

## SYNTHESIS OF POLYNUCLEAR HETEROCYCLIC POLYNITROGEN SYSTEMS BASED ON CYANURIC CHLORIDE AND ITS DERIVATIVES

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*Polynuclear structures containing several heterocycles of various types were synthesized by the reaction of cyanuric chloride and its mono- and dichloro derivatives with triazoles and tetrazoles in the presence of bases.*

**Keywords:** tetrazoles, triazines, triazoles, polynuclear heterocyclic systems.

In our earlier papers we demonstrated the fundamental possibility of the synthesis of noncondensed polynuclear triazole- and tetrazole-containing units by the gradual insertion of new heterocycles into the initial azole [1, 2]. In a continuation of these investigations in the present work we have examined a version of the synthesis of polynuclear structures based on the molecules of cyanuric chloride (**1**), 2-chloro-4,6-dimethoxy-1,3,5-triazine (**2**), 2-chloro-4,6-dimorpholino-1,3,5-triazine (**3**), 2,4-dichloro-6-methoxy-1,3,5-triazine (**4**), and 2,4-dichloro-6-diethylamino-1,3,5-triazine (**5**). As known, cyanuric chloride readily enters into reaction with various nucleophiles [3, 4]. It was assumed that this compound and its derivatives would react no less vigorously with azoles, forming polynuclear structures. It is known that one of the chlorine atoms in cyanuric chloride initially reacts quite readily in substitution reactions [3, 4]. Actually, the reaction of 1 mol of 5-phenyltetrazole with cyanuric chloride at 0–5°C leads to the production of 4,6-dichloro-2-(5-phenyltetrazol-1-yl)-1,3,5-triazine (**6**). Substitution of the other chlorine atoms already requires a somewhat higher reaction temperature. Thus, trisubstituted polynuclear azolyl-containing compounds **7a–c**, based in a 1,3,5-triazine ring, are formed during the reaction of cyanuric chloride with 3 mol of tetrazole, 5-phenyltetrazole, and ethyl (tetrazole-5-yl)acetate in the form of triethylammonium salts or in the presence of sodium hydrocarbonate in a water–acetone medium at 15–25°C. As a rule the isolated compounds are high-melting substances poorly soluble in organic solvents. In order to produce polycyclic compounds with lower melting points and soluble in organic solvents methoxy and alkylamino groups were inserted into the molecule of the triazine ring. Here the monochlorotriazines **2** and **3** and the dichlorotriazines **4** and **5** were synthesized, and they were then brought into substitution reactions with azoles.

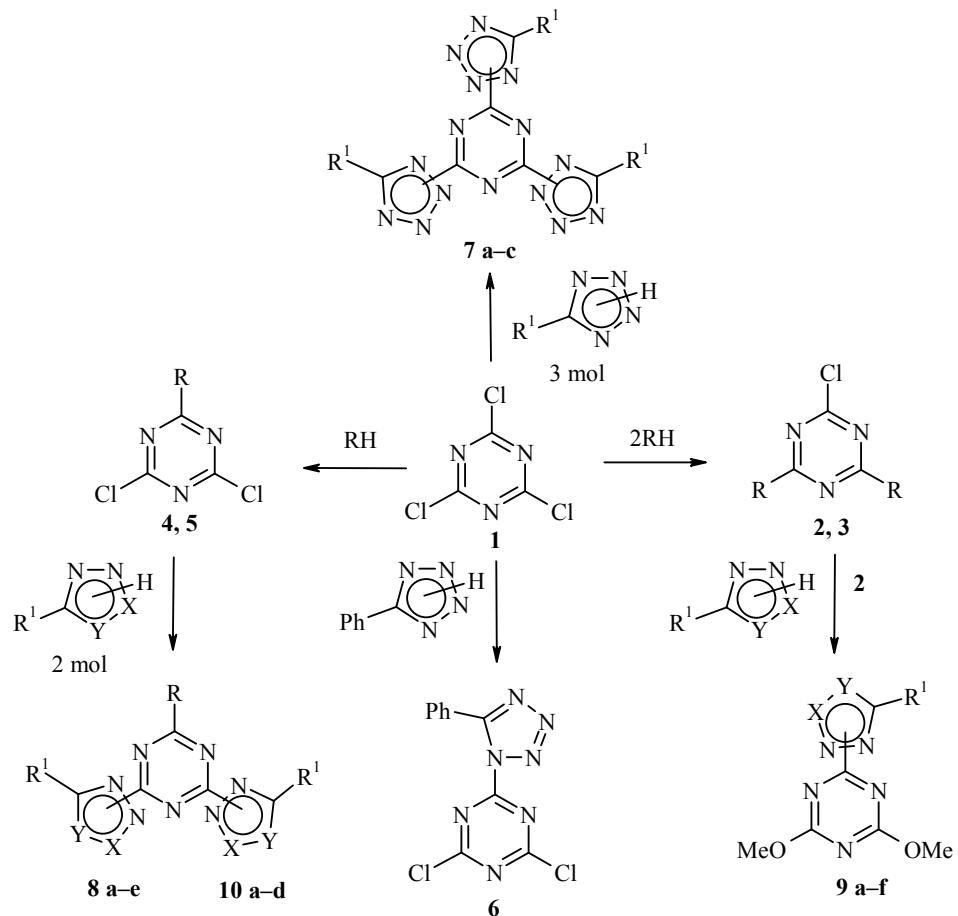
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In the literature [3] there is a method for the production of dichlorotriazine **4** by the reaction of cyanuric chloride with a large excess of methanol. However, when this method was reproduced a difficultly separable mixture of methoxy-substituted mono- and dichlorotriazines **2** and **4** was often formed. By using a threefold excess of methanol in the reaction with cyanuric chloride it was possible to obtain a high yield of the individual dichlorotriazine **4**.

The dichlorotriazine **4** proved more active in reaction with azoles than the monochloro derivative **2**. Its reaction with these heterocycles at room temperature leads to the formation of the tricyclic compounds **8a–e**. The two chlorine atoms of the dichlorotriazine **4** are easily substituted by tetrazole, 1,2,4-triazole, and 4-nitro-1,2,3-triazole rings.



**2, 4** R = OMe; **3** R = N(CH<sub>2</sub>)<sub>4</sub>O; **5** R = NEt<sub>2</sub>; **7a** R<sup>1</sup> = H, **b** R<sup>1</sup> = Ph, **c** R<sup>1</sup> = CH<sub>2</sub>CO<sub>2</sub>Et;  
**8a–e** R = OMe; **a** R<sup>1</sup> = H, X = Y = N, **b** R<sup>1</sup> = Ph, X = Y = N, **c** R<sup>1</sup> = CH<sub>2</sub>CO<sub>2</sub>Et, X = Y = N,  
**d** R<sup>1</sup> = NO<sub>2</sub>, X = N, Y = CH, **e** R<sup>1</sup> = H, X = CH, Y = N; **9 a** R<sup>1</sup> = H, X = Y = N,  
**b** R<sup>1</sup> = Ph, X = Y = N, **c** R<sup>1</sup> = CH<sub>2</sub>CO<sub>2</sub>Et, X = Y = N, **d** R<sup>1</sup> = NO<sub>2</sub>, X = N, Y = CH, **e** R<sup>1</sup> = NO<sub>2</sub>,  
X = N, Y = CPh, **f** R<sup>1</sup> = H, X = CH, Y = N; **10a–d** R = NET<sub>2</sub>; **a** R<sup>1</sup> = H, X = Y = N, **b** R<sup>1</sup> = Ph,  
X = Y = N, **c** R<sup>1</sup> = NO<sub>2</sub>, X = N, Y = CH, **d** R<sup>1</sup> = H, X = CH, Y = N

Under more rigorous conditions, with prolonged boiling in acetone, the chlorine in the triazine **2** is substituted by the above-mentioned azoles in the presence of sodium bicarbonate, and 4,6-dimethoxy-2-tetrazolyl(triazolyl)-1,3,5-triazines **9a–f** are formed. In all the cases of substitution of chlorine the formation of isomeric compounds involving various nitrogen atoms in the heterocycle of the azoles is possible. As a rule, however, one of the isomers can be isolated by fractional crystallization of the reaction products.

The IR spectra of the obtained methoxy-substituted compounds contain bands for the stretching vibrations of the C—O—C bond in the region of 1271–1186 and the vibrations of the C=N bonds of the heterocycles at 1567–1603 cm<sup>−1</sup>. In the <sup>13</sup>C NMR spectra of the methoxy-substituted triazines in the region of 172–174 ppm there are characteristic signals corresponding to the carbon atoms of the triazine rings attached to the methoxy group. In the region of 160–163 ppm there are characteristic signals for the carbon atoms of the triazine rings as substituents carrying the azole heterocycle; the signals of the carbon atoms of the methoxy group itself are in the region of 55–57 ppm.

During the reaction of dichlorotriazine **5** with azoles the corresponding noncondensed polynuclear structures **10a–d** with a dialkylamino group in the triazine ring were obtained. The reaction was conducted in the presence of sodium bicarbonate with prolonged boiling in acetone. In contrast to the dichlorotriazine **5** in the reaction of azoles with dimorpholinotriazine **3** it was not possible to obtain the desired polynitrogen compounds even with the stronger base sodium hydroxide.

In the <sup>13</sup>C NMR spectra of the amino-substituted triazines in the region of 163–165 there are signals for the carbon atoms of the triazine rings carrying a diethylamino group; at 156–162 there are signals for the carbon atoms of the triazine rings having an azolyl substituent; in the region of 12–14 there are signals for the carbon atoms of the methyl groups; in the region of 41–45 ppm there are signals for the methylene groups at the nitrogen atom of the diethylamine fragment.

By inserting amino and methoxyl fragments it was possible to reduce the melting point a little and to increase the solubility of the obtained substances in organic solvents. All the tetrazole-containing polynuclear triazines **7c**, **8b,c**, **9b**, and **10b** are thermally unstable and decompose at the melting point.

## EXPERIMENTAL

The <sup>13</sup>C NMR spectra were recorded on a Varian VXR-500S spectrometer (126 MHz) in DMSO (compounds **6**, **7a–c**, **8a,b,d,e**, **9b,e**, and **10a–d**) and acetone (compounds **8c**, **9a,c,d,f**), the signals of which were used as internal standard (29.5 and 39.5 ppm respectively). The IR spectra were obtained on an Infracam FT-801 instrument in vaseline oil on KBr glasses. Elemental analysis was performed on a FLASH BA 1112 Series CHN analyzer. Compounds **2**, **3**, and **5** were obtained by the methods in [3, 4].

**2,4-Dichloro-6-methoxy-1,3,5-triazine (4).** To a suspension of cyanuric chloride **1** (6 g, 32 mmol), methanol (2.8 g, 90 mmol), and water (3 ml) at room temperature with stirring, we added in portions 2.9 g of NaHCO<sub>3</sub>. When the release of carbon dioxide had ceased, the reaction mass was stirred for 1 h and poured into 200 ml of cold water with ice. The precipitate was filtered off and dried in air. It was packed into a paper filter and extracted with boiling hexane. After removal of the solvent the yield was 8.2 g (83%); mp 88–89°C (mp 89–90°C [3]).

**4,6-Dichloro-2-(5-phenyltetrazol-1-yl)-1,3,5-triazine (6).** To a solution of cyanuric chloride **1** (1 g, 5.4 mmol) in acetone (15 ml) at 2–4°C, we added dropwise 5-phenyltetrazole (0.79 g, 5.4 mmol) and triethylamine (0.54 g, 5.4 mmol) in acetone (15 ml). The reaction mass was stirred at 2–4°C for 1 h and was then poured into cold water, and the precipitate was filtered off. Yield 0.8 g (50%); mp 192–195°C (decomp.). IR spectrum,  $\nu$ , cm<sup>−1</sup>: 1636 (C=N heterocycle). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 165.6 (C-2 of triazine); 149.4 (2C-4,6 of triazine); 142.5 (C tetrazole); 124.6–132.2 (C Ph). Found, %: C 39.92; H 1.03; N 33.87. C<sub>10</sub>H<sub>5</sub>C<sub>12</sub>N<sub>7</sub>. Calculated, %: C 40.82; H 1.7; N 33.33.

**2,4,6-Tri(tetrazol-1-yl)-1,3,5-triazine (7a).** To a solution of tetrazole (0.9 g, 12.9 mmol) and cyanuric chloride **1** (0.72 g, 3.9 mmol) in acetone (10 ml) and water (1 ml) we added in portions at room temperature with stirring NaHCO<sub>3</sub> (1.1 g, 12.9 mmol). The mixture was boiled for 30 min, cooled, and poured into cold water.

The precipitate was filtered off and washed with boiling ethanol. Yield 0.2 g (18%); mp >350°C; in a burner flame it decomposes with explosion. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1636 (C=N heterocycle). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 159.8 (3C triazine); 142.6 (3C tetrazole).

**2,4,6-Tri(5-phenyltetrazol-2-yl)-1,3,5-triazine (7b).** To a solution of the triethylammonium salt obtained from 5-phenyltetrazole (1.5 g, 10 mmol) and triethylamine (1.02 g, 10 mmol) in acetone (10 ml), we added dropwise at 13–15°C with stirring cyanuric chloride **1** (0.61 g, 3 mmol) in acetone (15 ml). The mixture was stirred at room temperature for 1 h and poured into 100 ml of cold water. The cream-colored precipitate was filtered off and dried in air. Yield 1.3 g (74%); mp >300°C (sublimes). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1620 (Ph), 1636 (C=N heterocycle). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 164.4 (3C tetrazole); 164.3 (3C triazine); 130.8 (3C-*p* Ph); 128.9 (3C-*m* Ph); 126.1 (3C-*o* Ph); 125.5 (3C-*ipso* Ph). Found, %: C 55.21; H 3.01; N 41.20. C<sub>24</sub>H<sub>15</sub>N<sub>15</sub>. Calculated, %: C 56.14; H 2.92; N 40.94.

**2,4,6-Tri(5-ethoxycarbonylmethyltetrazol-2-yl)-1,3,5-triazine (7c).** The compound was obtained similarly to compound **7a** from cyanuric chloride **1** (0.86 g, 4.7 mmol), ethyl (tetrazol-5-yl)acetate (2.3 g, 15.4 mmol) and NaHCO<sub>3</sub> (1.3 g, 15.4 mmol). Yield 0.65 g (26%); mp 180°C (decomp., ethanol). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1640 (C=N heterocycle), 1710 (C=O). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 166.9 (3C, C=O); 161.5 (3C triazine); 159.7 (3C tetrazole); 60.5 (3C, CH<sub>3</sub>CH<sub>2</sub>O); 31.5 (3C, CH<sub>2</sub>C=O); 13.4 (3C, CH<sub>3</sub>CH<sub>2</sub>). Found, %: C 38.84; H 3.23; N 39.78. C<sub>18</sub>H<sub>21</sub>N<sub>15</sub>O<sub>6</sub>. Calculated, %: C 39.78; H 3.87; N 38.67.

**6-Methoxy-2,4-di(tetrazol-1-yl)-1,3,5-triazine (8a).** To a solution of triazine **4** (0.65 g, 3.5 mmol) and tetrazole (0.52 g, 7.5 mmol) in acetone (25 ml) and water (3 ml) at 25°C with stirring we added in portions NaHCO<sub>3</sub> (0.22 g, 7.6 mmol). After stirring for 2 h the reaction mass was left overnight, and was it then poured into 50 ml of cold water. The precipitate was filtered off. Yield 0.48 g (54%); at 165°C it decomposes with explosion, and it is sensitive to heat, friction, and impact. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1186 (–O–), 1625 (C=N heterocycle). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 172.3 (C-6 triazine); 160.5 (2C-2,4 triazine); 143.7 (2C tetrazole), 56.7 (C, CH<sub>3</sub>).

**Compounds 8b-d.** These compounds were obtained similarly to compound **8a**.

**6-Methoxy-2,4-di(5-phenyltetrazol-2-yl)-1,3,5-triazine (8b).** Compound **8b** was obtained from dichlorotriazine **4** (0.29 g, 1.6 mmol), phenyltetrazole (0.5 g, 3.4 mmol), and NaHCO<sub>3</sub> (0.29 g, 3.4 mmol) in acetone (10 ml) and water (1 ml). Yield 0.53 g (54%); mp 154°C (decomp.). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1271 (–O–), 1590 (Ph), 1640 (C=N heterocycle). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 173.2 (C-6 triazine); 163.5 (2C tetrazole); 162.1 (2C-2,4 triazine); 131.2 (2C-*p* Ph); 129.1 (2C-*m* Ph); 126.8 (2C-*o* Ph), 125.5 (2C-*ipso* Ph), 55.9 (C, CH<sub>3</sub>). Found, %: C 53.34; H 3.03; N 37.48. C<sub>18</sub>H<sub>13</sub>N<sub>11</sub>O. Calculated, %: C 54.14; H 3.26; N 38.6.

**2,4-Di(5-ethoxycarbonyltetrazol-2-yl)-6-methoxy-1,3,5-triazine (8c).** Compound **8c** was obtained from triazine **4** (1 g, 5.6 mmol), ethyl (tetrazol-5-yl)acetate (1.9 g, 12.2 mmol), and NaHCO<sub>3</sub> (1 g, 12.2 mmol) in acetone (10 ml) and water (2 ml). Yield 0.7 g (30%); mp 168°C (decomp.). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1186 (–O–), 1530 (C=N heterocycle), 1720 (C=O). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 172.7 (C-6 triazine); 167.5 (2C, C=O); 161.5 (2C-2,4 triazine); 159.5 (2C tetrazole); 61.8 (2C, CH<sub>3</sub>CH<sub>2</sub>O); 56.2 (C, OCH<sub>3</sub>); 32.9 (2C, CH<sub>2</sub>C=O); 13.8 (2C, CH<sub>3</sub>CH<sub>2</sub>). Found, %: C 39.02; H 3.54; N 35.14. C<sub>14</sub>H<sub>17</sub>N<sub>11</sub>O<sub>5</sub>. Calculated, %: C 40.1; H 4.06; N 36.75.

**6-Methoxy-2,4-di(4-nitro-1,2,3-triazol-2-yl)-1,3,5-triazine (8d).** Compound **8d** was obtained from triazine **4** (0.5 g, 2.8 mmol), 4-nitro-1,2,3-triazole (0.7 g, 6.1 mmol), and NaHCO<sub>3</sub> (0.51 g, 6.1 mmol) in acetone (10 ml) and water (1 ml). Yield 0.62 g (69%); mp 131–133°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1219 (–O–), 1565 (NO<sub>2</sub>), 1603 (C=N of heterocycle). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 173.2 (C-6 triazine); 160.5 (2C-2,4 triazine); 153.6 (2C-4 triazole); 124.7 (2C-5 triazole); 56.6 (C, CH<sub>3</sub>). Found, %: C 28.95; H 1.03; N 46.24. C<sub>8</sub>H<sub>5</sub>N<sub>11</sub>O<sub>5</sub>. Calculated, %: C 28.66; H 1.49; N 45.97.

**6-Methoxy-2,4-di(1,2,4-triazol-1-yl)-1,3,5-triazine (8e).** Compound **8e** was obtained from triazine **4** (0.6 g, 3 mmol), 1,2,4-triazole (0.4 g, 6 mmol), and NaHCO<sub>3</sub> (0.59 g, 7 mmol) in acetone (15 ml) and water (2 ml). Yield 0.27 g (33%); mp 207°C (ethanol). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1236 (–O–). <sup>13</sup>C NMR spectrum,  $\delta$ ,

ppm: 173.2 (C-6 triazine); 162.1 (2C-2,4 triazine); 153.4 (2C-3 triazole); 146.1 (2C-5 triazole); 56.6 (C, CH<sub>3</sub>). Found, %: C 39.50; H 3.01; N 51.83. C<sub>8</sub>H<sub>7</sub>N<sub>9</sub>O. Calculated %: C 39.18; H 2.86; N 51.43.

**4,6-Dimethoxy-2-(tetrazol-1-yl)-1,2,3-triazine (9a).** To a solution of the triethylammonium salt from tetrazole (0.4 g, 5.7 mmol), triethylamine (0.57 g, 5.7 mmol) in acetone (10 ml) at 25°C with stirring, a solution of the triazine **2** (1 g, 5.7 mmol) in acetone (5 ml) was added dropwise. The mixture was boiled for 3 h and left overnight. The reaction mixture was poured into 100 ml of cold water with ice, and the precipitate was filtered off. Yield 0.65 g (55%); mp 154-156°C (ethanol). IR spectrum, v, cm<sup>-1</sup>: 1219 (-O-). <sup>13</sup>C NMR spectrum, δ, ppm: 173.7 (2C-4,6 triazine); 161.1 (C-2 triazine); 143.1 (C tetrazole); 55.9 (2C, CH<sub>3</sub>). Found, %: C 34.71; H 3.05; N 45.95. C<sub>6</sub>H<sub>7</sub>N<sub>7</sub>O<sub>2</sub>. Calculated, %: C 34.45; H 3.35; N 46.89.

**Compounds 9b-e.** The compounds were obtained similarly to compound **9a**.

**4,6-Dimethoxy-2-(5-phenyltetrazol-2-yl)-1,3,5-triazine (9b).** Compound **9b** was obtained from 5-phenyltetrazole (0.9 g, 6 mmol), triethylamine (0.6 g, 6 mmol), and triazine **2** (1 g, 5.6 mmol) in acetone (15 ml). Yield 0.8 g (47%) of a light-cream-colored substance; mp 132-133°C (decomp., ethanol). IR spectrum, v, cm<sup>-1</sup>: 1171 (-O-), 1595 (Ph). <sup>13</sup>C NMR spectrum, δ, ppm: 173.5 (2C-4,6 triazine); 164.4 (C tetrazole); 161.5 (C-2 triazine); 131.2 (C-p Ph); 129.1 (C-m Ph); 126.8 (C-o Ph); 125.5 (C-ipso Ph); 55.9 (2C, CH<sub>3</sub>). Found, %: C 49.11; H 4.09; N 35.43. C<sub>12</sub>H<sub>11</sub>N<sub>7</sub>O<sub>2</sub>. Calculated, %: C 50.53; H 3.86; N 34.39.

**Ethyl [2-(4,6-Dimethoxy-1,3,5-triazin-2-yl)tetrazol-5-yl]acetate (9c).** Compound **9c** was obtained from triazine **2** (1 g, 5.7 mmol), ethyl (tetrazol-5-yl)acetate (0.9 g, 5.7 mmol), and triethylamine (0.58 g, 5.7 mmol) in acetone (15 ml). Yield 0.5 g (30%); mp 167°C (decomp., ethanol). IR spectrum, v, cm<sup>-1</sup>: 1150 (-O-), 1570 (C=N heterocycle), 1690 (COO). <sup>13</sup>C NMR spectrum, δ, ppm: 173.9 (2C-4,6 triazine); 167.4 (C, C=O); 162.1 (C-2 triazine); 159.8 (C tetrazole); 61.8 (C, CH<sub>3</sub>CH<sub>2</sub>O); 56.2 (2C, CH<sub>3</sub>); 32.9 (C, CH<sub>2</sub>C=O); 13.8 (C, CH<sub>3</sub>CH<sub>2</sub>). Found, %: C 41.15; H 4.78; N 32.87. C<sub>10</sub>H<sub>13</sub>N<sub>7</sub>O<sub>4</sub>. Calculated, %: C 40.68; H 4.41; N 33.22.

**4,6-Dimethoxy-2-(4-nitro-1,2,3-triazol-2-yl)-1,3,5-triazine (9d).** Compound **9d** was obtained from triazine **2** (1.4 g, 8 mmol), 4-nitro-1,2,3-triazole (1 g, 8.8 mmol), and triethylamine (0.88 g, 8.8 mmol) in acetone (10 ml). Yield 0.6 (30%); mp 122-124°C (ethanol). IR spectrum, v, cm<sup>-1</sup>: 1180 (-O-), 1560 (NO<sub>2</sub>). <sup>13</sup>C NMR spectrum, δ, ppm: 173.2 (2C-4,6 triazine); 162.3 (C-2 triazine); 153.5 (C-4 triazole); 122.8 (C-5 triazole); 55.4 (2C, CH<sub>3</sub>). Found, %: C 33.74; H 2.82; N 37.12. C<sub>7</sub>H<sub>7</sub>N<sub>7</sub>O. Calculated, %: C 33.2; H 2.77; N 38.74.

**4,6-Dimethoxy-2-(4-nitro-5-phenyl-1,2,3-triazol-2-yl)-1,3,5-triazine (9e).** Compound **9e** was obtained from triazine **2** (0.87 g, 5 mmol), 4-nitro-5-phenyl-1,2,3-triazole (1 g, 5.3 mmol), and triethylamine (0.53 g, 5.3 mmol) in acetone (10 ml). Yield 0.75 g (47%); mp 142-144°C (washed with hot ethanol). IR spectrum, v, cm<sup>-1</sup>: 1565 (NO<sub>2</sub>), 1600 (Ph). <sup>13</sup>C NMR spectrum, δ, ppm: 173.2 (2C-4,6 triazine); 163.1 (C-2 triazine); 151.5 (C-4 triazole); 143.9 (C-5 triazole); 130.3 (C-p Ph); 129.1 (C-m Ph); 128.3 (C-o Ph); 126.3 (C-ipso Ph); 56 (2C, CH<sub>3</sub>). Found, %: C 46.72; H 3.02; N 31.11. C<sub>13</sub>H<sub>11</sub>N<sub>7</sub>O<sub>4</sub>. Calculated, %: C 47.42; H 3.34; N 29.79.

**4,6-Dimethoxy-2-(1,2,4-triazol-1-yl)-1,3,5-triazine (9f).** To a solution of compound **2** (1 g, 5.7 mmol) and 1,2,4-triazole (0.41 g, 6 mmol) in acetone (10 ml) and water (1 ml), NaHCO<sub>3</sub> (0.5 g, 6 mmol) was added in portions. The reaction mixture was boiled for 3 h, cooled, and poured into cold water. The precipitate was filtered off. Yield 0.63 g (56%); mp 128-130°C (ethanol). IR spectrum, v, cm<sup>-1</sup>: 1190 (-O-). <sup>13</sup>C NMR spectrum, δ, ppm: 172.6 (2C-4,6 triazine); 162.2 (C-2 triazine); 153.4 (C-3 triazole); 145.4 (C-5 triazole); 55.7 (2C, CH<sub>3</sub>). Found, %: C 40.87; H 4.02; N 39.79. C<sub>7</sub>H<sub>8</sub>N<sub>6</sub>O<sub>2</sub>. Calculated, %: C 40.38; H 3.85; N 40.38.

**6-Diethylamino-2,4-di(tetrazol-1-yl)-1,3,5-triazine (10a).** To a solution of triazine **5** (1.2 g, 5 mmol) in acetone (7 ml), a solution of tetrazole (1 g, 15 mmol) and triethylamine (1.6 g, 16 mmol) in acetone (7 ml) and water (2 ml) was added. The mixture was boiled for 2 h, cooled, and poured into water. The precipitate was filtered off. Yield was 1.1 g (71%); mp 147-148°C (water). IR spectrum, v, cm<sup>-1</sup>: 1640 (C=N). <sup>13</sup>C NMR spectrum, δ, ppm: 164.3 (C-6 triazine); 159.9 (2C-2,4 triazine); 143.6 (2C tetrazole); 43.9 (2C, CH<sub>2</sub>); 13.0 (2C, CH<sub>3</sub>). Found, %: C 37.27; H 3.93; N 57.46. C<sub>9</sub>H<sub>12</sub>N<sub>12</sub>. Calculated, %: C 37.5; H 4.17; N 58.33.

**6-Diethylamino-2,4-di(5-phenyltetrazol-1-yl)-1,3,5-triazine (10b).** To a mixture of the triazine **5** (0.5 g, 2.3 mmol) and 5-phenyltetrazole (0.66 g, 4.5 mmol) in acetone (10 ml) and water (1 ml), NaHCO<sub>3</sub> (0.38 g, 4.5 mmol) was added. The mixture was boiled for 3 h, cooled, and poured into cold water with ice. The precipitate was filtered off. Yield 0.5 g (51%); mp 130°C (decomp.). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1605 (Ph). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 164.6 (C-6 triazine); 158.5 (2C-2,4 triazine); 145.6 (2C tetrazole); 43.2 (2C, CH<sub>2</sub>); 13.2 (2C, CH<sub>3</sub>). Found, %: C 57.85; H 3.83; N 37.75. C<sub>21</sub>H<sub>20</sub>N<sub>12</sub>. Calculated, %: C 57.27; H 4.55; N 38.18.

**Compounds 10c,d.** These compounds were obtained similarly.

**6-Diethylamino-2,4-di(4-nitro-1,2,3-triazol-2-yl)-1,3,5-triazine (10c).** Compound **10c** was obtained from triazine **5** (0.5 g, 2.3 mmol), 4-nitro-1,2,3-triazole (0.52 g, 4.5 mmol), and NaHCO<sub>3</sub> (0.38 g, 4.5 mmol) in acetone (10 ml) and water (1 ml). Yield 0.63 g (75%); mp 206–208°C (a mixture of DMF and ethanol). IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1560 (NO<sub>2</sub>). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 163.2 (C-6 of triazine); 159.2 (2C-2,4 triazine); 152.3 (2C-4 triazole); 123.8 (2C-5 triazole); 41.5 (2C, CH<sub>2</sub>); 12.5 (2C, CH<sub>3</sub>). Found, %: C 35.03; H 3.44; N 44.21. C<sub>11</sub>H<sub>12</sub>N<sub>12</sub>O<sub>4</sub>. Calculated, %: C 35.11; H 3.19; N 44.68.

**6-Diethylamino-2,4-di-(1,2,4-triazol-1-yl)-1,3,5-triazine (10d).** Compound **10d** was obtained from triazine **5** (0.5, 2.3 mmol), 1,2,4-triazole (0.31 g, 4.5 mmol), and NaHCO (0.38 g, 4.5 mmol) in acetone (10 ml) and water (1 ml) for 10 h. Yield 0.4 g (62%); mp 134–136°C (water). <sup>13</sup>C NMR spectrum,  $\delta$ , ppm: 164.5 (C-6 triazine); 160.8 (2C-2,4 triazine); 153.7 (2C-3 triazole); 146.1 (2C-5 triazole); 43.2 (2C, CH<sub>2</sub>); 12.7 (2C, CH<sub>3</sub>). Found, %: C 46.54; H 4.81; N 48.32. C<sub>11</sub>H<sub>14</sub>N<sub>10</sub>. Calculated, %: C 46.15; H 4.90; N 48.95.

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