# POLYMETHINE DYES — FURO[2,3-b]-6-PYRIDINE DERIVATIVES

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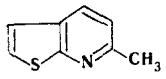
Polymethine dyes — furo[2,3-b]-6-pyridine derivatives — were synthesized. Replacement of the vinylene group in the benzene ring of the quinoline residue by an oxygen atom and by a sulfur atom causes a bathochromic shift of the absorption maximum of the corresponding cyanine dyes.

It has been shown that replacement of the vinylene group by a sulfur atom in the benzene ring of the quinoline residue in cyanine dyes leads to a bathochromic shift of their absorption maxima [1, 2]. To ascertain the effect on the spectra of the dyes of a similar replacement of the vinylene group by an oxygen atom we synthesized polymethine dyes of the cyanine (A) and merocyanine (B) series and p-dimethylaminostyryl dyes (C) containing a thieno- or furo[2,3-b]-6-pyridine residue (I, II) [3].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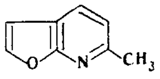
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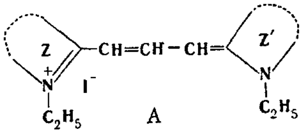
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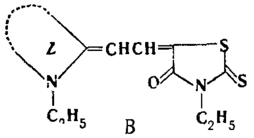
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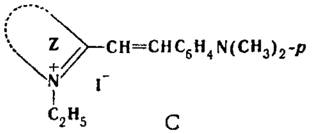
C

TABLE 1. Absorption Maxima of Carbocyanines (A) in Alcohol

| Compound | Z | Z′ | $\lambda_{max}$, nm | Hypsochromic shift,* nm |
|---|---|---|---|---|
| III | Furo [2,3-b]-6-pyridine | Furo [2,3-b]-6-pyridine | 620 | — |
| | 2-Quinoline | Benzoxazole | 545[4] | 1,0 |
| IV | Thieno [2,3-b]-6-pyridine | Benzoxazole | 542 | 9,5 |
| V | Furo [2,3-b]-6-pyridine | Benzoxazole | 536 | 16,5 |
| | 2-Quinoline | Benzothiazole | 580[5] | 2,5 |
| VI | Thieno [2,3-b]-6-pyridine | Benzothiazole | 572 | 16,0 |
| | Furo [2,3-b]-6-pyridine | Benzothiazole | 571 | 18,0 |
| | Thieno [2,3-b]-6-pyridine | 2-Quinoline | 608 | 4,5 |
| VII | Furo [2,3-b]-6-pyridine | 2-Quinoline | 609 | 4,5 |
| | 2-Quinoline | 4-Quinoline | 656 | 3,0 |
| VIII | Thieno [2,3-b]-6-pyridine | 4-Quinoline | 662 | 2,5 |
| IX | Furo [2,3-b]-6-pyridine | 4-Quinoline | 663 | 2,5 |

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*The $\lambda_{max}$ values in ethanol of symmetrical carbocyanines with benzoxazole, benzothiazole, 2-quinoline, 4-quinoline, and thieno[2,3-b]-6-pyridine residues are, respectively, 485, 558, 607, 711 [5], and 618 nm [1, 2].

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TABLE 2. Absorption Maxima of Dimethinemerocyanines (B) and p-Dimethylaminostyryl Dyes (C) in Alcohol

| Compound | Z | $\lambda_{max}$, nm | Hypsochromic shift,* nm |
|---|---|---|---|
| B | 2-Quinoline | 565 | 9,5 |
| B | Thieno [2,3-b]-6-pyridine | 576 | 4,0 |
| B (X) | Furo [2,3-b]-6-pyridine | 574 | 7,0 |
| C | 2-Quinoline | 532 | 76,5 |
| C (XI) | Thieno [2,3-b]-6-pyridine | 502 | 112 |
| C (XII) | Furo [2,3-b]-6-pyridine | 488 | 127,0 |

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*These are the deviations in the $\lambda_{max}$ values of the dyes from the arithmetic mean values calculated from the $\lambda_{max}$ values of the corresponding symmetrical carbocyanines and monomethineoxanine derivative of 3-ethylrhodanine ($\lambda_{max}$ in alcohol 542 nm [6]) or the hydrol of Michler's blue ($\lambda_{max}$ in nitromethane 610 nm).

TABLE 3. Excitation Energies of Cyanine Dyes

| Compound | $E_{theor}$ |  | $E_{exp}$, eV | $\lambda_{max}$, nm |  |
|---|---|---|---|---|---|
|  | β units | eV |  | theor. | exptl. |
| Bis (7-ethylfuro [2,3-b]-6-pyridine) trimethinecyanine (III) | 0,553 | 1,980 | 2,00 | 626 | 620 |
| 1,1'-Diethylquino-2,2'-carbocyanine | 0,571[7] | 2,04 | 2,04 | 607 | 607 |
| Bis (7-ethylthieno [2,3-b]-6-pyridine) trimethinecyanine (XIII) | 0,556 | 1,990 | 2,006 | 623 | 618 |
| 3,3'-Diethylthiacarbocyanine | 0,650[7] | 2,32 | 2,21 | 534 | 558 |
| Bis (3-ethylthieno [2,3-d]-2-thiazole(trimethinecyanine (XIV) | 0,577 | 2,062 | 2,08 | 600 | 594 |

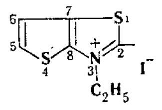
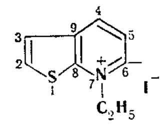
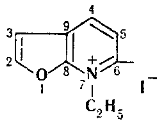
The dyes were obtained by known methods for the synthesis of such compounds (see [4]). The data in Table 1 show that replacement of the vinylene groups by an oxygen atom in the benzene ring of the 2-quinoline residue in the carbocyanines causes a somewhat greater bathochromic shift of the absorption maxima of the dyes than replacement of it by a sulfur atom. A comparison of the magnitudes of the hypsochromic shifts for unsymmetrical carbocyanines shows that the basicities of the furo[2,3-b]-6-pyridine and thieno[2,3-b]-6-pyridine residues are higher than the basicity of the 2-quinoline residue. The basicity of the furo[2,3-b]-6-pyridine residue somewhat exceeds the basicity of the thieno[2,3-b]-6-pyridine residue.

A comparison of the magnitudes of the hyposchromic shifts for p-dimethylaminostyryl dyes (C, Table 2) leads to the same conclusion.

The excitation energies calculated by the molecular orbital method within the Hückel approximation ($E_{theor}$) [7] and the corresponding maxima on the absorption curves of alcohol solutions of the dyes ($E_{exp}$) are presented in Table 3. The coulombic and exchange integrals (Table 4) were taken with allowance for the electronegativities of the heteroatoms [8] and the C–X bond lengths (where X is a heteroatom; see [7]). The coulombic integrals of the heteroatoms ($\alpha_X$) and the carbon atoms bonded to them [$\alpha_{C(X)}$] were calculated from the formulas $\alpha_X = \alpha + h_X\beta$ and $\alpha_{C(X)} = \alpha + 0.1\ h_X\beta$ for $h_{-NR-,\overset{+}{=}NR-}$ 1.5, $h_{-O-}$ 2.0, and $h_{-S-}$ 0.7; 3.58 eV was adopted for $|\beta|$ [7].

The calculated excitation energies of the electron from the higher occupied level to the lower vacant level increase on passing from the furo[2,3-b]-6-pyridine derivative (dye III) to the thienopyridocarbocyanine and, especially, to the quino-2,2'-carbocyanine; this is in agreement with the observed absorption maxima of these dyes. It has been shown that dyes with thieno[2,3-d]thiazole residues [9] have considerably deeper colors than the corresponding benzothiazole derivatives. These results are also in agreement with the calculated values.

TABLE 4. Exchange Integrals ($\beta_{CC}$, $\beta_{CX}$) and Energy Levels of Carbocyanine Molecules

| Compound | Heterocycle residue | Bond | $k_{CC}$ or $k_{CX}$* | Energy levels, β units | |
|---|---|---|---|---|---|
| | | | | vacant | occupied |
| XIV |  | $S_1$—$C_2$ | 0,4 | −1,7765 | 0,2405 |
| | | $S_1$—$C_7$ | | −1,6565 | 0,5745 |
| | | $S_4$—$C_5$ | | −1,6405 | 0,6565 |
| | | $S_4$—$C_8$ | | −1,1915 | 0,6655 |
| | | | | −0,8695 | 0,8235 |
| | | $C_2$—$N_3$ | 1,0 | −0,7765 | 0,9185 |
| | | $N_3$—$C_8$ | | −0,3365 | 1,0685 |
| | | | | | 1,4895 |
| | | | | | 1,6575 |
| | | | | | 1,7705 |
| | | | | | 2,6075 |
| | | | | | 2,6350 |
| XIII |  | $N_7$—$C_8$ | 0,8 | −1,9652 | 0,2548 |
| | | $N_7$—$C_6$ | | −1,8762 | 0,6564 |
| | | | | −1,6842 | 0,6817 |
| | | $S_1$—$C_8$ | 0,6 | −1,3920 | 0,7335 |
| | | $S_1$—$C_2$ | | −1,1282 | 0,9667 |
| | | | | −0,9375 | 1,2692 |
| | | $C_3$—$C_9$ | 0,9 | −0,8248 | 1,4234 |
| | | $C_8$—$C_9$ | | −0,6711 | 1,5622 |
| | | $C_4$—$C_9$ | | −0,3008 | 1,7494 |
| | | $C_5$—$C_6$ | | | 1,8476 |
| | | | | | 2,4407 |
| | | | | | 2,4736 |
| III |  | $N_7$—$C_8$ | 0,7 | −1,9740 | 0,3031 |
| | | | | −1,8673 | 0,7625 |
| | | $N_7$—$C_6$ | 0,8 | −1,6701 | 0,8927 |
| | | | | −1,3964 | 1,0446 |
| | | $C_3$—$C_9$ | 0,9 | −1,0876 | 1,1551 |
| | | $C_8$—$C_9$ | | −0,7988 | 1,2629 |
| | | $C_4$—$C_9$ | | −0,6341 | 1,5678 |
| | | $C_5$—$C_6$ | | −0,5377 | 1,6096 |
| | | | | −0,2502 | 2,1758 |
| | | | | | 2,2414 |
| | | | | | 2,5952 |
| | | | | | 2,6069 |

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*$\beta_{CC} = k_{CC}\beta$; $\beta_{CX} = k_{CX}\beta$.

## EXPERIMENTAL METHOD

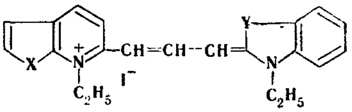
The electronic absorption spectra of ethanol solutions of the dyes were recorded with an SF-2 spectrophotometer.

Bis(7-ethylfuro[2,3-b]-6-pyridine)trimethinecyanine Iodide (III). A 0.58-g (2 mmole) sample of the ethiodide of II was heated for 5-10 min with 0.87 g (2 mmole) of 6-β-acetanilidovinylfuro[2,3-b]pyridine and 0.20 g (1 mmole) of triethylamine in 4 ml of acetic anhydride at 100-105°. The mixture was cooled and diluted with ether, and the resinous precipitate was dissolved by heating in 5 ml of ethanol. A 6-ml sample of 10% potassium iodide solution was added to the ethanol solution, the mixture was cooled, and the precipitated dye was removed by filtration and purified by recrystallization from ethanol to give dark-blue prisms (from ethanol) with mp > 200° (dec.) in 13% yield. Found: C 54.7; H 4.5; I 27.4%. $C_{21}H_{21}IN_2O_2$. Calculated: C 54.8; H 4.6; I 27.5%.

Unsymmetrical Carbocyanines (IV-IX, Table 5). A 2-mmole sample of the ethiodide of I or II was heated with 2 mmole of the ethiodide of 2-β-acetanilidovinyl-substituted benzoxazole, benzothiazole, or quinoline or the ethiodide of 4-β-acetanilidovinylquinoline and 2 mmole of triethylamine in 5-6 ml of acetic anhydride at 125-130° for 20-30 min, after which the mixture was cooled, and the precipitated dyes were removed by filtration. The products were purified by chromatography on aluminum oxide in chloroform and by recrystallization from ethanol. The dyes crystallized in the form of violet (IV-VII) or green (VIII, IX) prisms.

2-Thioxo-3-ethyl-5-(7-ethylfuro[2,3-b]dihydro-6-pyridylideneethylidene)-4-thiazolidone (X). A mixture of 0.58 g (2 mmole) of the ethiodide of II, 0.60 g (2 mmole) of 2-thioxo-5-

TABLE 5



| Compound | X | Y | mp, °C | Empirical formula | Found, % |  |  | Calc., % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | C | H | I | C | H | I |  |
| IV | S | O | 226—227 | $C_{21}H_{21}IN_2OS$ | 56,7 | 4,6 | 28,5 | 56,7 | 4,7 | 28,6 | 29 |
| V | O | O | 232—233 | $C_{21}H_{21}IN_2O_2$ | 54,7 | 4,5 | 27,5 | 54,8 | 4,6 | 27,5 | 24 |
| VI | O | S | 240—242 | $C_{21}H_{21}IN_2OS$ | 56,6 | 4,6 | 28,5 | 56,7 | 4,7 | 28,6 | 36 |
| VII | O | CH=CH | 256—257 | $C_{23}H_{23}IN_2O$ | 58,4 | 4,8 | 26,9 | 58,5 | 4,9 | 27,0 | 34 |
| VIII* | S | — | 192—194 | $C_{23}H_{23}IN_2S$ | 56,7 | 4,7 | N 5,7 | 56,8 | 4,7 | N 5,8 | 33 |
| IX* | O | — | 222—223 | $C_{23}H_{23}IN_2O$ | 58,4 | 4,8 | 26,9 | 58,5 | 4,9 | 27,0 | 31 |

*Unsymmetrical carbocyanines with a 4-quinoline residue.

acetanilidomethylene-4-thiazolidone, and 0.25 g (2.5 mmole) of triethylamine in 10 ml of anhydrous ethanol was heated at 95° for 1 h. Workup gave violet prisms (from ethanol) with mp 134-136° in 32% yield. Found: C 57.6; H 4.7%. $C_{16}H_{16}N_2O_2S_2$. Calculated: C 57.6; H 4.8%.

6-(p-Dimethylaminostyryl)furo[2,3-b]pyridine Ethiodide (XII). A mixture of 0.58 g (2 mmole) of the ethiodide of II, 0.34 g (2 mmole) of p-dimethylaminobenzaldehyde, and 0.09 g (1 mmole) of piperidine in 5 ml of pyridine was heated at 95° for 1 h. The dye was isolated and purified as in the case of the carbocyanines to give brown prisms (from ethanol) with mp 234-236° in 21% yield. Found: C 54.2; H 4.9; I 30.1%. $C_{19}H_{21}IN_2O$. Calculated: C 54.3; H 5.0; I 30.2%.

6-(p-Dimethylaminostyryl)thieno[2,3-b]pyridine Ethiodide (XI). This compound was similarly obtained as dark-violet prisms (from ethanol) with mp 256-257° in 23% yield. Found: C 52.1; H 4.8; N 6.3%. $C_{19}H_{21}IN_2S$. Calculated: C 52.3; H 4.8; N 6.4%.

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