spectrum, which has two doublets of 4-H and 5-H protons (7.56 and 7.76 ppm, $J_{4,5}$ = 9.7 Hz).



VI VII VIII

B= furo [3,2], X=$C(CH_3)_2$, S or CH=CH, B′=H or furo [3,2]

Alkylation of base III gave the ethiodide, from which symmetrical and unsymmetrical carbocyanines (VI), a dimethylidynemerocyanine (VII), and a p-dimethylaminostyryl dye (VIII) were synthesized by the usual methods [4].

The positions of the absorption maxima (in ethanol) of the synthesized dyes and, for comparison, the corresponding benzo[e]- and thieno[3,2-e]indolenine derivatives are presented in Tables 1 and 2.

The data in Table 1 show that the carbocyanine that is a furo[3,2-e]indolenine derivative is considerably more deeply colored than the indocarbocyanine. However, the introduction of a furo[3,2] group in the 4,5 positions of the 3,3-dimethylindolenine residue in the cyanines leads to a smaller bathochromic effect than when thieno or benzo groups are introduced in the same positions of the dyes.

TABLE 3. Cyanine Dyes

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	I	C	H	I	
IX	>300[a]	$C_{31}H_{33}IN_2O_2$	62,7	5,4	24,3	62,8	5,6	24,45	29
X	198—199[b]	$C_{26}H_{27}IN_2OS$	57,5	4,9	23,3	57,6	5,0	23,4	62
XI	244—245[c]	$C_{28}H_{29}IN_2O$	62,6	5,3	23,5	62,7	5,4	23,7	53
XII	205—206[d]	$C_{21}H_{22}N_2O_2S_2$	—	7,0[e]	15,9[f]	—	7,0[e]	16,1[f]	44
XIII	213—214[d]	$C_{24}H_{27}IN_2O$	—	5,7[e]	26,0	—	5,7[e]	26,1	41

[a]Green needles. [b]Dark-violet prisms. [c]Green prisms. [d]Violet prisms. [e]This is the percentage of nitrogen. [f]This is the percentage of sulfur.

A comparison of the hypsochromic shifts presented in Tables 1 and 2 shows that the basicity of the furo-[3,2-e]indolenine residue is substantially higher than the basicity not only of the indolenine residue but also of the thieno[3,2-e]indolenine residue.

EXPERIMENTAL

The absorption spectra of solutions of the dyes in ethanol were obtained with an SF-2 spectrophotometer. The PMR spectrum of III in carbon tetrachloride (on the δ scale) was recorded with a Varian T-60 spectrometer.

5-Aminobenzofuran (IV). This compound was obtained by decomposition of the double tin salt of the hydrochloride of IV [2]. Workup gave a colorless oil with bp 133-135° (8 mm). Found %: C 72.0; H 5.1; N 10.3. C_8H_7NO. Calculated %: C 72.2; H 5.26; N 10.5. The hydrochloride was obtained as colorless prisms (from anhydrous ethanol) with mp 237-238°. Found %: C 56.4; H 4.5; Cl 20.7. $C_8H_7NO \cdot HCl$. Calculated %: C 56.6; H 4.6; Cl 20.9.

5-Hydrazinobenzofuran (V). A 14.5-g (0.109 mole) sample of IV was diazotized at 0-2° in 80 ml of water and 80 ml of concentrated hydrochloric acid with a solution of 7.6 g (0.11 mole) of sodium nitrite in 35 ml of water. The reaction mixture was filtered, and an ice-water-cooled solution of 49 g (0.217 mole) of stannous chloride dihydrate in 49 ml of concentrated hydrochloric acid was added to the filtrate with vigorous stirring. The mixture was then stirred for another 20 min, after which the tin complex was removed by filtration and suspended in 200 ml of water. A 40% solution of sodium hydroxide was added to the suspension with cooling and stirring until it gave an alkaline reaction. The mixture was then treated with ether, and the extract was dried with magnesium sulfate. The ether was evaporated to a small volume, and a solution of hydrogen chloride in anhydrous ether was added. The precipitated hydrochloride was removed by filtration and recrystallized from ethanol to give colorless prisms (from ethanol) with mp 194-195° in 60% yield. Found %: C 52.0; H 4.7; Cl 19.1. $C_8H_9ClN_2O$. Calculated %: C 52.0; H 4.9; Cl 19.2.

7,8,8'-Trimethylfuro[3,2-e]indolenine (III). A 4.3-g (0.05 mole) sample of methyl isopropyl ketone was added dropwise with vigorous stirring at 92-95° to a solution of 9.25 g (0.05 mole) of V in a mixture of 60 ml of water and 60 g of concentrated sulfuric acid, after which the mixture was heated at 94-97° for 2.5 h. It was then cooled and made alkaline with 10% sodium hydroxide solution (with cooling). The resulting base was removed by steam distillation and extracted with ether. The extract was dried with potassium carbonate, the ether was removed by distillation, and the residue was vacuum distilled to give 2.99 g (30%) of a greenish oil with 155-158° (7-8 mm). Found %: C 78.2; H 6.3; N 6.9. $C_{13}H_{13}NO$. Calculated %: C 78.4; H 6.5; N 7.0. The picrate was obtained as light-yellow needles (from anhydrous ethanol) with mp 174-175°. Found %: N 13.1. $C_{19}H_{16}N_4O_8$. Calculated %: N 13.07. The ethiodide was obtained as light-yellow prisms (from ethanol) with mp 239-240°. Found %: I 35.6. $C_{15}H_{18}INO$. Calculated %: I 35.8.

Dyes (Table 3). p-Dimethylaminostyryl dye XIII was obtained by heating 0.001 mole of the ethiodide of III with 0.001 mole of p-dimethylaminobenzaldehyde in 2 ml of pyridine in the presence of piperidine at 100-110° for 30 min. Carbocyanine IX was obtained by condensation of 0.001 mole of the ethiodide of III with 0.002 mole of ethyl orthoformate in 3 ml of acetic anhydride at 125-130° for 15 min.

Unsymmetrical carbocyanines X and XI were obtained by heating 0.001 mole of the ethiodide of III with 0.001 mole of the ethiodide of 2-(β-acetanilidovinyl)benzazole or -quinoline in 3 ml of acetic anhydride at 120-130° for 15 min in the presence of 0.001 mole of triethylamine.

The iodides of IX-XI and XIII were isolated by dilution of the cooled reaction mixture with ether, dissolving of the precipitate or resinous mass in ethanol, and addition of an equal volume of 10% potassium iodide solution to the alcohol solution. The dyes were purified by recrystallization from ethanol.

Dimethylidynemerocyanine XII was synthesized by condensation of 0.001 mole of the ethiodide of III with 0.001 mole of 5-acetanilidomethylene-3-ethylrhodanine in 2 ml of anhydrous ethanol in the presence of 0.002 mole of triethylamine by heating on a boiling-water bath for 30 min. The mixture was cooled, and the precipitated dye was removed by filtration and purified by recrystallization from ethanol.

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POLYMETHINE DYES – FURO[2,3-g]BENZOTHIAZOLE DERIVATIVES

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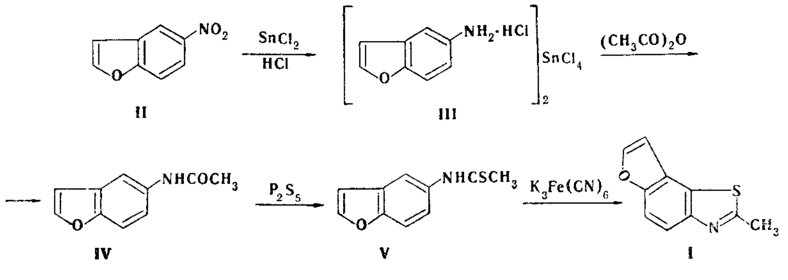
UDC 541.651:547.728'789.6

A new heterocyclic base – 2-methylfuro[2,3-g]benzothiazole – and cyanine dyes with residues of this base were synthesized. It is shown that introduction of a furo[2,3] group in the 6,7 positions of the benzothiazole residue in the cyanines leads to a smaller bathochromic effect than the introduction of a thieno[2,3] and, particularly, a benzo group in the same positions.

Polymethine dyes that are thieno[2,3-g]benzothiazole derivatives have been previously described [1]. It was shown that a considerable bathochromic shift of the absorption maximum is observed on passing from dyes with a benzothiazole residue to the corresponding thieno[2,3-g]benzothiazole derivatives.

We have synthesized a new heterocyclic base – 2-methylfuro[2,3-g]benzothiazole (I) – from 5-nitrobenzofuran (II) [2] via the scheme



Reduction of II with stannous chloride in concentrated hydrochloric acid at 40–45°C gave 5-aminobenzofuran hydrochloride double tin salt (III), which was converted to 5-acetamidobenzofuran (IV) by acetylation with

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All-Union State Scientific-Research and Design Institute of the Photographic-Chemical Industry, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1603–1606, December, 1975. Original article submitted December 16, 1974.