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Supporting Information

for

Synthesis, structure, ionochromic and cytotoxic properties of new 2-(indolin-2-yl)-1,3-tropolones

Yurii A. Sayapin, Eugeny A. Gusakov, Inna O. Tupaeva, Alexander D. Dubonosov, Igor V. Dorogan, Valery V. Tkachev, Anna S. Goncharova, Gennady V. Shilov, Natalia S. Kuznetsova, Svetlana Y. Filippova, Tatyana A. Krasnikova, Yanis A. Boumber, Alexey Y. Maksimov, Sergey M. Aldoshin and Vladimir I. Minkin

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Experimental procedures and characterization data for all novel compounds 7a, 7b, 8a and 8b

Synthesis

2-(1,1-Dimethyl-1*H*-benzo[*e*]indolin-2-yl)-5,6,7- trichloro-1,3-tropolone (**7a**).

A solution of 1,1,2-trimethyl-1*H*-benzo[*e*]indoline (**2a**, 1.05 g, 5 mmol) and *o*-chloranil (**3**, 1.23 g, 5 mmol) in dioxane (10 mL) was refluxed for 1.5 h. The solvent was removed *in vacuo* and the residue was dissolved in methylene chloride. The solution was purified by silica gel column chromatography with hexane/CH_2Cl_2 1:2. The yellow-orange fraction of **7a** with R_f 0.4 was collected and recrystallized from *n*-hexane. Orange crystals. Yield 30%, mp 164-165 ºC (*n*-hexane). ^{1}H NMR (DMSO-d_6) δ (ppm), *J*/Hz: 1.85 (s, 6H, 2Me), 7.10 (s, 1H, H*4*), 7.51 (t, 1H, H_{Ar}, *J* = 7.8), 7.63 (t, 1H, H_{Ar}, *J* = 7.8), 7.94 (d, 1H, H_{Ar}, *J* = 8.4), 7.97 (d, 1H, H_{Ar}, *J* = 8.4) 8.02 (d, 1H, H_{Ar}, *J* = 7.8), 8.17 (d, 1H, H_{Ar}, *J* = 8.4), 14.23 (s, 1H, OH). ^{13}C NMR (DMSO-d_6) δ (ppm): 22.9, 53.6, 111.7, 114.2, 122.4, 125.0, 127.0, 127.4, 128.0, 129.8, 129.8, 130.6, 132.0, 134.0, 134.4, 134.8, 136.6, 178.3, 182.5, 182.7. ^{1}H NMR ($CDCl_3$) δ (ppm), *J*/Hz: 1.98 (s, 6H, 2Me), 6.92 (s, 1H, H*4*), 7.45 (d, 1H, H_{Ar}, *J* = 9), 7.51 (t, 1H, H_{Ar}, *J* = 7.8), 7.64 (t, 1H, H_{Ar}, *J* = 8.4), 7.89 (d, 1H, H_{Ar}, *J* = 8.4), 7.96 (d, 1H, H_{Ar}, *J* = 8.4), 8.09 (d, 1H, H_{Ar}, *J* = 8.4), 15.15 (br. s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.1, 23.4, 31.6, 54.6, 112.7, 122.5, 125.3, 127.6, 127.9, 130.1, 130.3, 132.6, 133.5, 135.0, 135.9, 180.7. IR (v, cm^{-1}): 3040, 2975, 2934, 2867, 1736, 1638, 1536, 1520, 1494, 1466, 1442, 1399, 1372, 1364, 1323, 1261, 1215, 1207, 1174, 1082, 1057, 945, 907, 874, 856, 815, 788, 763, 748, 689. ESI-MS, *m/z* (rel. int.): 419 (44) [M^+], 417 (44), 389 (66), 378 (27), 374 (82), 353 (17), 339 (60), 304 (18), 275 (24), 241 (35), 194 (72), 191 (26), 165 (60), 152 (100), 147 (26), 139 (30), 127 (35), 121 (35), 115 (21), 106 (16), 87 (12), 84 (21), 77 (15), 63 (23). Anal. Calcd (%) for $C_{21}H_{14}Cl_3NO_2$: C, 60.24; H, 3.37; N, 3.35. Found (%): C, 60.12; H, 3.20; N, 3.22.

(2-(3,3-Dimethyl-3*H*-benzo[*g*]indolin-2-yl)-5,6,7- trichloro-1,3-tropolone (**7b**).

A solution of 2,3,3-trimethyl-3*H*-benzo[*g*]indoline (**2b**, 1.05 g, 5 mmol) and *o*-chloranil (**3**, 1.23 g, 5 mmol) in dioxane (10 mL) was refluxed for 1.5 h. The solvent was removed *in vacuo* and the residue was dissolved in methylene chloride. The solution was purified by silica gel column chromatography with hexane/CH_2Cl_2 1:1. The orange fraction of **7b** with R_f 0.4 was collected and recrystallized from *n*-hexane. Orange crystals. Yield 28%, mp 209-210 ºC (*n*-hexane). ^{1}H NMR ($CDCl_3$) δ (ppm), *J*/Hz: 1.75 (s, 6H, 2Me), 6.93 (s, 1H, H^4), 7.44 (d, 1H, H_{Ar}, *J* = 8.4), 7.54 (t, 1H, H_{Ar}, *J* = 7.8), 7.63 (t, 1H, H_{Ar}, *J* = 8.4), 7.78 (d, 1H, H_{Ar}, *J* = 8.4), 7.91 (d, 1H, H_{Ar}, *J* = 8.4), 7.98 (d, 1H, H_{Ar}, *J* = 7.8), 15.76 (br. s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ (ppm): 25.4, 53.6, 112.4, 115.1, 122.3, 124.4, 126.8, 127.2, 128.0, 128.2, 129.0, 129.9, 130.1, 130.3, 130.8, 132.0, 133.4, 134.2, 135.4, 136.9, 140.0, 177.1, 191.0, 196.4. IR (v, cm^{-1}): 3277, 3058, 3001, 2980, 2938, 2870, 1649, 1558, 1503, 1469, 1377, 1369, 1318, 1294, 1256, 1205, 1095, 1055, 944, 895, 866, 820, 790, 763, 747, 699, 686. ESI-MS, *m/z* (rel. int.): 419 (7) [M^+], 417 (7), 391 (13), 389 (13), 376 (20), 374 (20), 341 (12), 339 (18), 304 (10), 275 (13), 240 (25), 238 (10), 220 (16), 204 (14), 194 (51), 191 (39), 178 (19), 165 (92), 156 (22), 152 (100), 149 (52), 147 (77), 139 (48), 131 (15), 127 (43), 121 (53), 119 (74), 115 (41), 107 (15), 102 (16), 86 (32), 84 (75), 77 (45), 65 (24), 63 (77), 51 (26). Anal. Calcd (%) for $C_{21}H_{14}Cl_3NO_2$: C, 60.24; H, 3.37; N, 3.35. Found (%): C, 60.10; H, 3.24; N, 3.20.

2-(1,1-Dimethyl-1*H*-benzo[*e*]indolin-2-yl)-4,5,6,7-tetrachloro-1,3-tropolone (**8a**).

A solution of 1,1,2-trimethyl-1*H*-benzo[*e*]indoline (**2a**, 1.05 g, 5 mmol) and *o*-chloranil (**3**, 2.46 g, 10 mmol) in AcOH (10 mL) was kept at 50–60 °C for 20 h. The solution was diluted with water and extracted with chloroform (2 × 50 mL). The chloroform solution was washed in a separating funnel with water (3 × 50 mL) and then dried for 2 h with anhydrous Na_2SO_4. The solvent was removed *in vacuo*, the residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 1:1. The yellow fraction of **8a** with R_f 0.9 was collected and recrystallized from *n*-hexane. Bright yellow crystals. Yield 26%, mp 226-227 ºC (*n*-hexane). ^{1}H NMR ($CDCl_3$) *δ* (ppm), *J*/Hz: 1.99 (s, 6H, 2Me), 7.42 (d, 1H, H_{Ar}, *J* = 8.4), 7.53 (t, 1H, H_{Ar}, *J* = 7.8), 7.65 (t, 1H, H_{Ar}, *J* = 8.4), 7.91 (d, 1H, H_{Ar}, *J* = 8.4), 7.97 (d, 1H, H_{Ar}, *J* = 8.4), 8.08 (d, 1H, H_{Ar}, *J* = 8.6), 14.29 (br. s, 1H, OH). ^{13}C NMR ($CDCl_3$) *δ* (ppm): 14.1, 22.6, 23.1, 54.5, 112.1, 112.5, 122.4, 125.4, 127.7, 127.9, 130.2, 130.5, 132.7, 134.7, 135.6, 179.0. IR (v, cm^{-1}): 3128, 3058, 2973, 2929, 2869, 1666, 1626, 1599, 1561, 1524, 1495, 1471, 1443, 1380, 1366, 1345, 1246, 1213, 1129, 1105, 1067, 962, 940, 924, 867, 813, 803, 773, 752, 740, 696. ESI-MS, *m/z* (rel. int.): 453 (80) [M+], 424 (27), 416 (17), 402 (100), 389 (22), 380 (17), 374 (21), 338 (22), 309 (15), 275 (30), 238 (23), 220 (17), 194 (69), 190 (29), 165 (55), 155 (27), 152 (63), 139 (22), 126 (25), 120 (23), 118 (17), 115 (17), 111 (12), 106 (12), 87 (10), 63 (12). Anal. Calcd (%) for $C_{21}H_{13}Cl_4NO_2$: C, 55.66; H, 2.89; N, 3.09. Found (%): C, 55.44; H, 2.66; N, 2.90.

(2-(3,3-Dimethyl-3*H*-benzo[*g*]indolin-2-yl)-4,5,6,7-tetrachloro-1,3-tropolone (**8b**).

A solution of 2,3,3-trimethyl-3*H*-benzo[*g*]indoline (**2b**, 1.05 g, 5 mmol) and *o*-chloranil (**3**, 2.46 g, 10 mmol) in AcOH (10 mL) was kept at 60 °C for 72 h. The solution was diluted with water and extracted with chloroform (2 × 50 mL). The chloroform solution was washed in a separating funnel with water (3 × 50 mL) and then dried for 2 h with anhydrous Na_2SO_4. The solvent was removed *in vacuo*, the residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 1:1. The yellow-orange fraction of **8b** with R_f 0.8 was collected and recrystallized from *n*-hexane. Bright yellow crystals. Yield 24%, mp 152-153 ºC (*n*-hexane). IR (v, cm^{-1}): 3312, 3007, 2979, 2933, 2872, 1665, 1578, 1561, 1544, 1495, 1466, 1445, 1396, 1370, 1322, 1279, 1249, 1219, 1207, 1071, 1037, 980, 898, 869, 823, 798 ,777, 756, 688, 675. ^{1}H NMR ($CDCl_3$) δ (ppm), *J*/Hz: 1.75 (s, 6H, 2Me), 7.44 (d, 1H, H_{Ar}, *J* = 7.8), 7.55 (t, 1H, H_{Ar}, *J* = 7.8), 7.63 (t, 1H, H_{Ar}, *J* = 8.4), 7.79 (d, 1H, H_{Ar}, *J* = 8.4), 7.92 (d, 1H, H_{Ar}, *J* = 8.4), 7.98 (d, 1H, H_{Ar}, *J* = 8.4), 14.84 (br. s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ (ppm): 23.8, 53.7, 112.9, 119.2, 120.6, 120.7, 126.7, 126.9, 127.5, 128.8, 133.5, 133.7, 138.4, 177.9. ESI-MS, *m/z* (rel. int.): 453 (76) [M^+], 424 (17), 416 (14), 402 (100), 400 (98), 389 (15), 380 (16), 373 (19), 338 (27), 309 (15), 275 (36), 238 (27), 220 (27), 207 (18), 194 (85), 190 (48), 180 (21), 165 (89), 155 (42), 152 (86), 139 (38), 137 (25), 126 (41), 120 (42), 118 (29), 115 (29), 111 (22), 106 (16), 87 (17), 77 (17), 63 (24), 57 (17). Anal. Calcd (%) for $C_{21}H_{13}Cl_4NO_2$: C, 55.66; H, 2.89; N, 3.09. Found (%): C, 55.48; H, 2.70; N, 2.88.