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Synthesis of new merocyanine dyes of thiophene series

Valerii Z. Shirinian, Igor V. Zavarzin, Evgeniya S. Leonova and Ashot I. Markosyan

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer. The mass spectra were measured on a Kratos instrument (70 eV) with direct sample inlet into the ion source, and the high-resolution mass spectra were measured on a Bruker maXis instrument. Melting points were determined using a Boethius apparatus and were not corrected. The IR spectra were recorded on a Specord M80 or M82 instrument in KBr pellets, and the elemental analysis was performed using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. The electronic absorption spectra were measured on a LOMO SF-56 spectrophotometer; the experiments were performed in acetonitrile (Acros) solutions with concentrations $C = 2 \cdot 10^{-5}$ mol·L^{-1} at 293 K in the presence of air.

Commercially available reagents and solvents (Acros, Merck) were used in this work. The completion of reactions was monitored on TLC plates (Merck UV-254); silica gel from Merck (0.060–0.200) was used for column chromatography. Commercially available diphenyl propargyl alcohol, sodium acetylide and *p*-toluenesulfonic acid were used. Benzothienophen-3-one **1a**,[1] thieno[2,3-*b*]pyridin-3(2*H*)-one **1b**[2] and propargylic alcohols **2a-e**[3] were prepared as described.

(2*Z*)-2-[3-(2,4-Dimethoxyphenyl)-3-(4-fluorophenyl)prop-2-en-1-ylidene]-1-benzothiophen-3(2*H*)-one (3b)

Mp 156-158 °C (MeOH). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 3.62 (s, 3H, CH_3), 3.89 (s, 3H, CH_3), 6.59 (m, 2H, H^{arom}), 6.89 (d, 1H, *J* =11.8,), 7.03 (m, 3H, H^{arom}), 7.26 (m, 1H, H^{arom}), 7.36 (m, 2H, H^{arom}), 7.48 (d, 1H, *J*=11.8,), 7.49 (m, 1H, H^{arom}), 7.55 (m, 1H, H^{arom}), 7.86 (d, 1H, *J* = 7.88, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 55.6 (OMe), 55.7 (OMe), 99.6, 104.9, 115.2, 115.6, 119.4, 124, 125.3, 126.8, 129, 129.2, 131.6, 132.1, 132.9, 133.4, 134.9, 137.3, 145.1, 150.2, 158.6, 161.3, 161.9, 165.3, 187.9 (C=O). Mass spectrum, *m/z* (%): 418 $[M]^{+}$. IR (KBr), cm^{-1}: 832, 876 (C-$H^{arom.}$); 1304 (C-F); 1668 (C=O); 2836 (=C-H), 2951 (O-Me). Absorption

(CH_3CN), λ_{max}/nm (ε): 465 ($1.9x10^4$). Found (%): C, 71.59; H, 4.59. Calc. for $C_{25}H_{19}FO_3S$ (%): C, 71.75; H, 4.58.

(2*Z*)-2-[3-(2,4-Dimethoxyphenyl)-3-(2-fluorophenyl)prop-2-en-1-ylidene]-1-benzothiophen-3(2*H*)-one (3c)

Mp 149-151 °C (hexane). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 3.76 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 6.47 (m, 2H, H^{arom}), 7.03 (d, J=7.87, 1H, H^{arom}), 7.12 (m, 1H, H^{arom}), 7.18 (m, 1H, H^{arom}), 7.22 (m, 2H, H^{arom}), 7.26 (m, 1H, H^{arom}), 7.37 (m, 1H, H^{arom}), 7.44 (m, 1H, H^{arom}), 7.48 (m, 1H, H^{arom}), 7.54 (m, 1H, H^{arom}), 7.85 (d, 1H, *J* = 7.22, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 56 (2C, OMe), 100.3, 106.3, 116.3, 122.3, 124.8, 125.2, 126.2, 126.7, 127.9, 130.1, 130.5, 131.6, 132.2, 133.0, 133.2, 133.8, 135.9, 145.4, 145.7, 160.1, 160.3, 187.9 (C=O). Mass spectrum, *m/z* (%): 418 $[M]^+$. IR (KBr), cm^{-1}: 830 (C-$H^{arom.}$); 1308 (C-F); 1664 (C=O); 2852 (=C-H), 2924 (O-Me). Absorption (CH_3CN), λ_{max}/nm (ε): 466 ($1.93x10^4$). Found (%): C, 71.66; H, 4.61. Calc. for $C_{25}H_{19}FO_3S$. C, 71.75; H, 4.58.

2-[3-(4-Fluorophenyl)-3-(5-methyl-2-thienyl)prop-2-en-1-ylidene]-1-benzothiophen-3(2*H*)-one (3d).

Mp 110-112 °C (hexane). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.54 (s, 3H, CH_3), 6.85 (m, 1H, H^{arom}), 6.93 (m, 1H, H^{arom}), 7.14 (d, 1H, *J* = 12.11), 7.36 (m, 1H, H^{arom}), 7.38 (m, 1H, H^{arom}), 7.41 (m, 2H, H^{arom}), 7.43 (m, 1H, H^{arom}), 7.45 (m, 1H, H^{arom}), 7.7 (m, 1H, H^{arom}), 7.77 (m, 2H, H^{arom}). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 14.3 (Me), 114.82, 116.42, 124.0, 125.2, 126.18, 131.12, 132.22, 133.10, 133.32, 133.5, 133.61, 133.78, 135.11, 141.51, 145.08, 152.54, 154.00, 159.2, 159.52, 166.01, 188.12 (C=O). Mass spectrum, *m/z* (%): 378 $[M]^+$. IR (KBr), cm^{-1}: 808, 868 (C-$H^{arom.}$); 1288 (C-F); 1656 (C=O). Absorption (CH_3CN), λ_{max}/nm (ε): 476 ($1.96x10^4$). Found (%): C, 69.58; H, 4.05. Calc. for $C_{22}H_{15}FOS_2$. C, 69.81; H, 3.99.

2-[3-(2,4-Dimethoxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-ylidene]-1-benzothiophen-3(2*H*)-one (3e).

Mp 135-137 °C (hexane). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 3.66 (s, 3H, CH_3), 3.83 (s, 6H, CH_3), 3.89 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 6.48 (m, 1H, H^{arom}), 6.61 (s, 2H, H^{arom}), 6.9 (d, 1H, *J* = 11.74), 7.07 (d, 1H, *J* = 8.43, H^{arom}), 7.25 (m, 1H, H^{arom}), 7.3 (m, 1H, H^{arom}), 7.46 (m, 1H, H^{arom}), 7.5 (s, 1H, H^{arom}), 7.56 (m, 1H, H^{arom}), 7.88 (m, 1H, H^{arom}). Mass spectrum, *m/z* (%): 490 $[M]^+$. IR (KBr), cm^{-1}: 1668 (C=O); 2932 (=C-H); 2996 (O-Me). Absorption (CH_3CN), λ_{max}/nm (ε): 473 ($2.34x10^4$). Found (%): C, 68.67; H, 5.27. Calc. for $C_{28}H_{26}O_6S$. C, 68.55; H, 5.34.

2-[3-(2,4-Dimethoxyphenyl)-3-(4-fluorophenyl)prop-2-en-1-ylidene]thieno[2,3-*b*]pyridin-3-(2*H*)-one (4b).

Mp 177-179 °C (EtOH). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 3,63 (s, 3H, CH_3), 3.9 (s, 3H, CH_3), 6.59 (d, 2H, H^{arom}), 6.9 (d, 1H, *J* =11.74), 7.04 (m, 2H, H^{arom}), 7.23 (m, 2H, H^{arom}), 7.38 (m, 2H, H^{arom}), 7.57 (d, 1H, *J* =12.1), 8.07 (m, 1H, H^{arom}), 8.68 (m, 1H, H^{arom}). Mass spectrum, *m/z* (%): 419 $[M]^+$. IR (KBr), cm^{-1}: 760 (C-$H^{Py.}$); 832, 880 (C-$H^{arom.}$); 1304 (C-F); 1668 cm^{-1} (C=O); 2928 cm^{-1} (=CH). Absorption (CH_3CN), λ_{max}/nm (ε): 465 ($2.08x10^4$). Found (%): C, 68.81; H, 4.35; N, 3.38. Calc. for $C_{22}H_{15}FNO_3S$. C, 68.72; H, 4.33; N, 3.34.

2-[3-(2,4-Dimethoxyphenyl)-3-(2-fluorophenyl)prop-2-en-1-ylidene]thieno[2,3-*b*]pyridin-3-(2*H*)-one (4c).

Mp 134-136 ^{o}C (diethyl ether : heptane, 1:5). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 3.62 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 6.56 (m, 2H, H^{arom}), 6.98 (d, 1H, *J* =12.1), 7.1 (m, 3H, H^{arom}), 7.22 (m, 2H, H^{arom}), 7.29 (m, 1H, H^{arom}), 7.62 (d, 1H, J=12.1), 8.06 (m, 1H, H^{arom}), 8.66 (m, 1H, H^{arom}). Mass spectrum, *m/z* (%): 419 $[M]^+$. IR (KBr), cm^{-1}: 756 ($CH^{Py.}$); 825 (C-$H^{arom.}$); 1288 (C-F); 1680 (C=O); 2852, 2924, 2956 (=CH). Absorption (CH_3CN), λ_{max}/nm (ε): 465 ($1.78x10^4$). Found (%): C, 69.01; H, 4.37. Calc. for $C_{22}H_{15}FNO_3S$. C, 68.72; H, 4.33.

2-[3-(4-Fluorophenyl)-3-(5-methyl-2-thienyl)prop-2-en-1-ylidene]thieno[2,3-*b*]pyridin-3-(2*H*)-one (4d).

Mp 175-177 °C (diethyl ether : heptane, 1:5). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.53 (s, 3H, CH_3), 6.73 (m, 2H, H^{arom}), 6.83 (d, 1H, *J* =12.1), 7.17 (m, 2H, H^{arom}), 7.25 (m, 1H, H^{arom}), 7.34 (m, 2H, H^{arom}), 7.48 (d, 1H, *J* =12.1), 8.07 (m, 1H, H^{arom}), 8.68 (m, 1H, H^{arom}). Mass spectrum, *m/z* (%): 379 $[M]^+$. IR (KBr), cm^{-1}: 760 (C-$H^{Py.}$); 796, 872 ($CH^{arom.}$); 1288 (CF); 1660 (C=O). Absorption (CH_3CN), λ_{max}/nm (ε): 479 ($2.11x10^4$). Found (%): C, 66.50; H, 3.68; N, 3.57. Calc. for $C_{21}H_{14}FNOS_2$. C, 66.47; H, 3.72; N, 3.69.

2-[3-(2,4-Dimethoxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-en-1-ylidene]-thieno[2,3-*b*]pyridin-3-(2*H*)-one (4e).

Mp 135-137 °C (diethyl ether : heptane, 1:5). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 3.66 (s, 3H, CH_3), 3.83 (s, 6H, CH_3), 3.89 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 6.48 (s, 1H, H^{arom}), 6.58 (m, 1H, H^{arom}), 6.62 (s, 2H, H^{arom}), 6.9 (d, 1H, *J* = 11.74), 7.07 (m, 1H, H^{arom}), 7.23 (m, 1H, H^{arom}), 7.55 (d, 1H, *J* = 12.11), 8.08 (m, 1H, H^{arom}), 8.68 (m, 1H, H^{arom}). Mass spectrum, *m/z* (%): 491 $[M]^+$. IR (KBr), cm^{-1}: 764 (C-$H^{Py.}$); 840 (C-$H^{arom.}$); 1668 (C=O); 2924 (=CH).

Absorption (CH_3CN), λ_{max}/nm (ε): 477 ($2.51x10^4$)Found (%): C, 65.86; H, 5.19; N, 2.72. Calc. for $C_{27}H_{25}NO_6S$. C, 65.97; H, 5.13; N, 2.85.

Solid-state preparation of merocyanines 3a and 4a.

The mixture of benzothienone **1a** or thieno[2,3-*b*]pyridin-3-one **1b** (3 mmol), diphenylpropargyl alcohol **2a** (3 mmol), catalyst (0.3 mmol for **1a** and 3.1 mmol for **1b**) and 1g of silica gel was well ground for 20 min at room temperature using a mortar and pestle and was kept for several days. After completion of the reaction, the product was purified by chromatography on silica gel using the light petroleum / ethyl acetate (8:1) solvent system as an eluent.

(2*Z*)-2-(3,3-Diphenylprop-2-en-1-ylidene)-1-benzothiophen-3(2*H*)-one (3a)

The reaction mixture was kept for 10 days. Yield 0.5 g (49%). Mp 141–143 °C (methanol).

(2*Z*)-*2-(3.3-Diphenylprop-2-en-1-yliden)thieno[2,3-b]pyridin-3-(2H)-one* (4a)

The reaction mixture was kept for 6 days. Yield 0.58 g (57%), Mp 194–195 °C (ethanol).

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