

## The first synthesis of 3-nitro-4-[(s-tetrazin-3-yl)amino]furazans

Aleksei B. Sheremetev,\* Nadezhda V. Palysaeva and Marina I. Struchkova

### Experimental

*3-[6-(3,5-Dimethyl-1H-pyrazol-1-yl)[1,2,4,5]tetrazin-3-ylamino]-4-nitrofurazan 2*: mp 188–190 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 2.25 (s, 3H, Me), 2.52 (s, 3H, Me), 6.28 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>), δ: 13.2, 13.4, 110.3, 142.6, 145.5, 151.9, 155.4, 158.4, 159.2. <sup>14</sup>N NMR (DMSO-*d*<sub>6</sub>) δ: -33.4 (Δ*v*<sub>1/2</sub> = 191 Hz, NO<sub>2</sub>). IR (KBr, *v*/cm<sup>-1</sup>): 3400–3300, 2928, 1604, 1576, 1540, 1480, 1424, 1372, 1348, 1076, 1052, 1028, 976. MS, *m/z*: 304 (M<sup>+</sup>). Found (%): C, 35.61; H, 2.69; N, 45.92. Calc. for C<sub>9</sub>H<sub>8</sub>N<sub>10</sub>O<sub>3</sub> (304.23) (%): C, 35.53; H, 2.65; N, 46.04.

*4,4'-Azobis{3-[6-(3,5-dimethyl-1H-pyrazol-1-yl)[1,2,4,5]tetrazin-3-ylamino]furazan}* **3**: mp 260–261 °C. IR (KBr, *v*/cm<sup>-1</sup>): 3100–2800, 1576, 1516, 1484, 1468, 1416, 1284, 1168, 1072, 1048, 1028, 980, 948. MS, *m/z*: 544 (M<sup>+</sup>). Found (%): C, 39.80; H, 2.99; N, 51.37. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>20</sub>O<sub>2</sub> (544.45) (%): C, 39.71; H, 2.96; N, 51.45.

*4,4'-Azoxybis{3-[6-(3,5-dimethyl-1H-pyrazol-1-yl)[1,2,4,5]tetrazin-3-ylamino]furazan}* **4**: mp 168–170 °C. <sup>1</sup>H NMR (Py-*d*<sub>5</sub>) δ: 3.33 (s, 3H, Me), 3.39 (s, 3H, Me), 3.51 (s, 3H, Me), 3.63 (s, 3H, Me), 7.12 (s, 1H), 7.18 (s, 1H). <sup>13</sup>C NMR (Py-*d*<sub>5</sub>) δ: 14.4, 15.0, 112.0, 144.1, 144.2, 148.8, 151.8, 153.9, 156.0, 160.4, 160.6, 162.1, 162.4. MS, *m/z*: 560 (M<sup>+</sup>). Found (%): C, 38.64; H, 2.95; N, 49.86. Calc. for C<sub>18</sub>H<sub>16</sub>N<sub>20</sub>O<sub>2</sub> (560.45) (%): C, 38.57; H, 2.88; N, 49.98.

*3,6-Bis(4-nitrofurazan-3-ylamino)-s-tetrazine 9*: mp 240–242 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ: 12.8 (broad, NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ: 145.6, 155.3, 159.2. <sup>14</sup>N NMR (DMSO-*d*<sub>6</sub>) δ: -33.6 (Δ*v*<sub>1/2</sub> = 190 Hz, NO<sub>2</sub>). MS, *m/z*: 338 (M<sup>+</sup>), 292 (M<sup>+</sup> - NO<sub>2</sub>). Found (%): C, 21.38; H, 0.58; N, 49.59. Calc. for C<sub>6</sub>H<sub>2</sub>N<sub>12</sub>O<sub>6</sub> (338.16) (%): C, 21.31; H, 0.60; N, 49.70.

*3,6-Bis(4-nitrofurazan-3-ylamino)-s-tetrazine N-oxide 10*: mp 264–268 °C (decomp.). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 12.3 (broad, NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ: 145.5, 145.7, 149.2, 155.2, 155.3, 156.8. <sup>14</sup>N NMR (DMSO-*d*<sub>6</sub>) δ: -33.0 and -33.5 (NO<sub>2</sub>). MS, *m/z*: 354 (M<sup>+</sup>), 338 (M<sup>+</sup> - O), 308

(M<sup>+</sup> - NO<sub>2</sub>). Found (%): C, 21.38; H, 0.58; N, 49.59. Calc. for C<sub>6</sub>H<sub>2</sub>N<sub>12</sub>O<sub>7</sub> (354.16) (%): C, 20.35; H, 0.57; N, 47.46.

*3,6-Bis(4-nitrofurazan-3-ylamino)-s-tetrazine N,N'-dioxide 11*: mp >300 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ: 12 (broad, NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>), δ: 145.2, 146.5, 155.3. <sup>14</sup>N NMR (DMSO-*d*<sub>6</sub>), δ: -33.4 (Δ*v*<sub>1/2</sub> = 175 Hz, NO<sub>2</sub>). MS, m/z: 370 (M<sup>+</sup>), 354 (M<sup>+</sup> - O), 338 (M<sup>+</sup> - 2O), 324 (M<sup>+</sup> - NO<sub>2</sub>), 308 (M<sup>+</sup> - O - NO<sub>2</sub>), 278 (M<sup>+</sup> - 2NO<sub>2</sub>). Found (%): C, 19.50; H, 0.51; N, 45.33. Calc. for C<sub>6</sub>H<sub>2</sub>N<sub>12</sub>O<sub>8</sub> (370.16) (%): C, 19.47; H, 0.54; N, 45.41.

*3-Nitro-4-{[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazin-3-ylamino}furazan 14*: mp 235–236 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 9.81 (s, 1H, CH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ: 137.3, 145.3, 150.0, 151.5, 154.9. <sup>14</sup>N NMR (DMSO-*d*<sub>6</sub>) δ: -33.7 (Δ*v*<sub>1/2</sub> = 183 Hz, NO<sub>2</sub>). IR (KBr, *ν*/cm<sup>-1</sup>): 3364, 3160, 3144, 1604, 1572, 1536, 1452, 1392, 1348, 1324, 1220, 1188, 1148, 1140, 1052, 1028, 988, 960 cm<sup>-1</sup>. MS, m/z: 250 (M<sup>+</sup>). Found (%): C, 24.09; H, 0.85; N, 55.93. Calc. for C<sub>5</sub>H<sub>2</sub>N<sub>10</sub>O<sub>3</sub> (250.14) (%): C, 24.01; H, 0.81; N, 56.00.

*4,4'-Azobis{3-([1,2,4]triazolo[4,3-b][1,2,4,5]tetrazin-3-ylamino)furazan} 15*: mp >300 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 9.83 (s, 2H, CH), 12.5 (broad, 2H, NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ: 137.4, 145.1, 149.9, 151.8, 157.4. Found (%): C, 27.66; H, 0.98; N, 64.15. Calc. for C<sub>10</sub>H<sub>4</sub>N<sub>20</sub>O<sub>2</sub> (436.27) (%): C, 27.53; H, 0.92; N, 64.21.

*4,4'-Azoxybis{3-([1,2,4]triazolo[4,3-b][1,2,4,5]tetrazin-3-ylamino)furazan} 16*: mp 297–298 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 9.79 (s, 1H, CH), 9.82 (s, 1H, CH), 12.0 (broad, 2H, NH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) δ: 137.3, 145.0, 146.6, 148.8, 149.8, 149.9, 151.5, 151.8, 153.4. Found (%): C, 26.67; H, 0.95; N, 61.83. Calc. for C<sub>10</sub>H<sub>4</sub>N<sub>20</sub>O<sub>3</sub> (436.27) (%): C, 26.56; H, 0.89; N, 61.94.