Novel synthesis of new symmetrical bis-heterocyclic compounds: synthesis of bis-thiazolo, bis-pyrazolo-, bis-benzotriazolo, bis-indolo- and bis-pyrazolyl thiazolo-2,6-diamino pyridine derivatives

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The reaction of 2,6-diaminopyridine with chloroacetyl chloride yielded 2,6-bis-(2-chloroacetamido-N-yl) pyridine. The later reacted with KCN, KSCN, indole and benzotriazole separately to give 2,6-bis-(cyanoacetamido-N-yl)pyridine [which on coupling with benzenediazonium chloride yielded the bis-cyanophenyl hydrazone derivative and by refluxing the later compound with chloroacetonitrile afforded 2,6-diamido-bis-(4-amino-5-cyano-1-phenylpyrazol-3-yl)pyridine], 2,6-bis-(thiocyanate acetamido-N-yl)pyridine, 2,6-bis-[2-(1H-indol-3-yl)acetamido-N-yl] pyridine and 2,6-bis-[2-(1,2,3-benzotriazol-1-yl)acetamido-N-yl]pyridine, respectively. Acetylation of 2,6-diaminopyridine with acetic anhydride afforded 2,6-bis-(acetamido-N-yl) pyridine which on coupling with benzenediazoniunm chloride yielded the bis-phenyl-hydrazone derivative. By reacting the later with chloroacetoniitrile afforded 2,6-diamino-bis-(5-cyano-1-phenylpyrazol-4-yl)pyridine. Under basic conditions the reaction of 2,6-diaminopyridine with CS₂ followed by ethyl-α-bromocyanoacetate and phenacyl bromide separately afforded 2,6-bis-(5-cyano-4-hydroxythiazol-3-yl-2-thione)pyridine and 2,6-bis-(4-phenyl thiazol-3-yl-2-thione)pyridine respectively. Condensation of the later compounds separately with malononitrile yielded the dicyanomethinothiazole derivatives. The reaction of either hydrazine hydrate or phenyl hydrazine with the thiazolyl thione derivatives or with the dicyanomethinothiazole derivatives afforded the hydrazono-thiazole and the pyrazole derivatives respectively.

Key words: 2,6-diaminopyridine; bis-(thiazolo)pyridine; bis-(pyrazolo)pyridine; bis-(hydrazonopyrazolo)pyridine.

INTRODUCTION

The incorporation of two moieties increases biological activity of both and thus it was of value to synthesize some new heterocyclic derivatives having two moieties in the same molecules. In continuation to our programme [1–10], this research has been devoted to the development of new classes of bis-heterocycle systems which incorporate the bis-thiazolo-, bis-pyrazolo-, bis-benzotriazolo-, bis-indolo-, bis-triazolo- and bis-pyrazolyl thiazolo- pyridine derivatives moiety. The importance of such compounds lies in their diverse pharmaceutical activities namely antibacterial [11, 12], antidiabetic [13], anti HIV [14], antiviral [15, 16] and analgesic activities.

RESULTS AND DISCUSSION

Mixing 2,6-diaminopyridine with chloroacetyl chloride in dioxane afforded the 2,6-bis-(2-chloroacetamido)pyridine 2 (Scheme 1). Compound 2 could be converted into 7 on treatment with potassium cyanide and into 8 on treatment with potassium thio-

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The reaction of compounds 19 and 23 respectively (Scheme 3); their formation took place via elimination of hydrogen sulphide. The reaction of 19 and 23 with either hydrazine hydrate or phenyl hydrazine afforded the pyrazole derivatives 20, 21, 24 and 25 (Scheme 3). The structures of the latter compounds were confirmed by analytical and spectral data.

EXPERIMENTAL

All melting points are uncorrected. IR spectra (KBr) were recorded on a Pye Unicam SP-100 spectrophotometer. \(^1\)H and \(^13\)C NMR spectra (DMSO-d\(_6\) as a solvent) were obtained on a Varian Gemini 200 and on a Bruker AC200 and AC600 MHz spectrometers respectively, TMS as internal standard, chemical shifts in \(\delta\) (ppm); mass spectra: AEI MS 30 mass spectrometer operating at 70 eV; elemental analysis were obtained from Microanalytical Data Unit at Cairo University, Egypt.

2,6-Bis-(2-chloroacetamido-N-yl) pyridine (2): A mixture of 1 (1.09 g, 10 mmol) and chloroacetyl-chloride (2.30 g, 20 mmol) in 20 ml of dioxane was refluxed for 45 min. The mixture was allowed to cool to room temperature then poured onto cold water. The obtained solid was collected by filtration and crystallized from methanol to give pale pink crystals (93% yield), m.p. 105°C; IR (KBr) ν (cm\(^{-1}\)): 3118 (NH) and 1700 (C=O); \(^1\)H NMR (DMSO-d\(_6\)) \(\delta\) (ppm): 4.58 (s, 4H, 2CH\(_2\)), 8.10–8.30 (m, 3H, pyr-H), 8.50 (s, 2H, 2NH); \(^13\)C NMR (DMSO-d\(_6\)) \(\delta\) (ppm): 190.5 (2CO), 154.2 (C-2 and C-6 pyridine), 149.3 (C-3 and C-5 pyridine), 138.5 (C-4 pyridine), 53.23 (CH\(_2\)); MS: m/z = 262 [M\(^+\)]; Anal. Calcd. for C\(_9\)H\(_9\)N\(_3\)Cl\(_2\)O\(_2\) (262.09): C, 41.24; H, 3.46; N, 16.03; Cl, 27.05. Found: C, 41.35; H, 3.76; N, 16.25; Cl, 27.35.

2,6-Bis-(acetamido-N-yl) pyridine (3): Reflux gently 1 g of 1 and 3 ml of acetic anhydride for 15 min. Pour in 20 ml of cold water then boil to destroy any excess of acetic anhydride. Filter the precipitate, wash with a little cold water and dry in air. Crystallization from ethanol afforded 0.18 g of a creamy crystals (95% yield), m.p. 95°C; IR (KBr) ν (cm\(^{-1}\)): 3225 (NH), 1700 (C=O); \(^1\)H NMR (DMSO-d\(_6\)) \(\delta\) (ppm): 1.5 (s, 6H, 2CH\(_3\)), 8.10–8.30 (m, 3H, pyr-H), 8.55 (s, 2H, 2NH); \(^13\)C NMR (DMSO-d\(_6\)) \(\delta\) (ppm): 184.5 (2CO), 153.5 (C-2 and C-6 pyridine), 148.4 (C-3 and C-5 pyridine), 138.7 (C-4 pyridine), 24.15 (CH\(_3\)); MS: m/z = 193 [M\(^+\)]; Anal. Calcd. for C\(_9\)H\(_{11}\)N\(_3\)O\(_2\) (193.21): C, 55.95; H, 5.74; N, 21.75. Found: C, 55.90; H, 5.76; N, 21.90.

2,6-Bis-(5-cyano-4-hydroxythiazol-3-yl-2-thione) pyridine (5): To a solution of 1 (1.09 g, 0.01 mol) in 30 ml of DMF, carbon disulphide (1.52 g, 0.02 mol) and potassium hydroxide (1.12 g, 0.02 mol) in 30 ml of DMF, carbon disulphide (1.52 g, 0.02 mol) and potassium hydroxide (1.12 g, 0.02 mol) in 10 ml of water were added. The whole reaction mixture was heated in a boiling water bath for 1 h then left to cool till 20°C. To a cold solution of the reaction mixture (3.84 g, 0.02 mol) of ethyl α-bromocynoacetate was added. The reaction mixture was stirred at room temperature for one night. The solid product, formed upon acidification with hydrochloric acid, was collected by filtration and crystallized from dioxane to give orange crystals (87% yield), m.p. 150°C; IR (KBr) ν (cm\(^{-1}\)): 3480–3340 (OH), 2225 (2 CN), 1210–1195 (2 C=S); \(^1\)H NMR (DMSO-d\(_6\)) \(\delta\) (ppm): 7.90–8.25 (m, 3H, pyr-H), 10.33 (s, 2H, 2NH); \(^13\)C NMR (DMSO-d\(_6\)) \(\delta\) (ppm): 153.2 (C-2 and C-6 pyridine), 150.2 (C-4 and C-4′ thiazole), 148.1 (C-3 and C-5 pyridine), 140.8 (C-5 and C-5′ thiazole), 138.1 (C-4 pyridine), 119.7 (2CN); MS: m/z = 391 [M\(^+\)]; Anal. Calcd. for C\(_{12}\)H\(_9\)N\(_5\)S\(_4\)O\(_2\)
(391.47): C, 39.89; H, 1.29; N, 17.89; S, 32.76. Found: C, 39.95; H, 1.31; N, 18.01; S, 32.80.

2,6-Bis-(4-phenylthiazol-3-yl-2-thione)pyridine (6): To a solution of 1 (1.09 g, 0.01 mol) in 30 ml of DMF, (1.52 g, 0.02 mol) of carbon disulphide and (1.12 g, 0.02 mol) of potassium hydroxide in 10 ml of water were added. The whole reaction mixture was heated in boiling water bath for 1 h then left to cool down to 20°C; (3.96 g, 0.02 mol) of phenacyl-bromide was added to this cold solution. The reaction mixture was stirred at room temperature for one night. The solid product formed upon acidification with hydrochloric acid was collected by filtration. Crystallization from dioxane gave red crystals (80% yield), m.p. 99°C; IR (KBr) v (cm⁻¹): 3060 (CH aromatic), 1200–1190 (C=S); ¹H NMR (DMSO-d₆) δ (ppm): 6.95 (s, 2H, thiazole H-5), 7.32–7.55 (m, 10H, 2C₆H₅), 7.95–8.30 (m, 3H, pyr-H); ¹³C NMR (DMSO-d₆) δ (ppm): 180.4 (C-5 and C-5’ thiazole), 164.1 (2C=S), 153.4 (C-2 and C-6 pyridine), 148.8 (C-3 and C-5 pyridine), 146.5 (C-4 and C-4’ thiazole), 138.5 (C-4 pyridine), 152.1, 143.2, 132.1, 129.5, 128.5, 126.2 (C-arom.); MS: m/z = 461 [M⁺]; Anal. Calcd. for C₂₃H₁₅N₃S₄ (461.65): C, 59.84; H, 3.28; N, 9.10; S, 27.78. Found: C, 59.80; H, 3.27; N, 9.11; S, 27.82.
Scheme 3.

2,6-Bis-(cyanoacetamido-N-yl) pyridine (7): To a warmed solution of 2 (1.31 g, 5 mmol) in 10 ml benzene, were added (0.78 g, 12 mmol) of potassium cyanide in 10 ml of water. The reaction mixture was stirred at 50°C (bath temperature) for 1 h, then the aqueous layer was separated and poured onto acidified cooled water. The product, so formed, was collected by filtration and dried. Crystallization from acetic acid gave creamy crystals (95% yield), m.p. 235°C; IR (KBr) ν (cm⁻¹): 2252 (CN), 3220 (NH), 1638 (C=O); ¹H NMR (DMSO-d₆) δ (ppm): 4.48 (s, 4H, 2 CH₂), 8.10–8.30 (m, 3H, pyr-H), 9.45 (s, 2H, 2NH); MS: m/z = 243 [M⁺]; Anal. Calcd. for C₁₁H₉N₅O₂ (243.23): C, 54.32; H, 3.73; N, 28.79. Found: C, 54.37; H, 3.74; N, 28.84.

2,6-Bis-(thiocyanate acetamido-N-yl)pyridine (8): To a warmed solution of 2 (1.13 g, 5 mmol) in 10 ml acetonitrile, were added (0.92 g, 12 mmol) of potassium thiocyanate. The reaction mixture was stirred at 50°C (bath temperature) for 1 h, then
poured onto ice cold water. The product, so formed, was collected by filtration, crystallized from ethanol to give faint pink crystals (95% yield), m.p. 130°C; IR (KBr) ν (cm⁻¹): 3440, 3234 (NH), 2215 (CN), 1700 (C=O); ¹H NMR (DMSO-d₆) δ (ppm): 4.48 (s, 4H, 2CH₂), 8.10–8.30 (m, 3H, pyr-H), 9.20 (s, 2H, 2NH); MS: m/z = 307 [M⁺]; Anal. Calcd. for C₁₉H₁₇N₃O₂ (307.35): C, 67.71; H, 3.86; N, 28.43. Found: C, 67.72; H, 3.84; N, 28.42.

**General procedure for the synthesis of compounds 9 and 10**

A mixture of 2 (2.62 g, 10 mmol), (2.34 g, 20 mmol) of indole or (2.38 g, 20 mmol) of benzotriazole and 2 ml triethylamine (20 mmol) in 20 ml of toluene was refluxed for 2 h. The solvent was removed in vacuum and the remaining residue was triturated with 5% sodium hydroxide. The solid product was collected by filtration, washed with water and crystallized from the proper solvent. The crystals (78% yield), m.p. 162°C; IR (KBr) ν (cm⁻¹): 3440, 3230 (NH), 2225, 2220, 2215 (CN), 1655 (C=C); 1H NMR (DMSO-d₆) δ (ppm): 7.11–7.45 (m, 10H, 2C₆H₅), 8.10–8.30 (m, 3H, pyr-H), 8.35 (s, 2H, 2NH); MS: m/z = 451 [M⁺]; Anal. Calcd. for C₂₆H₂₁N₅O₂ (451.451): C, 61.19; H, 3.79; N, 27.92. Found: C, 61.23, H, 3.77; N, 28.15.

2,6-Bis-(1-oxo-2-phenylhydrazonoethanoneamido-N-yl)pyridine (15): Crystallization from dioxane gave yellow crystals (78% yield), m.p. 255°C; IR (KBr) ν (cm⁻¹): 3440, 3230 (NH), 1700 (C=O); ¹H NMR (DMSO-d₆) δ (ppm): 7.11–7.45 (m, 10H, 2C₆H₅), 7.56 (s, 2H, olefinic CH), 8.10–8.30 (m, 3H, pyr-H), 9.30 (s, 2H, 2NH), 12.04 (br, 2H, two hydrazone NH); MS: m/z = 401 [M⁺]; Anal. Calcd. for C₂₅H₁₉N₉O₂ (401.43): C, 62.83; H, 4.77; N, 24.42. Found: C, 62.85; H, 4.74; N, 24.46.

**General procedure for the synthesis of compounds 14 and 17**

To a solution of (5 mmol) of 12 or 15 in a 2 ml of DMF and 10 ml of triethylamine, was added (1.3 ml, 20 mmol) of chloroacetonitrile. The reaction mixture was refluxed for 1 h and then left to cool to room temperature. The obtained residual product was triturated with ethanol to give a solid product that was collected by filtration, washed with water and crystallized from the proper solvent.

2,6-Diamido-bis-(4-amino-5-cyano-1-phenylpyrazol-3-yl) pyridine (14): Crystallization from ethanol gave faint brown crystals (75% yield), m.p. 268–270°C; IR (KBr) ν (cm⁻¹): 1700 (C=O), 3450 (NH₂), 3200 (NH), 2220, 2215 (CN), 1650 (C=N); ¹H NMR (DMSO-d₆) δ (ppm): 6.52 (s, 4H, 2NH₂), 7.31–7.65 (m, 10H, 2C₆H₅), 8.10–8.30 (m, 3H, pyr-H), 8.90 (s, 2H, 2NH); MS: m/z = 529 [M⁺]; Anal. Calcd. for C₂₆H₁₉N₁₁O₂ (529.53): C, 61.24; H, 3.62; N, 29.10. Found: C, 61.25; H, 3.61; N, 29.40.

2,6-Diamino-bis-(5-cyano-1-phenylpyrazol-4-yl) pyridine (17): Crystallization from ethanol gave faint brown crystals (85% yield), m.p. 230°C; IR (KBr) ν (cm⁻¹): 3200(NH), 2220 (CN), 1600 (C≡N); ¹H NMR (DMSO-d₆) δ (ppm): 7.30 (s, 2H, pyrazolyl H-3), 7.41–7.65 (m, 10H, 2C₆H₅), 8.10–8.30 (m, 3H, pyr-H), 8.35 (s, 2H, 2NH); MS: m/z = 443 [M⁺]; Anal. Calcd. for C₂₅H₁₇N₉O₄ (443.48): C, 67.71; H, 3.86; N, 28.43. Found: C, 67.72; H, 3.84; N, 28.44.

2,6-Bis-(5-cyano-2-dicyanomethano-4-hydroxythiazol-N-yl)pyridine (19): A solution of 5 (3.91g, 0.01 mol) in 40 ml of DMF containing piperidine 0.5 ml, (1.32 ml, 0.02 mol) of malononitrile was added. The reaction mixture was heated under reflux for 10 h, then evaporated in vacuo. The remaining product was triturated with ethanol and the formed solid product was collected by filtration. Crystallization from dioxane gave brown crystals (75% yield), m.p. > 360°C; IR (KBr) ν (cm⁻¹): 3490 (OH), 2225, 2220, 2215 (CN), 1655 (C≡C); ¹H NMR
(DMSO-d$_6$) $\delta$ (ppm): 8.10–8.30 (m, 3H, pyr-H), 10.44 (s, 2H, 2OH); MS: m/z = 455 [M$^+$]; Anal. Calcd. for C$_{19}$H$_{13}$N$_7$S$_2$O$_2$ (455.44): C, 50.11; H, 1.11; N, 27.68; S, 11.71. Found: C, 50.15; H, 1.09; N, 27.72; S, 14.12.

**General procedure for the synthesis of compounds 18a, b, 20, 21 and 22a, b**

To a solution of 5, 19 or 6 (0.01 mol) in 30 ml of DMF, hydrazine hydrate or phenylhydrazine (0.04 mol) or (0.02 mol) were added, respectively. The reaction mixture was heated under reflux for 6–8 h then poured into ice/water mixture containing few drops of hydrochloric acid and the formed solid product was collected by filtration.

2.6-Bis-(3-amino-[1H]-5-hydrazonopyrazolo[4,5-d]thiazol-N-yl)pyridine (18a): Crystallization from ethanol gave pale yellow crystals (68% yield), m.p. > 360°C; IR (KBr) $\nu$ (cm$^{-1}$): 3465–3365 (NH$_2$, NH), 1660 (exocyclic C=N), 1650 (C=C); $^1$H NMR (DMSO-d$_6$) $\delta$ (ppm): 4.46, 5.35 (2s, 8H, 4NH$_2$), 8.10–8.30 (m, 3H, pyr-H), 8.44 (s, 2H, 2NH); MS: m/z = 415 [M$^+$]; Anal. Calcd. for C$_{29}$H$_{15}$N$_7$S$_2$O$_3$ (525.62): C, 66.27; H, 2.88; N, 18.65; S, 12.20. Found: C, 66.28; H, 2.87; N, 18.66; S, 12.19.

2.6-Bis-(3-amino-1-phenyl-5-hydrazonopyrazolo[4,5-d]thiazol-N-yl)pyridine (18b): Crystallization from dioxane gave yellow crystals (70% yield), m.p. > 360°C; IR (KBr) $\nu$ (cm$^{-1}$): 3450–3370 (NH$_2$, NH), 1665 (exocyclic C=N), 1650 (C=C); $^1$H NMR (DMSO-d$_6$) $\delta$ (ppm): 5.32 (s, 4H, 2NH$_2$), 7.36–7.48 (m, 20H, 4C$_6$H$_5$), 8.10–8.30 (m, 3H, pyr-H), 8.45 (s, 2H, 2NH$_2$); MS: m/z = 519 [M$^+$]; Anal. Calcd. for C$_{37}$H$_{29}$N$_{13}$S$_2$O$_3$ (851.94): C, 61.74; H, 4.06; N, 27.68; S, 8.90.

2.6-Bis-[3-amino-1-[1H]-5-(3',5'-diaminopyrazolo-4'-ylidino) pyrazolo[4,5-d]thiazol-N-yl]pyridine (20): Crystallization from ethanol gave white crystals (68% yield), m.p. > 360°C; IR (KBr) $\nu$ (cm$^{-1}$): 3460–3370 (NH$_2$, NH), 1665 (C=C), 1375 (C=N); $^1$H NMR (DMSO-d$_6$) $\delta$ (ppm): 5.31, 5.36, 7.42 (3s, 3H, pyr-H); MS: m/z = 851 [M$^+$]; Anal. Calcd. for C$_{43}$H$_{35}$N$_{17}$S$_2$O$_2$ (851.94): C, 60.62; H, 3.90; N, 27.95; S, 7.53. Found: C, 60.60; H, 3.91; N, 27.99; S, 7.50.

2.6-Bis-(2-hydrazono-4-phenylthiazol-N-yl)pyridine (22a): Crystallization from dioxane gave buff crystals (75% yield), m.p. 125°C; IR (KBr) $\nu$ (cm$^{-1}$): 3460 (NH$_2$), 1665 (exocyclic C=N), 1650 (C=C); $^1$H NMR (DMSO-d$_6$) $\delta$ (ppm): 6.35 (s, 4H, 2NH$_2$), 6.37 (s, 2H, thiazolyl H-5), 7.32–7.37 (m, 10H, 2C$_6$H$_5$), 8.10–8.30 (m, 3H, pyr-H); MS: m/z = 457 [M$^+$]; Anal. Calcd. for C$_{25}$H$_{19}$N$_7$S$_2$O$_2$ (457.59): C, 60.37; H, 4.19; N, 21.43; S, 15.44.

2.6-Bis-(2-hydrazono-4-phenylthiazol-N-yl)pyridine (22b): Crystallization from dioxane gave pale yellow crystals (73% yield), m.p. 120°C; IR (KBr) $\nu$ (cm$^{-1}$): 3460–3375 (NH), 1665 (exocyclic C=N), 1650 (C=C); $^1$H NMR (DMSO-d$_6$) $\delta$ (ppm): 6.37 (s, 2H, thiazolyl H-5), 7.32–7.48 (m, 20H, 4C$_6$H$_5$), 8.10–8.30 (m, 3H, pyr-H), 8.33 (s, 2H, 2NH$_2$); MS: m/z = 609 [M$^+$]; Anal. Calcd. for C$_{35}$H$_{22}$N$_7$S$_2$O$_2$ (609.78): C, 68.94; H, 4.46; N, 16.08; S, 10.52. Found: C, 68.97; H, 4.44; N, 16.10, S, 10.49.

2.6-Bis-(2-dicyanomethino-4-phenylthiazol-N-yl)pyridine (23): To a solution of 6 (4.61 g, 0.01 mol) in 30 ml of DMF, (1.32 ml, 0.02 mol) of mono-nitrolyl was added. The mixture was heated under reflux for 6 h till the evolution of H$_2$S was ceased. The solid product formed upon pouring into water was collected by filtration. Crystallization from dioxane gave brown crystals (80% yield), mp 145°C; IR (KBr) $\nu$ (cm$^{-1}$): 2225–2220 (CN), 1655 (C=C); $^1$H NMR (DMSO-d$_6$) $\delta$ (ppm): 6.34 (s, 2H, thiazolyl H-5), 7.34–7.45 (m, 10H, 2C$_6$H$_5$), 8.10–8.30 (m, 3H, pyr-H); MS: m/z = 525 [M$^+$]; Anal. Calcd. for C$_{30}$H$_{22}$N$_7$O$_2$S$_2$ (525.62): C, 66.27; H, 2.88; N, 18.65; S, 12.20. Found: C, 66.28; H, 2.87; N, 18.66; S, 12.19.

**General procedure for the synthesis of compounds 24 and 25**

To a solution of 23 (5.01 g, 0.01 mol) in 40 ml of dioxane, hydrazine hydrate or phenyl hydrazine (0.02 mol) was added. The reaction mixture was heated under reflux for 3–4 h, then left to cool. The solid product formed upon standing was collected by filtration.
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C_{20}H_{22}N_{11}S_{2} (589.71): C, 59.07; H, 3.93; N, 26.13; S, 10.87. Found: C, 59.05; H, 3.94; N, 26.17; S, 10.80.

2,6-Bis-[2-(3′-amino-5′-imino-1′-phenylpyrazolo-4′-ylidino)-4-phenylthiazol-N-y1] pyridine (25):

Crystallization from ethanol afforded pale yellow crystals (65% yield), m.p. > 360°C; IR (KBr) ν (cm⁻¹): 3465, 3390 (NH₂, NH), 1660 (C=N), 1645 (C=C); 1H NMR (DMSO-d₆) δ (ppm): 4.43 (s, 2H, thiazolyl H-5), 7.30–7.64 (m, 20H, 4C₆H₅), 8.10–8.30 (m, 3H, pyr-H), 8.37 (s, 2H, 2NH); MS: m/z = 741 [M +].

Anal. Calcd. for C_{41}H_{31}N_{11}S_{2} (741.91): C, 66.38; H, 4.21; N, 20.77; S, 10.87. Found: C, 66.40; H, 4.20; N, 20.80; S, 8.60.

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НОВИ СИНТЕЗИ НА НОВИ СИМЕТРИЧНИ БИС-ХЕТЕРОЦИКЛЕНИ СЪЕДИНЕНИЯ: СИНТЕЗ НА БИС-ТИАЗОЛ-, БИС-ПИРАЗОЛ-, БИС-БЕНЗОТРИАЗОЛ-, БИС-ИНДОЛ- И БИС-ПИРАЗОЛИТГИАЗОЛ-2,6-ДИАМИНИПРИДИНОВИ ПРОИЗВОДНИ

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При реакция на 2,6-диаминопирладин с хлорацетилхлорид се получава 2,6-бис-(2-хлорацетамид-Ν-ил)пирладин. Реакцията на продукта поотделно с KCl, KSCN, индол и бензотриазол води съответно до 2,6-бис-(цианатацетамид-Ν-ил)пирладин (продуктът при купуление с бензенидиазониев хлорид дава бис-цианидианил-хидразидновото производно и чрез дестилиране на последното съединение с обратен хладник и хлорацетониtrak се получава 2,6-диамино-5-циан-1-фенилацилазол-3-илпирладин), 2,6-бис-(тиощианат ацетамид-Ν-ил)пирладин, 2,6-бис-[2-{I(Ν-ил)азетамид-Ν-ил}ипридин и 2,6-бис-[2-{1,2,3-бензотриазол-1-ил}ациетамид-Ν-ил]пирладин. Ацетилиране на 2,6-диаминопирладина с оцетен ацетил води до 2,6-бис-(ациетамид-Ν-ил)пирладин, който при купуление с бензенидиазониев хлорид дава бис-фенилацилазолово производно. При реакцията на последното с хлорацетониtrak се получава 2,6-диамино-бис-(5-циан-1-фенил-пирладил-Ν-ил)пирладин. В алкална среда реакцията на 2,6-диаминопирладина с Cs₂S₃ последователно с etил-α-бромцианидат и фенацил-бромид дава съответно 2,6-бис-(3-циан-4-хидрокси-пирладил-3-ил)пирладин и 2,6-бис-(4-фенил-пирладил-3-ил-2-тионил)пирладин. При кондензация на получените съединения поотделно с малононитрил се получават дицианетнидициназолови производни. При реакция на хидразинхидрат или фенилгидразин с тиазолтрицианилинови производни или с дицианетнидициназолови производни съответно до хидразонтрицианилови и пиразолови производни.

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