Synthesis of Some Symmetrically Substituted Compounds Derived from 1,3-Bis(6-Azauracil-1-yl)benzene and 1,3,5-Tris(6-Azauracil-1-yl)benzene [1]

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The 3,5-bis(5-carboxy-6-azauracil-1-yl)aniline (**7**) and 1,3,5-tris(5-carboxy-6-azauracil-1-yl)benzene (**10**) were prepared from 3-amino-5-nitroacetanilide (**1**) *via* intermediates **2-6**. A series of other substituted 6-azauracil derivatives **9**, **11-14** were also prepared.

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Double 6-azauracil derivatives with two 6-azauracil nuclei bonded on the benzene ring in a *meta* orientation, relative to each other, might be interesting from the point of view of their possible interactions with various substrates. Thanks to the free rotation of heterocycles around the heterocycle-benzene bond they can assume various conformations with various distances of bonding hydrogen atoms. Some derivatives of that type have been prepared earlier [2-5]. However, these derivatives were either unsubstituted on benzene ring [2-4] or some vicinal amino-, hydroxy- and hydrazino derivatives where both 6-azauracil rings were connected by C atom in position 5 of the 6-azauracil ring.

The main topic of this communication is the synthesis of 1,3-di-6-azauracil derivatives of benzene, where both 6-azauracil rings are connected by N atom in position 1 of 6-azauracil ring that contain a amino group at the 5 position of benzene. Thus generating a symmetric compound with respect to both 6-azauracil rings. The main attention was dedicated to the synthesis of the symmetrical 1,3,5-tris(6-azauracil-1-yl)benzene derivative **10**. Such compound has never been described before.

As a starting material for the preparation of above described compounds we chose 3-amino-5-nitroacetanilide (**1**), which was prepared from 3,5-dinitroaniline by acetylation followed by the reduction of one nitro group using $(NH_4)_2S$.

Diazotization of **1** and further coupling of the formed diazonium salt with ethyl cyanoacetylcarbamate afforded the corresponding hydrazone **2** in a good yield. The hydrazone **2** was then cyclized thermally by boiling in dry pyridine to the 1-(3-acetylamino-5-nitrophenyl)-6-azauracil-5-carbonitrile (**3**). The reaction is very sensitive to the presence of moisture in the pyridine, which can cause hydrolytic splitting of the formed triazine ring. The traces of side product were removed by thorough washing of crude triazine **3** with acetic acid. In the next step, the nitro group of **3** was reduced to the corresponding amino derivative **4**. For the reduction, we used ferrous hydroxide, which is heavily employed for such type of synthesis in our laboratory. It is very convenient to prepare and is selective to nitro group only. However, it was necessary to wash the ferric hydroxide precipitate thoroughly since a lot of the desired amino derivative can be adsorbed on the huge surface of the hydroxide.

The second 6-azauracil nucleus was built in similar way as the first one. For the cyclization of hydrazone **5** to the *N*-[3,5-bis(6-azauracil)phenyl]acetamide (**6**), the alkaline cyclization in a solution of sodium carbonate at a room temperature was used. In this way, we received the desired derivative **6** in a very good yield.

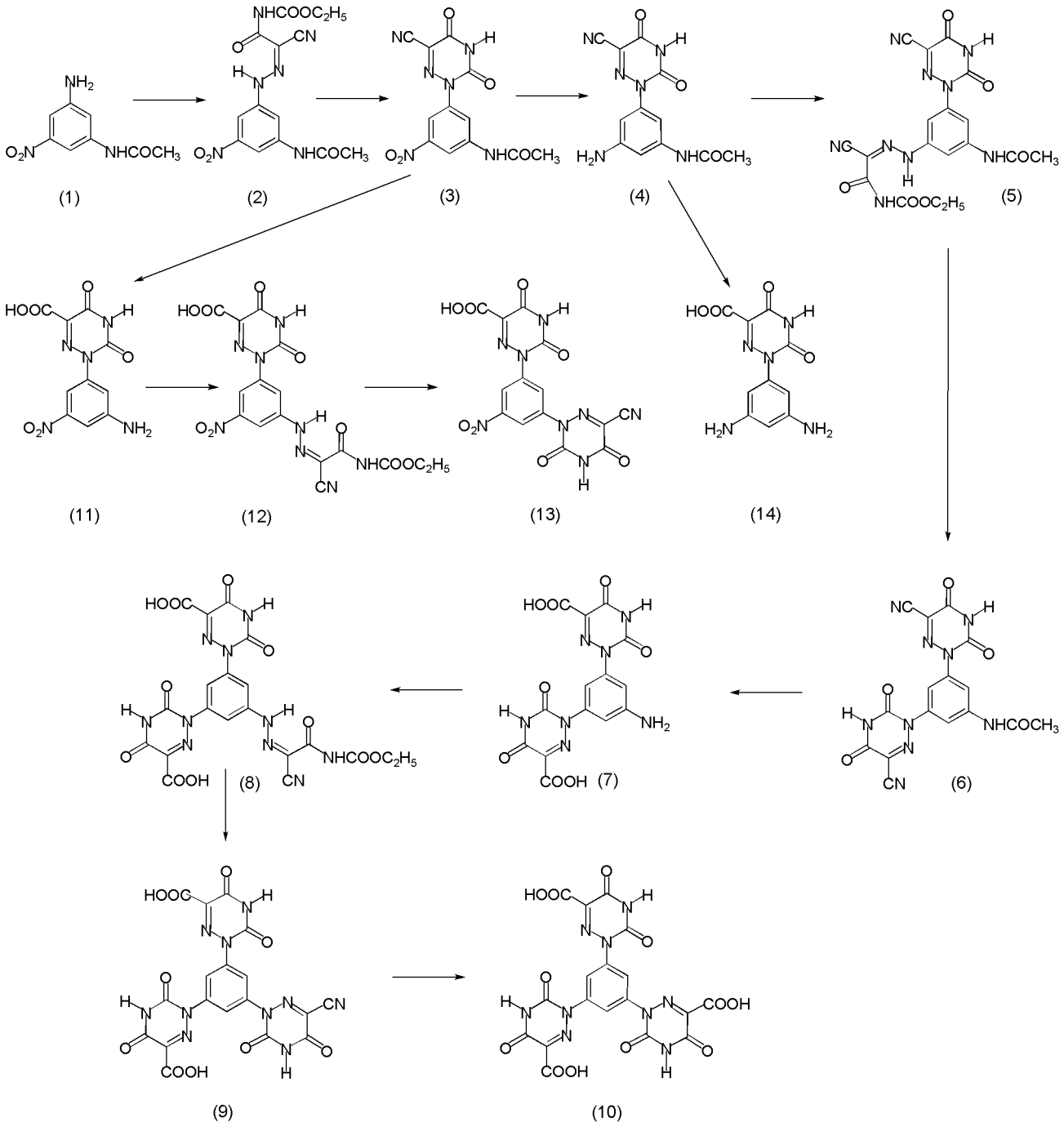
The protecting acetyl group was removed by acidic hydrolysis in hydrochloric acid. During this step, the nitrile groups were hydrolyzed to carboxyl groups. The desired amine **7** was isolated from the reaction mixture as the hydrochloride salt.

The third 6-azauracil nucleus was built in the same way as the second one *via* a hydrazone **8** that was again cyclized in alkaline solution of sodium carbonate to the desired triple 6-azauracil derivative **9**. The last nitrile group of derivative **9** was hydrolyzed in a mixture of acetic acid and hydrochloric acid resulting in symmetrical tris carboxylic acid **10**.

During the synthesis of desired amino compounds **7** or triple 6-azauracil derivative **9**, other synthetic ways were also studied. One of them began with the acetyl derivative **3** that was hydrolyzed by boiling in hydrochloric acid to the amino acid **11**. This amino derivative was used for the preparation of the double 6-azauracil derivative **13** *via* hydrazone **12**. The cyclization of hydrazone proceeded again by reflux of its pyridine solution. However, further reduction of nitro group of derivative **13** to the desired amino derivative failed due to isolation problems of the amino compound from the reaction mixture.

The other possible alternative way lead through diamino derivative **14**, which was prepared by acidic hydrolysis of amino derivative **4**. The further step should have employed the double diazotation and further coupling with ethyl cyanoacetylcarbamate to get the double hydrazono derivative. Unfortunately, the procedure failed.

Due to the free rotation of 6-azauracil nuclei around single benzene-6-azauracil bond, all double 6-azauracil derivatives (**6-8**, **13**) and both triple 6-azauracil derivatives (**9,10**) can assume various space conformations with



changing distance of 6-azauracil hydrogen atoms so they could bind into various substrates.

EXPERIMENTAL

The melting points were determined on a Boetius stage and are not corrected. The infrared spectra were measured using KBr disc technique and scanned on an ATI Unicam Genesis FTIR instrument. Wave numbers are in cm^{-1}. Elemental analyses were performed by using an EA 1108 Elemental Analyser (Fison Instrument). NMR spectra were measured on a Bruker AMX-360 (360 MHz) and Varian Unity+ 300 (300 MHz) spectrometers in DMSO-d_6 solutions; the chemical shifts δ are reported in ppm.

3-Amino-5-nitroacetanilide (**1**).

Ethanolic solution of $(NH_4)_2S$ was prepared in advance in this manner: A solution of 54 ml of 26% ammonia in 100 ml of 96%

ethanol was saturated under cooling with 10.5 g (0.3 mol) of sulphane. Resulting solution contains 0.14 g (2.05 mmoles) of $(NH_4)_2S$ in 1 ml.

A solution of 1.86 g (10 mmoles) of 3,5-dinitroaniline in 7 ml of acetanhydride was heated for 1 hour at 105 °C on an oil bath. Then, the resulting solution was poured into 370 ml of ice water. The precipitated solid was collected by suction and washed with water. Crude *N*-3,5-dinitrophenylacetamide was dissolved in 60 ml of ethanol and the solution was allowed to reflux. Into the boiling solution, 15 portions of $(NH_4)_2S$ (prepared as described above) was added in course of 75 minutes (each portion = 1 ml of $(NH_4)_2S$ solution). Then, the reaction mixture was allowed to reflux for 30 minutes then cooled and filtered. The filtrate was taken down on a boiling water bath. The residue was mixed with 6 ml of 36% HCl and 50 ml of water and the mixture was filtered. The filtrate was neutralized using 10% NaOH solution. The next day, the precipitated solid was collected by suction, washed with water and in air. Double recrystallization from water afforded orange solid with overall yield 70 %, mp 205-206 °C (ref. 204-205 °C [6]).

Anal. Calcd. for $C_8H_9N_3O_3$ (195.8): C, 49.23; H, 4.62; N, 21.54. Found: C, 49.26; H, 4.18; N, 21.29.

Ethyl 3-Acetamino-5-nitrophenylhydrazonocyanoacetylcarbamate (**2**).

A solution of 80 mg of $NaNO_2$ (1.15 mmol) in 3 ml of ice-cold water was added drop wise at 0-5 °C to a pre-cooled solution of 196 mg of amine **1** (1 mmol) in a mixture of 2.5 ml of 98% acetic acid, 3 ml of 36% hydrochloric acid and 15 ml of water. Reaction mixture was then left to stand in an ice bath for another 20 minutes. Then, the solution of diazonium salt was added drop wise to a cooled solution that was prepared in this manner: 500 mg (3 mmoles) of ethyl cyanoacetylcarbamate was dissolved in 230 ml of hot water and, after cooling to 0 °C, 10 g of sodium acetate was added. The reaction mixture was left to stand at 0-5 °C. The next day, the precipitated solid was collected by suction, thoroughly washed with water and dried in air to give 353.6 mg (97 %) of hydrazone **2**; mp 218-220 °C (ethanol); ^{1}H-nmr: δ 1.32 (t, 3H, J=7.3, CH_3); 2.15 (s, 3H, $COCH_3$); 4.24 (q, 2H, J=7.3, CH_2); 8.25 (m, 2H, J=2.1, H_2+H_4); 8.33 (t, 1H, J=2.1, H_6); 10.53 (s, 1H, NH); 10.88 (s, 1H, NH); 12.47 (s, 1H, NH); ir: 3334, 3223, 3098, 2990, 2223, 2191, 1765, 1681, 1607, 1541, 1488, 1447, 1371, 1348, 1296, 1266, 1235, 1215, 1159, 1131, 1025, 989, 920, 879, 779, 745, 674, 643, 574, 538.

Anal. Calcd. for $C_{14}H_{14}N_6O_6$ (362.2): C, 46.41; H, 3.87; N, 23.21. Found: C, 46.81; H, 3.90; N, 23.49.

2-(3-Acetamino-5-nitrophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-carbonitrile (**3**).

A solution of 362 mg (1 mmol) of hydrazone **2** in 30 ml of dry pyridine was refluxed for 20 hours and then taken down *in vacuo*. The residue was mixed with little water and a few drops of 36% HCl to adjust pH. The solid was collected with suction and mixed with 5 ml of 98% acetic acid. The mixture was refluxed for 5 minutes and filtered. The filtrate contains pure hydrazonecyanoacetamide derivative arose by hydrolytic splitting of triazine **3**. The filtration cake of pure triazine **3** was washed with water and dried in air to give 246 mg (75 %) of triazine **3**; mp 284 °C (decomp.) (ethanol); ^{1}H-nmr: δ 2.17 (s, 3H, $COCH_3$); 8.08 (t, 1H, J=2.0, H_2); 8.21 (t, 1H, J=2.0, H_4); 8.67 (t, 1H, J=2.0, H_6); 10.73 (s, 1H, NH); 13.23 (br, 1H, NH); ir: 3370, 3122, 2990, 2813, 2244, 1750, 1730, 1674, 1622, 1533, 1462, 1426, 1334, 1285, 1221, 1231, 1167, 1096, 1020, 895, 797, 750, 720, 689, 573, 548, 435.

Anal. Calcd. for $C_{12}H_8N_6O_5 \cdot H_2O$ (333.3): C, 43.11; H, 2.99; N, 25.15. Found: C, 42.90; H, 2.56; N, 25.35.

2-(3-Acetamino-5-aminophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-carbonitrile (**4**).

A solution of 2.225 g (8 mmoles) of $FeSO_4 \cdot 7H_2O$ in 8 ml of water was added to the warm solution of 2.525 g (8 mmoles) of $Ba(OH)_2 \cdot 8H_2O$ in 18 ml of warm water. The mixture of precipitated $Fe(OH)_2$ and $BaSO_4$ was added in small portions to the solution of 332 mg (1 mmol) of nitro triazine **3** and 2 ml of 25% ammonia in 30 ml of water. The reaction mixture was then heated for 5 minutes at 60 °C and then on a boiling water bath for 60 minutes with continuous stirring. Hot reaction mixture was then filtered and the precipitate was washed thoroughly with a warm 1% ammonia solution. Combined filtrates were then taken down *in vacuo*. The residue was mixed with little warm water, ammonia and charcoal and resulting solution was filtered. The filtrate was then acidified with 98% acetic acid. The next day the precipitated solid was collected by suction, washed with water and dried in air to give 249 mg (75 %) of aminotriazine **4**. mp 229-230 °C (water); ^{1}H-nmr: δ 2.05 (s, 3H, $COCH_3$); 5.50 (br, 2H, NH_2); 6.39 (t, 1H, J=1.9, H_4); 6.90 (t, 1H, J=1.9, H_6); 6.97 (t, 1H, J=1.9, H_2); 9.88 (s, 1H, NH); 12.95 (br, 1H, NH); ir: 3395, 2791, 2244, 1709, 1684, 1620, 1599, 1554, 1486, 1444, 1371, 1298, 1155, 996, 849, 577, 553.

Anal. Calcd. for $C_{12}H_8N_6O_5 \cdot H_2O$ (334.3): C, 43.12; H, 3.02; N, 25.14. Found: C, 43.32; H, 3.41; N, 24.99.

Ethyl 3-(3,5-Dioxo-2,3,4,5-tetrahydro-6-cyano-1,2,4-triazin-2-yl)-5-acetaminophenylhydrazonocyanoacetylcarbamate (**5**).

A solution of 30 mg (0.45 mmol) of $NaNO_2$ in 1 ml of ice-cold water was added drop wise at 0-5 °C to a pre-cooled solution of 100 mg (0.32 mmol) of aminotriazine **4** in a mixture of 4 ml of 98% acetic acid, 0.5 ml of 36% hydrochloric acid and 0.5 ml of water. Reaction mixture was then left to stand in an ice bath for another 20 minutes. Then, the solution of diazonium salt was added drop wise to a cooled solution that was prepared in this manner: 144 mg (1.1 mmol) of ethyl cyanoacetylcarbamate was dissolved in 60 ml of hot water and, after cooling to 0 °C, 4 g of sodium acetate was added. The reaction mixture was left to stand at 0-5 °C. The next day, the precipitated solid was collected by suction, thoroughly washed with water and dried in air to give 137 mg (91 %) of hydrazone **5**; mp 235 °C (decomp.) (ethanol); ^{1}H-nmr: δ 1.30 (t, 3H, J=7.0, CH_3); 4.23 (q, 2H, J=7.0, CH_2); 2.12 (s, 3H, $COCH_3$); 7.56 (t, 1H, J=2.0, H_4); 7.61 (t, 1H, J=2.0, H_2); 7.97 (t, 1H, J=2.0, H_6); 10.31 (s, 1H, NH); 10.51 (s, 1H, NH); 12.39 (br, 1H, NH); 12.72 (br, 1H, NH); ir: 3353, 2988, 2215, 1779, 1712, 1674, 1618, 1554, 1481, 1415, 1324, 1279, 1195, 1153, 1023, 918, 868, 692, 603, 563, 535, 464.

Anal. Calcd. for $C_{18}H_{15}N_9O_6 \cdot 3H_2O$ (507.2): C, 42.60; H, 4.14; N, 24.85. Found: C, 42.78; H, 4.12; N, 24.74.

3,5-Bis(3,5-dioxo-2,3,4,5-tetrahydro-6-cyano-1,2,4-triazin-2-yl)acetanilide (**6**).

A mixture of 100 mg (0,2 mmol) of hydrazone **5** and 72 mg (0.68 mmol) of Na_2CO_3 in 15 ml of water was left to stand for 10 days with intermittent stirring. Then, after addition of little charcoal, the mixture was filtered and filtrate was acidified with 12%

HCl to pH=1. The next day, the precipitated solid was collected by suction, washed with water and dried in air to give 75 mg (88 %) of double triazine **6**. mp >360 °C (water/ethanol); ^{1}H-nmr: δ 2.11 (s, 3H, $COCH_3$); 7.42 (t, 1H, J=2.0, H_4); 7.92 (t, 1H, J=2.0, H_6); 7.94 (t, 1H, J=2.0, H_2); 10.47 (s, 1H, NH); 12.69 (br, 1H, NH); 13.08 (br, 1H, NH); ir: 3493, 3382, 2979, 2786, 2244, 1720, 1613, 1557, 1475, 1424, 1307, 1159, 1076, 1016, 978, 880, 807, 739, 667, 585, 566, 476.

Anal. Calcd. for $C_{16}H_9N_9O_5$•H_2O (425.3): C, 45.18; H, 2.61; N, 29.64. Found: C, 45.47; H, 3.02; N, 29.34.

3,5-Bis(3,5-dioxo-2,3,4,5-tetrahydro-6-carboxy-1,2,4-triazin-2-yl)-aniline (**7**).

A solution of 106 mg (0.25 mmol) of triazine **6** in 10 ml of 20% HCl was refluxed for 4 hours. Upon cooling, needles of hydrochloride precipitated from reaction mixture. The next day, the precipitate was collected by suction and dried in air to give 93 mg (81 %) of amine **7** hydrochloride; mp >360 °C (10% HCl); ^{1}H-nmr: δ 6.75 (d, 2H, J=1.9, H_2+H_6); 6.77 (t, 2H, J=1.9, H_4); 12.55 (br, 2H, 2xNH); ir: 3448, 3082, 2833, 1729, 1618, 1553, 1410, 1311, 1154, 1055, 930, 870, 817, 740, 657, 588, 570, 460.

Anal. Calcd. for $C_{14}H_9N_7O_8$•HCl•H_2O (457.75): C, 36.74; H, 3.02; N, 21.42. Found: C, 36.44; H, 2.64; N, 21.42.

Ethyl 3,5-Bis(3,5-dioxo-2,3,4,5-tetrahydro-6-carboxy-1,2,4-triazin-2-yl) phenylhydrazonocyanoacetylcarbamate (**8**).

A solution of 25 mg (0.3 mmol) of $NaNO_2$ in 2 ml of ice-cold water was added drop wise at 0-5 °C to a pre-cooled solution of 139 mg (0.25 mmol) of amine **7** in 3 ml of 36% hydrochloric acid and 5 ml of water. Reaction mixture was then left to stand in an ice bath for another 30 minutes. Then, the solution of diazonium salt was added drop wise to a cooled solution that was prepared in this manner: 100 mg (0.7 mmol) of ethyl cyanoacetylcarbamate was dissolved in 100 ml of hot water and, after cooling to 0 °C, 4 g of sodium acetate was added. The reaction mixture was left to stand at 0-5 °C. The next day, the precipitated solid was collected by suction, thoroughly washed with water and dried in air to give 139 mg (98 %) of hydrazone **8**; mp >360 °C (ethanol); ^{1}H-nmr: δ 1.23 (t, 3H, J=7.2, CH_3); 4.13 (q, 2H, J=7.2, CH_2); 7.31 (t, 1H, J=1.8, H_4); 7.60 (d, 2H, J=1.8, H_2+H_6); 9.38 (br, 1H, NH); ir: 3442, 3082, 2988, 2799, 2219, 1777, 1705, 1614, 1444, 1414, 1371, 1304, 1279, 1176, 1155, 1017, 962, 892, 821, 735, 634, 564.

Anal. Calcd. for $C_{20}H_{14}N_{10}O_{11}$ (570.4): C, 42.12; H, 2.47; N, 24.56. Found: C, 42.45; H, 2.80; N, 24.49.

2-[3,5-Bis(3,5-dioxo-2,3,4,5-tetrahydro-6-carboxy-1,2,4-triazin-2-yl)phenyl]-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-carbonitrile (**9**).

A mixture of 114 mg (0.2 mmol) of hydrazone **8** and 106 mg (1 mmol) of Na_2CO_3 in 20 ml of water was left to stand for 10 days with intermittent stirring. Then, after addition of little charcoal, the mixture was filtered and filtrate was acidified with 12% HCl to pH=1. The next day, the precipitated solid was collected by suction, washed with water and dried in air to give 79 mg (75 %) of triple triazine **9**; mp >360 (water/ethanol); ^{1}H-nmr: δ 7.78 (d, 2H, J=2.0, H_2+H_6); 7.85 (t, 1H, J=2.0, H_4); ir: 3444, 3209, 2242, 1724, 1612, 1560, 1440, 1408, 1305, 1152, 1029, 818, 739, 626, 567.

Anal. Calcd. for $C_{18}H_8N_{10}O_{10}$•H_2O (532.4): C, 39.86; H, 1.86; N, 25.83. Found: C, 39.58; H, 2.02; N, 25.97.

1,3,5-Tris(3,5-dioxo-2,3,4,5-tetrahydro-6-carboxy-1,2,4-triazin-2-yl)benzene (**10**).

A solution of 107 mg (0.2 mmol) of triazine **9** in a mixture of 8 ml of 98% acetic acid and 8 ml of 36 % HCl was refluxed for 5 hours and then taken down on a boiling water bath. The solid was mixed with little water, collected by suction, washed with water and dried in air to give 108 mg (91 %) of triple triazino carboxylic acid **10**; mp 297-298 °C (ethanol/water); ^{1}H-nmr: 7.80 (s, 3H, H_2+H_4+H_6); ir: 3575, 3465, 3345, 3240, 1734, 1691, 1617, 1443, 1291, 1158, 1028, 812, 623.

Anal. Calcd. for $C_{18}H_9N_9O_{12}$•$3H_2O$ (597.4): C, 36.19; H, 2.53; N, 21.10. Found: C, 36.20; H, 2.37; N, 20.99

2-(3-Amino-5-nitrophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-carboxylic Acid (**11**).

A mixture of 400 mg (1.2 mmol) of triazine **3** and 20 ml of 20% HCl was refluxed for 5 hours. After the addition of little charcoal, the mixture was filtered and the filtrate was taken down on a boiling water bath. The residue was mixed with 15 ml of 20% Na_2CO_3 solution and filtered. The filtrate was acidified with 9% HCl. The next day, the precipitated solid was collected by suction, thoroughly washed with water and dried in air to give 326 mg (83 %) of acid **11**. mp 235 °C (decomp.) (water); ^{1}H-nmr: δ 6.21 (br, 2H, NH_2); 7.16 (t, 1H, J=2.1, H_2); 7.47 (t, 1H, J=2.1, H_4); 7.53 (t, 1H, J=2.1, H_6); 12.59 (br, 1H, NH); ir: 3425, 3356, 3230, 3037, 2807, 1720, 1704, 1637, 1537, 1401, 1358, 1300, 1157, 805, 768, 637, 574.

Anal. Calcd. for $C_{10}H_7N_5O_6$•$2H_2O$ (329.2): C, 36.48; H, 3.37; N, 21.28. Found: C, 36.75; H, 2.98; N, 21.37.

Ethyl 3-Nitro-5-(3,5-dioxo-2,3,4,5-tetrahydro-6-carboxy-1,2,4-triazin-2-yl)phenylhydrazonocyanacetylcarbamate (**12**).

A solution of 160 mg (2.32 mmoles) of $NaNO_2$ in 5 ml ice-cold water was added drop wise at 0-5 °C to a pre-cooled solution of 660 mg (2 mmoles) of amine **11** in a mixture of 10 ml of 36% hydrochloric acid and 30 ml of water. Reaction mixture was then left to stand in an ice bath for another 30 minutes. Then, the solution of diazonium salt was added drop wise to a cooled solution that was prepared in this manner: 900 mg (5.4 mmoles) of ethyl cyanoacetylcarbamate was dissolved in 250 ml of hot water and, after cooling to 0 °C, 20 g of sodium acetate was added. The reaction mixture was left to stand at 0-5 °C. The next day, 15 ml of 36% HCl was added to the solution of hydrazone and the precipitated solid was collected by suction, washed thoroughly with water and dried in air to give 541 mg (57 %) of hydrazone **12**. mp 226-228 °C (decomp.) (ethanol); ^{1}H-nmr: δ 1.32 (t, 3H, J=7.1, CH_3); 4.26 (q, 2H, J=7.1, CH_2); 8.21 (t, 1H, J=2.0, H_2); 8.32 (t, 1H, J=2.0, H_4); 8.73 (t, 1H, J=2.0, H_6); 11.03 (s, 1H, NH); 12.68 (s, 1H, NH); ir: 3559, 3417, 3096, 2220, 1771, 1716, 1709, 1626, 1541, 1498, 1472, 1466, 1405, 1353, 1317, 1279, 1239, 1215, 1184, 1150, 1094, 1024, 922, 668, 571.

Anal. Calcd. for $C_{10}H_{12}N_8O_9$•H_2O (478.3): C, 40.17; H, 2.93; N, 23.43. Found: C, 39.75; H, 2.64; N, 23.71.

2-[3-Nitro-5-(3,5-dioxo-2,3,4,5-tetrahydro-6-cyano-1,2,4-triazin-2-yl)phenyl]-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-carboxylic Acid (**13**).

A solution of 160mg (0.33 mmol) of hydrazone **12** in 40 ml of dry pyridine was refluxed for 21 hours and then taken down *in vacuo*. The residue was mixed with little water and a few drops of 36% HCl to adjust pH. The solid was collected with suction, washed with water and dried in air to give 123 mg

(87 %) of double triazine **13**; mp 205 °C (decomp.) (water); ^{1}H-nmr: δ 8.21 (t, 1H, J=2.0, H_4); 8.47 (t, 1H, J=2.0, H_2); 8.59 (t, 1H, J=2.0, H_6); 12.73 (br, 1H, NH); 13.95 (br, 1H, NH); ir: 3012, 2795, 2244, 1715, 1627, 1540, 1409, 1357, 1303, 1182, 1151, 1094, 891, 748, 568.

Anal. Calcd. for $C_{14}H_6N_8O_8 \cdot H_2O$ (432.2): C, 38.89; H, 1.85; N, 25.93. Found: C, 38.90; H, 1.76; N, 25.55.

2-(3,5-Diaminophenyl)-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-carboxylic Acid (**14**).

A solution of 108 mg (0.25 mmol) of amine **4** in 10 ml of 20% HCl was refluxed for 4 hours. Then, after the addition of little charcoal, the mixture was filtered. After standing overnight at 0-5 °C, the solid precipitated from the solution. The solid was collected with suction, washed with ether and dried in air to give 68 mg (82 %) of diamine **14** dihydrochloride; mp >360 °C (20% HCl); ^{1}H-nmr: δ 6.71 (t, 1H, J=1.8, H_4); 6.80 (d, 2H, J=1.8, H_2+H_6); 12.55 (br, 1H, NH); ir: 3456, 2963, 2795, 2569, 1720, 1644, 1562, 1518, 1405, 1339, 13002, 1213, 1157, 1069, 855, 732, 670, 648, 592, 540.

Anal. Calcd. for $C_{10}H_9N_5O_4 \cdot 2HCl$ (336.1): C, 35.73; H, 3.30; N, 20.83. Found: C, 35.42; H, 3.44; N, 20.98.

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