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SYNTHESIS OF NOVEL [1,2,4]TRIAZINO[5,6-*f*]-1,10-PHENANTHROLINES BASED ON THE AZOLYL-1-CARBOXAMIDRAZONES

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The possibility to obtain certain [1,2,4]triazino[5,6-*f*]-1,10-phenanthrolines and novel complex compounds based on them as promising photoactivated cytotoxins has been demonstrated in the studies [1-3]. It should be noted that the starting ligands were obtained by prolonged refluxing in alcohol of 1,10-phenanthroline-5,6-dione with amidrazones, in which the amidrazone fragment was linked with a carbon atom belonging to a heteroaromatic system.

In continuation of our work on the reactivity of *N*-heterocyclic amidrazones, we propose a convenient method for the preparation of azolyl-substituted [1,2,4]triazino[5,6-*f*]-1,10-phenanthrolines **3** and **6** from the different amidrazones **2** and **5**, in which the carboxamido hydrazone fragment is bonded to a nitrogen of the heterocycle. The starting amidrazones **2** and **5** were synthesized by treating hydrazine hydrate with the readily available *N*-cyanoheterocycles **1** and **4** (the preparation of which we have reported before [4]). The target compounds **3** and **6** were prepared in 68 and 74% yield respectively by brief (20 min) refluxing of compounds **2** or **5** with 1,10-phenanthroline-5,6-dione in isopropanol, which points to an increased reactivity of the carboxamido hydrazone fragment bonded to a heterocyclic nitrogen in heterocyclization reactions with 1,2-diketones.

Hence we propose a convenient method for preparing the previously unknown azolyl-substituted [1,2,4]triazino[5,6-*f*]-1,10-phenanthrolines as promising ligands, based on readily available *N*-heterocyclic amidrazones.

IR spectra were recorded on an FSM-1201 instrument for KBr pellets. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument (400 and 100 MHz, respectively) using DMSO-d_6 with TMS as internal standard. Elemental analysis was carried out on a vario EI cube analyzer. Melting points were measured on a Boetius hot stage apparatus and are not corrected.

The benzimidazol-1-ylcarboxamidohydrazone (**5**) was prepared by method [5].

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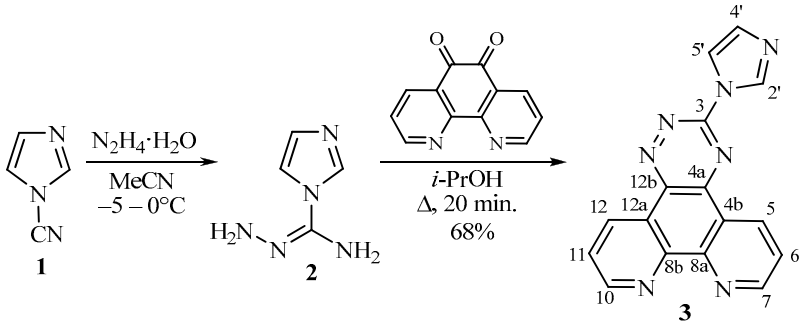
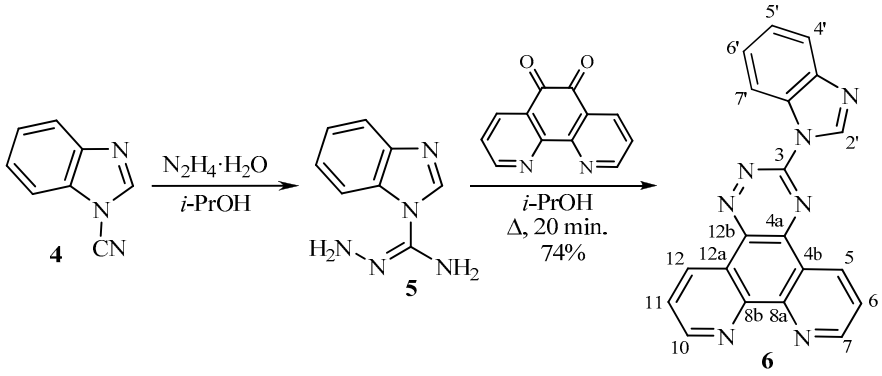
Imidazol-1-ylcarboxamidohydrazone (2). Hydrazine hydrate (0.70 ml, 21.6 mmol) was added to a stirred solution of compound **1** (2.00 g, 21.5 mmol) in MeCN (4 ml), and the temperature of the mixture was maintained in the range from -5 to 0°C. Stirring was continued for 10 min and the precipitate formed was filtered off, washed with cold EtOH, and recrystallized from MeCN. Yield 1.91 g (71%). White powder, turning pink in air. Mp 102-104°C (decomp.). IR spectrum, ν, cm^{-1}: 3321, 3101, 1693, 1643, 1493, 1327, 914, 768. ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.12 (1H, s, H-2); 7.58-7.53 (1H, m, H-4); 7.05-6.98 (1H, m, H-5); 6.57 (2H, br. s, =C–NH_2); 4.98 (2H, br. s, =N–NH_2). Found, %: C 38.25; H 5.67; N 56.09. $C_4H_7N_5$. Calculated, %: C 38.39; H 5.64; N 55.97.





3-(1*H*-Imidazol-1-yl)[1,2,4]triazino[5,6-*f*]-1,10-phenanthroline (3). 1,10-Phenanthroline-5,6-dione (1.68 g, 8 mmol) was added to a warmed solution of compound **2** (1.00 g, 8 mmol) in 2-PrOH (30 ml) with vigorous stirring. The solution was refluxed for 20 min, cooled, and the precipitate was filtered off, recrystallized from EtOH, and dried in a drying oven for 24 h at 60°C. Yield 1.63 g (68%). Yellowish-green crystalline powder. Mp > 300°C. IR spectrum, ν, cm^{-1}: 3123, 3074, 1579, 1518, 1384, 1253, 1072, 758. ^1H NMR spectrum, δ, ppm (*J*, Hz): 9.69 (1H, dd, *J* = 4.3, *J* = 1.8, H-10); 9.51 (1H, dd, *J* = 4.3, *J* = 1.8, H-7); 9.29 (1H, ddd, *J* = 8.0, *J* = 1.8, *J* = 0.7, H-5); 8.92 (1H, ddd, *J* = 7.9, *J* = 1.8, *J* = 0.7, H-12); 8.34 (1H, s, H-2'); 8.02-7.98 (1H, m, H-5'); 7.95 (1H, dd, *J* = 7.9, *J* = 4.3, H-11); 7.84 (1H, dd, *J* = 8.0, *J* = 4.3, H-6); 7.72-7.65 (1H, m, H-4'). ^{13}C NMR spectrum, δ, ppm: 122.9 (C-6); 123.8 (C-11); 127.1 (C-4b); 127.8 (C-5'); 128.8 (C-12a); 131.0 (C-5); 131.5 (C-12); 131.9 (C-4'); 140.3 (C-12b); 144.0 (C-8a); 145.8 (C-8b); 146.0 (C-4a); 148.1 (CH-2'); 151.2 (C-7); 151.9 (C-10); 158.6 (C-3). Found, %: C 64.09; H 3.10; N 32.83. $C_{16}H_9N_7$. Calculated, %: C 64.21; H 3.03; N 32.76.

3-(1*H*-Benzimidazol-1-yl)[1,2,4]triazino[5,6-*f*]-1,10-phenanthroline (6) was prepared similarly from the compound **5** (1.4 g, 8 mmol). The product was recrystallized from DMF and dried in a drying oven for 24 h at 60°C. Yield 2.07 g (74%). Yellowish-green crystalline powder. Mp > 300°C. IR spectrum, ν, cm^{-1}: 3135, 3066, 1571, 1507, 1487, 1451, 1383, 1074, 745. ^1H NMR spectrum, δ, ppm (*J*, Hz): 9.71 (1H, dd, *J* = 4.4, *J* = 1.9, H-10); 9.58 (1H, dd, *J* = 4.4, *J* = 1.9, H-7); 9.3 (1H, ddd, *J* = 8.0, *J* = 1.9, *J* = 0.7, H-5); 8.84 (1H, ddd, *J* = 8.0,

J = 1.9, *J* = 0.7, H-12); 8.56 (1H, s, H-2'); 7.97 (1H, dd, *J* = 8.0, *J* = 4.4, H-11); 7.88 (1H, dd, *J* = 8.0, *J* = 4.4, H-6); 7.79-7.77 (1H, m, H-4'); 7.73-7.68 (1H, m, H-7'); 7.40-7.37 (1H, m, H-6'); 7.32-7.30 (1H, m, H-5'). ^{13}C NMR spectrum, δ, ppm: 111.6 (C-7'); 120.5 (C-4'); 123.0 (C-6); 123.5 (C-5'); 123.7 (C-11); 125.1 (C-6'); 126.7 (C-4b); 127.9 (C-12a); 131.1 (C-5); 131.5 (C-12); 139.2 (C-7a'); 140.0 (C-12b); 142.1 (C-3a'); 144.9 (C-8a); 145.2 (C-8b); 146.3 (C-4a); 150.7 (C-7); 150.9 (C-10); 152.6 (CH-2'); 159.2 (C-3). Found, %: C 68.59; H 3.21; N 28.20. $C_{20}H_{11}N_7$. Calculated %: C 68.76; H 3.17; N 28.06.

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