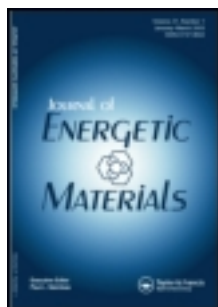


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### 1,2,4,5-tetrazine based energetic materials

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## **1,2,4,5-TETRAZINE BASED ENERGETIC MATERIALS**

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### **ABSTRACT**

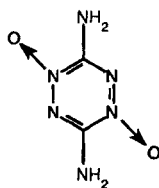
The synthesis and properties of several new energetic 1,2,4,5-tetrazine derivatives are described. These include energetic salts of 3,6-dihydrazino-1,2,4,5-tetrazine and several symmetrically and unsymmetrically substituted tetrazines with energetic substituents, in addition to a new nitro-tetrazine.

### **INTRODUCTION**

High-nitrogen energetic materials offer distinct advantages to conventional carbon-based energetic materials. High-nitrogen materials have a large number of N-N and C-N bonds and therefore possess large positive heats of formation. The low percentage of carbon and hydrogen in these compounds has a double positive effect: it enhances the density and allows a good oxygen balance to be achieved more easily. However, since nitrogen does not catenate well, several nitrogens in a row should be avoided, as these compounds are typically very sensitive to impact.

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The tetrazine ring is only exceeded in its nitrogen content by tetrazoles and yet this ring system has been relatively unexploited for use in energetic materials. The only tetrazine extensively evaluated as an explosive has been 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide or LAX-112 (1).



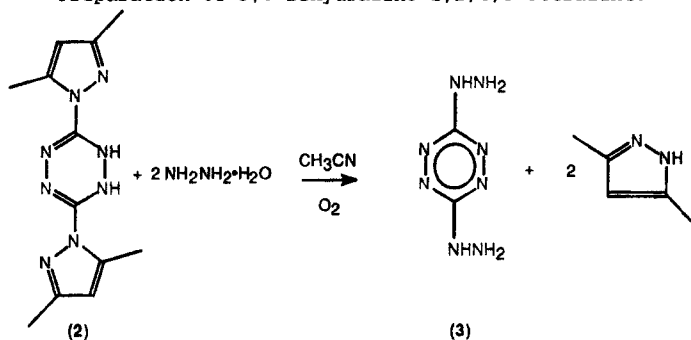
(1)  
LAX-112

In the process of scaling up (1) for evaluation, large quantities of intermediates were prepared. This allowed for a more thorough investigation by permitting access to materials containing the tetrazine ring.

### RESULTS

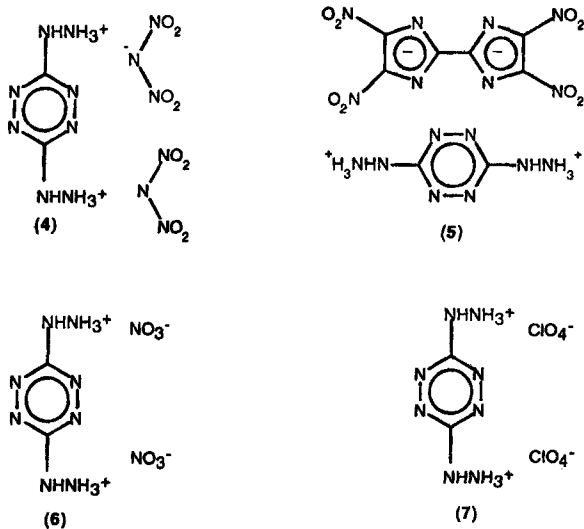
More than 75 lb of the di-hydro compound (2) was available from the scale up process of (1), which is easily prepared from triaminoguanidine hydrochloride and 2,4-pentanedione.<sup>1</sup> Treatment of (2) with hydrazine hydrate in the presence of atmospheric oxygen resulted not only in the displacement of 3,5-dimethylpyrazole but also in aromatization of the ring (FIGURE 1) to give an excellent yield of the previously known 3,6-dihydrazino-1,2,4,5-tetrazine (3).<sup>2,3</sup>

FIGURE 1  
Preparation of 3,6-Dihydrazino-1,2,4,5-Tetrazine.



Previous to the discovery of the air oxidation for the preparation of (3), a separate oxidation of (2) was required.<sup>1</sup> Dinitrogen tetroxide in DMF or NMP was used to aromatize the ring followed by treatment with hydrazine to produce (3). Compound (3) is best described as a highly energetic fuel having a heat of formation measured at +128 kcal/mol. Pellets 0.5 inches in diameter will detonate unconfined if the density is less than 97% of the theoretical maximum of 1.61 g/cm<sup>3</sup>. Pellets 0.25 inches in diameter will not detonate. This material calculates to perform well in both rocket and gun propellants. Compound (3) has also been utilized for smoke-free pyrotechnics.<sup>2</sup> The dihydrazino derivative is sparingly soluble in water, but dissolves readily in acidic media. This allowed for the preparation of the energetic salts of (3), namely the bis-dinitramide (4), tetranitro-biimidazolite (5), di-nitrate (6), and the di-perchlorate (7) (FIGURE 2).

FIGURE 2  
Energetic Salts of 3,6-Dihydrazino-1,2,4,5-Tetrazine



Some of the physical and explosive properties of compounds (4)-  
(7) are given in TABLE 1.

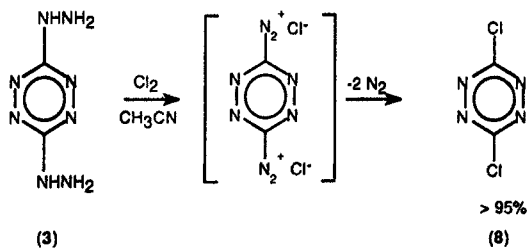
TABLE 1  
Physical and Explosive Properties of the Energetic Salts of 3,6-Dihydrazino-1,2,4,5-Tetrazine

Compound	DTA Exotherm [°C]	Drop Weight Impact Height [cm]	Density (flotation) [g/cm <sup>3</sup> ]
(4)	136	11	1.82
(5)	217	60	1.83
(6)	117	16	1.80
(7)	200	13	1.96

3,6-Dihydrazino-1,2,4,5-tetrazine (3) is easily converted  
to 3,6-dichloro-1,2,4,5-tetrazine (8) via the diazonium salt by

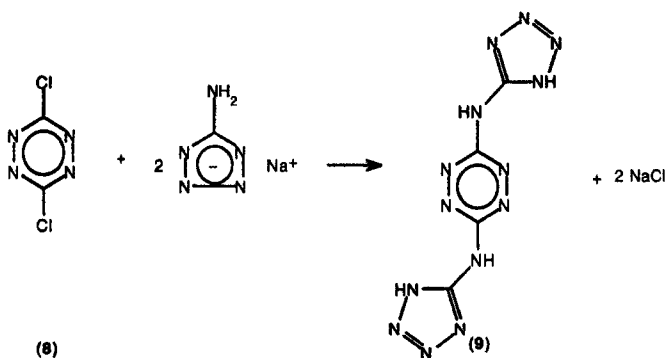
oxidation with chlorine gas (FIGURE 3).<sup>4</sup> The previous preparation of (8) was tedious and time consuming.<sup>5</sup>

FIGURE 3  
Preparation of 3,6-Dichloro-1,2,4,5-Tetrazine



3,6-Dichloro-1,2,4,5-tetrazine is a powerful electrophile being similar in reactivity to picryl fluoride and readily condenses with 2 equivalents of the sodium salt of 5-amino-tetrazole to yield the di-substituted compound, 3,6-bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (9) (FIGURE 4).

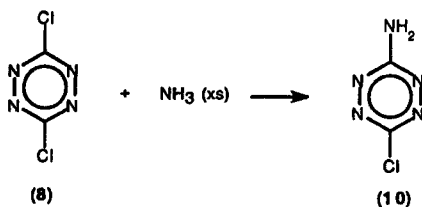
FIGURE 4  
Condensation Reaction of 3,6-Dichloro-1,2,4,5-Tetrazine with Sodium 5-Aminotetrazolate



The structure of this compound was determined by x-ray crystallography of its solvate with DMSO.<sup>15</sup> Compound (9) has a very high heat of formation measured at +211 kcal/mole.

Unsymmetrically substituted tetrazines were prepared from 3-amino-6-chloro-1,2,4,5-tetrazine (10) which was obtained from (8) by treatment with excess ammonia gas (FIGURE 5).

FIGURE 5  
Preparation of 3-Amino-6-Chloro-1,2,4,5-Tetrazine

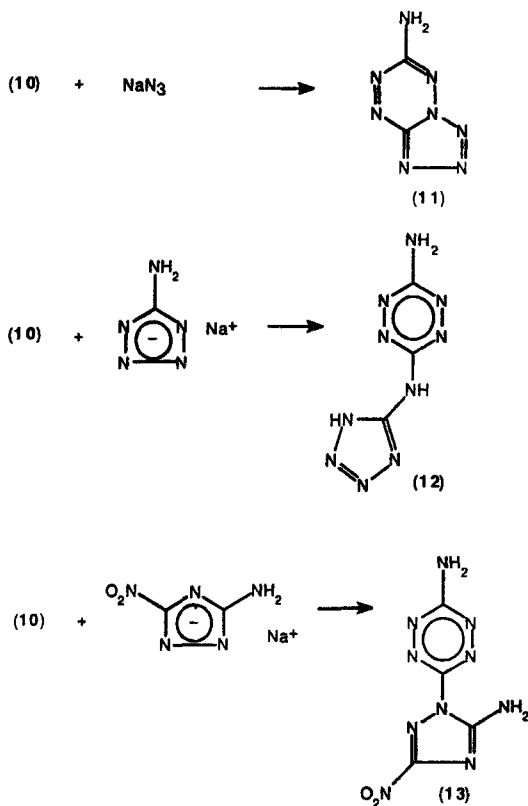


The remaining leaving group on (10) was very difficult to displace. These reactions required several days at reflux to obtain a reasonable yield. The energetic nucleophiles used were azide and the sodium salts of 5-aminotetrazole and 5-amino-3-nitro-1,2,4-triazole (ANTA) to produce compounds (11)-(13) (FIGURE 6).

The structures of compounds (12) and (13) were not established by x-ray crystallography but were deduced from the analogous bis-substituted compounds. When the sodium salt of ANTA is used as a nucleophile it has been shown to substitute through the N-1 nitrogen.<sup>6</sup> The sodium salt of 5-amino-tetrazole was shown

to substitute at the 5-amino position earlier in this paper as shown in structure (9).

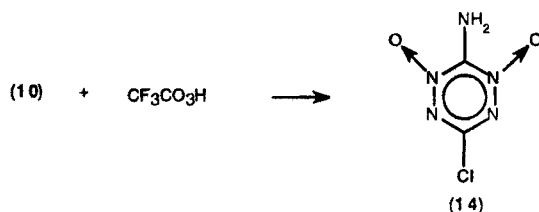
FIGURE 6  
Preparation of Unsymmetrical Amino-Tetrazines



Oxidation of (10) with peroxytrifluoroacetic acid produced the di-N-oxide (14) (FIGURE 7). The remaining leaving group on (14) could not be displaced even with extended reaction times.

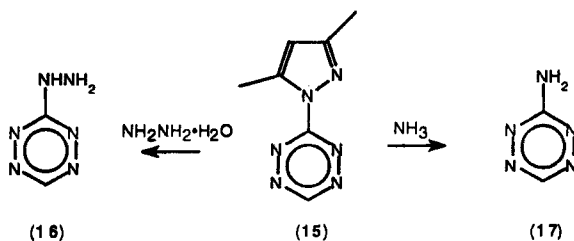


FIGURE 7  
Preparation of 3-Amino-6-Chloro-1,2,4,5-Tetrazine-2,4-Dioxide



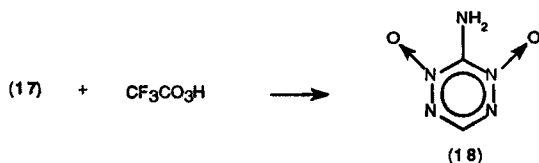
We have previously reported the synthesis of 3-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (15).<sup>7</sup> Compound (15) was readily converted to the amine (17) and hydrazine (16) derivatives (FIGURE 8).

FIGURE 8  
Preparation of Mono-Substituted Tetrazines



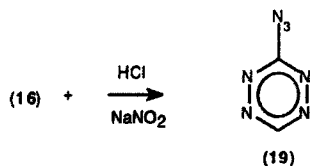
Compound (17) was oxidized with peroxytrifluoroacetic acid to give the dioxide (18) (FIGURE 9).

FIGURE 9  
Oxidation of 3-Amino-1,2,4,5-Tetrazine with Peroxytrifluoroacetic Acid



The energetic salts (nitrate and perchlorate) of (16) were extremely hygroscopic and work on them was abandoned. Diazotization of (16) produced the previously unknown 3-azido-1,2,4,5-tetrazine (19) (FIGURE 10).

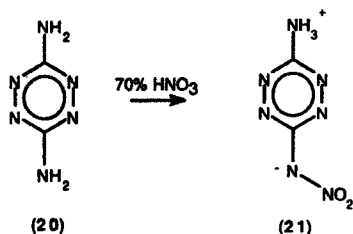
FIGURE 10  
Preparation of 3-Azido-1,2,4,5-Tetrazine



Compound (19) was determined to be in the azido-form rather than the fused tetrazolo-form shown for compound (11)<sup>8</sup> by infrared spectroscopy as it exhibited a strong absorption band at 2150  $\text{cm}^{-1}$ .

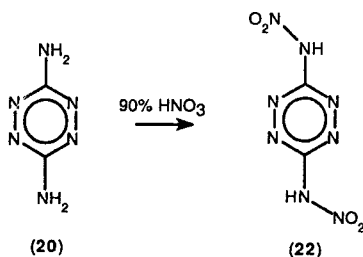
The reaction of 3,6-diamino-1,2,4,5-tetrazine (20) with nitric acid was first reported in 1979, by Guither et al.,<sup>9</sup> to yield the di-nitrate salt. We have shown that this reaction actually yields the zwitterionic mono-nitramine (21) (FIGURE 11).

FIGURE 11  
Preparation of 3-Amino-6-Nitramino-1,2,4,5-Tetrazine



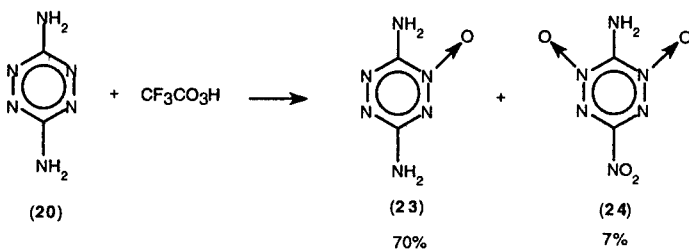
Chinese workers have reported the synthesis of the dinitramine (22) with concentrated nitric acid.<sup>10</sup> We have found that nitric acid of at least 90% was required for this transformation to occur (FIGURE 12). Compound (22) was readily hydrolyzed back to starting material with even traces of moisture.

FIGURE 12  
Preparation of 3,6-Bis-Nitramino-1,2,4,5-Tetrazine



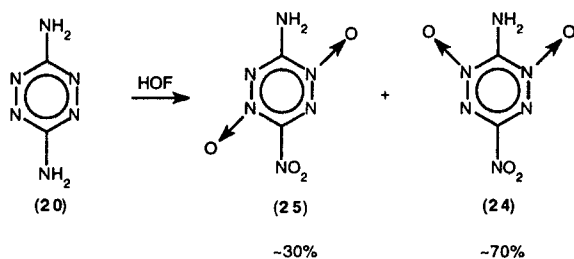
It has previously been reported by Coburn et al. that the oxidation of (20) with peroxytrifluoroacetic acid yielded the mono-N-oxide (23) and a small amount of the nitro-compound (24) (FIGURE 13).<sup>11</sup>

FIGURE 13  
Oxidation of 3,6-Diamino-1,2,4,5-Tetrazine with Peroxytrifluoroacetic Acid



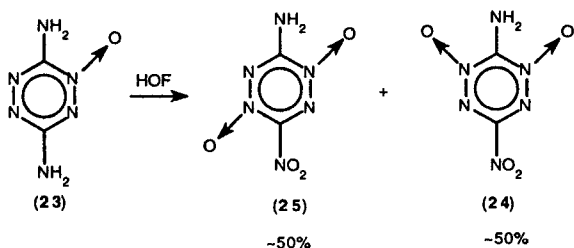
We found that the oxidation of (20) with hypofluorous acid (HOF),<sup>12,13</sup> which is a much stronger oxygen transfer reagent, yielded two main products in addition to small quantities of LAX-112 (1), one was compound (24) the other was the isomeric nitrotetrazine (25) (FIGURE 14).

FIGURE 14  
Oxidation of 3,6-Diamino-1,2,4,5-Tetrazine with Hypofluorous Acid



Similarly oxidation of (23) with hypofluorous acid yielded the same two products but in different ratios (FIGURE 15).

FIGURE 15  
Oxidation of 3,6-Diamino-1,2,4,5-Tetrazine-1-Oxide with Hypofluorous Acid



Oxidation of LAX-112 (1) with hypofluorous acid resulted in very little conversion due to the low solubility of (1) in the oxidizing medium.

### **EXPERIMENTAL**

All starting materials were obtained from commercial sources or prepared from the referenced literature. All NMR spectra were obtained on a JEOL GSX-270 spectrometer, and chemical shifts are reported relative to internal tetramethylsilane. Elemental analyses were performed by W.F. King at Los Alamos National Laboratory. Thin layer chromatography was performed on MK6F silica gel plates (Whatman) and visualized by UV radiation. All melting points were determined at 2°C/min with a Mettler FP1 apparatus and are corrected. IR spectra were obtained on a Bio-Rad FTS-40 FTIR spectrometer. Poor agreement between theoretical and measured results in elemental analysis may be explained by the well known problem of microanalysis of high-nitrogen content compounds. However all compounds were purified to the point that agreement to at least two elements was within 0.4%.

**3,6-Dihydrazino-1,2,4,5-tetrazine Bis-Dinitramide, (4).** Ammonium dinitramide (0.25 g, 2.01 mmol) was dissolved in 2 ml of water and loaded on a Dowex-W H<sup>+</sup>-form water column of approximately 20 ml of volume. The column was eluted with 3 column volumes of water. The solution of dinitramidic acid was neutralized by adding 3,6-dihydrazino-1,2,4,5-tetrazine (0.142 g,

1 mmol). The water was removed by rotary evaporation to afford the dinitramide salt in quantitative yield.

**3,6-Dihydrazino-1,2,4,5-tetrazine (4,4',5,5'-Tetranitro-2,2'-bi-imidazolate), (5).** To 4,4',5,5'-tetranitro-2,2'-bi-imidazole dihydrate (0.35 g, 1 mmol) dissolved in 8 ml of water was added 3,6-dihydrazino-1,2,4,5-tetrazine (0.142 g, 1 mmol). An orange precipitate formed immediately, which was filtered and air dried to give the salt in quantitative yield.

**3,6-Dihydrazino-1,2,4,5-tetrazine Di-nitrate, (6).** To nitric acid (1 M, 5 ml) was added 3,6-dihydrazino-1,2,4,5-tetrazine (0.355 g, 2.5 mmol). The solution was allowed to stand for 30 minutes and the solvent removed by rotary evaporation to afford the di-nitrate salt in quantitative yield.

**3,6-Dihydrazino-1,2,4,5-tetrazine Di-perchlorate, (7).** To perchloric acid (1 M, 5 ml) was added 3,6-dihydrazino-1,2,4,5-tetrazine (0.355 g, 2.5 mmol). The solution was allowed to stand for 30 minutes and the solvent removed by rotary evaporation to afford the di-perchlorate salt in quantitative yield.

**3,6-Dichloro-1,2,4,5-tetrazine, (8).** To 3,6-dihydrazino-1,2,4,5-tetrazine (3) (4.26 g, 30 mmol) was added to acetonitrile (75 ml). The suspension was stirred at room temperature as chlorine gas was bubbled into the slurry. After approximately 45 min a solution was obtained and the reaction was

complete. The solution was purged with air to remove any excess chlorine, filtered through a bed of Celite, and then concentrated under reduced pressure to yield 4.3 g (95%) of product identical in all respects to that previously reported.<sup>5</sup>

**3,6-Bis(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine, (9).** To a solution of 3,6-dichloro-1,2,4,5-tetrazine (1.51 g, 10 mmol) in acetonitrile (70 ml) was added the sodium salt of 5-aminotetrazole (2.14 g, 10 mmol). The mixture was refluxed for 24 hours then allowed to cool to room temperature. The suspension was centrifuged until the supernatant liquid was clear. The liquid was decanted and the brown solid washed successively with acetonitrile and water. With each wash the solid was separated from the solvent by centrifugation followed by decantation. The isolated crude yield was 1.5 g (60%), this material was recrystallized from DMSO/methanol yielding an orange brown powder mp 264°C dec; <sup>1</sup>H NMR (deuteriomethylsulfoxide-d<sub>6</sub>) 12.5 (br s, 4H); <sup>13</sup>C NMR (deuteriomethylsulfoxide-d<sub>6</sub>) 151.74, 158.25; IR (KBr) 3421, 3000, 1615, 1436, 1127 cm<sup>-1</sup>. A gas pycnometer density of 1.76 g/cm<sup>3</sup> was also determined and a drop height of 195 cm was measured (Type 12, HMX-24-27 cm).

Anal. Calcd for C<sub>4</sub>H<sub>4</sub>N<sub>14</sub>: C, 19.36; H, 1.63; N, 79.02. Found: C, 19.33; H, 1.56; N, 75.59.

**3-Amino-6-chloro-1,2,4,5-tetrazine, (10).** Ammonia was bubbled through a solution of 3,6-dichloro-1,2,4,5-tetrazine

(5 g, 33 mmol) in methyl t-butyl ether (150 ml) with stirring for 20 minutes. The slurry was filtered through a bed of Celite and the filtrate concentrated to yield 4.0 g (92%) of (10). An analytical sample was obtained by recrystallization from chloroform, mp 146-148°C;  $^1\text{H}$  NMR (deuteriomethylsulfoxide)  $\delta$  8.25 (s, 2H);  $^{13}\text{C}$  NMR (deuteriomethylsulfoxide)  $\delta$  159.5, 163.7; IR (KBr) 3312, 3192, 1618, 1507, 1391, 1193, 1054, 935  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_2\text{H}_2\text{N}_5\text{Cl}$ : C, 18.27; H, 1.53; N, 53.25.  
Found: C, 18.24; H, 1.40; N, 50.99.

**6-Amino-tetrazolo[1,5-b]-1,2,4,5-tetrazine, (11).**

To a solution of sodium azide (0.065 g, 1 mmol) in 80% aqueous ethanol (10 ml) was added (10) (0.132 g, 1 mmol). The solution was stirred 7 days at room temperature. The solution was then concentrated and treated with chloroform and filtered to yield a yellow crystalline material 83 mg, (60%); identical in all respects to that previously reported.<sup>8</sup>  $^1\text{H}$  NMR (deuterio-p-dioxane)  $\delta$  7.64 (s, 2H);  $^{13}\text{C}$  NMR (deuterio-p-dioxane)  $\delta$  150.8, 160.4; IR (KBr) 3400, 3324, 3236, 3173, 1700, 1636, 1557, 1319, 1250  $\text{cm}^{-1}$ .

**3-Amino-6-(1H-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine, (12).** To a solution of (10) (1.31 g, 10 mmol) in acetonitrile (50 ml) was added the sodium salt of 5-aminotetrazole (1.07 g, 10 mmol) and the mixture refluxed for 14 days. The suspension was filtered, washed with water and dried to yield 1.38 g (77%), mp 267°C dec;  $^1\text{H}$  NMR (deuteriomethylsulfoxide)  $\delta$  7.0 (s,



4H);  $^{13}\text{C}$  NMR (deuteriomethylsulfoxide) $\delta$  157.6, 159.7, 161.6; IR (KBr) 3515, 3369, 3305, 1594, 1492, 1432, 1067, 959  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_3\text{H}_4\text{N}_{10}$ : C, 20.00; H, 2.24; N, 77.76.

Found: C, 20.29; H, 2.07; N, 78.25.

**3-Amino-6-(3-amino-5-nitro-1H-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine, (13).** To a solution of (10) (1.31 g, 10 mmol) in acetonitrile (50 ml) was added the sodium salt of 3-amino-5-nitro-1,2,4-triazole (1.51 g, 10 mmol) and the mixture refluxed for 14 days. The suspension was filtered, washed with water and dried to yield 1.52 g. (68%) mp 287°C dec;  $^1\text{H}$  NMR (deuteriomethylsulfoxide) $\delta$  7.73 (s, 2H), 8.53 (s, 2H);  $^{13}\text{C}$  NMR (deuteriomethylsulfoxide) $\delta$  155.8, 157.1, 161.5, 163.7; IR (KBr) 3412, 3374, 3236, 3299, 3202, 1647, 1523, 1456, 1406, 1334, 1312, 1112, 1050, 1015, 976, 862, 849  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_4\text{H}_4\text{N}_{10}\text{O}_2$ : C, 21.43; H, 1.80; N, 62.49.

Found: C, 21.66 ; H, 1.80 ; N, 60.81.

**3-Amino-6-chloro-1,2,4,5-tetrazine-2,4-dioxide, (14).** To a slurry of 90% hydrogen peroxide (0.7 ml, 25 mmol) in methylene chloride (20 ml) was added trifluoroacetic anhydride (4 ml, 28 mmol) with stirring and ice cooling below 10°C. Compound (10) (1.0 g, 7.6 mmol) was added at 0°C and stirred for 30 minutes at 0°C, then for 2 hours at room temperature. The yellow precipitate was filtered to yield 0.53 g of product. The mother liquor was concentrated, treated with ether and filtered to yield an additional 3.0 g of product to give an overall yield of 64%, mp

191°C dec. An analytical sample was obtained by recrystallization from  $\text{CHCl}_3$ /hexanes.  $^1\text{H}$  NMR (deuteriomethylsulfoxide)  $\delta$  8.76 (s, 2H);  $^{13}\text{C}$  NMR (deuteriomethyl sulfoxide)  $\delta$  145.6, 147.1; IR (KBr) 3283, 3234, 3148, 1674, 1499, 1416, 1326, 1304, 1268, 1224, 1083, 1003, 949  $\text{cm}^{-1}$ . A drop height of 183 cm was measured (Type 12) (HMX=24-27 cm).

Anal. Calcd for  $\text{C}_2\text{H}_2\text{N}_5\text{ClO}_2$ : C, 14.69; H, 1.23; N, 42.83.

Found: C, 14.97; H, 1.17; N, 40.84.

**3-Amino-1,2,4,5-tetrazine, (17).** This material was previously reported but we were unable to repeat the synthesis and no spectral or physical data was given.<sup>14</sup> Ammonia was bubbled through a solution of (15) (1.76 g, 10 mmol) in toluene (15 ml) with stirring at room temperature for twenty minutes. The resulting solid was collected by filtration, washed with toluene and air dried to yield 780 mg (81%) of pure (17), mp 176-177°C;  $^1\text{H}$  NMR (deuteriomethylsulfoxide)  $\delta$  8.0 (s, 2H), 9.7 (s, 1H);  $^{13}\text{C}$  NMR (deuteriomethyl sulfoxide)  $\delta$  153.5, 165.0; IR (KBr) 3319, 3129, 3076, 1639, 1520, 1483, 1124, 1084, 1048, 959, 862, 801  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_2\text{H}_3\text{N}_5$ : C, 24.74; H, 3.12; N, 72.14. Found: C, 24.67; H, 3.18; N, 70.78.

**3-Amino-1,2,4,5-tetrazine-2,4-dioxide, (18).** To a slurry of 90% hydrogen peroxide (0.7 ml, 25 mmol) in methylene chloride (20 ml) was added trifluoroacetic anhydride (4 ml, 28 mmol) with stirring and ice cooling below 10°C. Compound (17) (0.808 g, 8 mmol) was added at 0°C and stirred for 30 minutes at

0 °C, then for 2 hours at room temperature. The yellow precipitate was filtered to yield 0.85 g of product (82%), mp 276 °C dec; <sup>1</sup>H NMR (deuteriomethylsulfoxide) δ 8.5 (s, 1H), 8.6 (s, 2H); <sup>13</sup>C NMR (deuteriomethylsulfoxide) δ 143.7, 148.5; IR (KBr) 3283, 3218, 3137, 3111, 1641, 1535, 1417, 1377, 1332, 1238, 1083, 937, 918 cm<sup>-1</sup>. The density was determined to be 1.77 g/cm<sup>3</sup> by x-ray crystallography.<sup>15</sup> A drop height of 41 cm (Type 12) (HMX=24-27 cm) was also measured.

*Anal.* Calcd for C<sub>2</sub>H<sub>3</sub>N<sub>5</sub>O<sub>2</sub>: C, 18.61; H, 2.34; N, 54.26.  
Found: C, 18.54; H, 2.37; N, 54.55.

**3-Azido-1,2,4,5-tetrazine, (19).** To 5 ml of 4 N HCl was added (16) (0.112 g, 1 mmol). The solution was cooled to -3 °C and sodium nitrite (0.086, 1.25 mmol) in 1 ml of water was added dropwise. The mixture was stirred for 30 minutes and extracted with methylene chloride (3 x 5 ml). The combined organic extracts were dried with magnesium sulfate and concentrated to yield 110 mg (90%), mp 43-44 °C. Due to the explosive nature of this compound an elemental analysis was not performed. <sup>1</sup>H NMR (deuteriochloroform) δ 10.1 (s, 1H); <sup>13</sup>C NMR (deuteriochloroform) δ 156.8, 168.1; IR (KBr) 3100, 2150, 1435, 1371, 1185, 1085 cm<sup>-1</sup>.

**3-Amino-6-nitramino-1,2,4,5-tetrazine, (21).** To 3,6-diamino-1,2,4,5-tetrazine (0.5 g, 4.46 mmol) was added 5 ml of 70% nitric acid dropwise until dissolution was complete. The solution was then allowed to stand at room temperature for two hours. The

resulting red-orange crystalline solid was collected, washed with water and air dried to give 0.5 g, (76%) mp 164°C dec;  $^1\text{H}$  NMR (deuteriomethylsulfoxide)- $\delta$  8.47 (s, 3H);  $^{13}\text{C}$  NMR (deuteriomethylsulfoxide)- $\delta$  155.3, 163.1; IR (KBr) 3359, 3315, 3197, 3159, 1637, 1602, 1513, 1432, 1314, 1277, 1072, 956  $\text{cm}^{-1}$ . A drop height of approximately 10 cm was measured (Type 12) (HMX=24-27 cm).

Anal. Calcd for  $\text{C}_2\text{H}_3\text{N}_7\text{O}_2$ : C, 15.29; H, 1.92; N, 62.41.

Found: C, 15.20; H, 1.95; N, 62.60.

**3-Amino-6-Nitro-1,2,4,5-Tetrazine-1,4-Dioxide, (25) and 3-Amino-6-Nitro-1,2,4,5-Tetrazine-2,4-Dioxide, (24).** A mixture of 200 ml of acetonitrile and 20 ml of water was cooled to 0°C with a dry ice bath with stirring. Through the cooled solution was bubbled a mixture of 10% fluorine in helium for 1.5 hours. A 5 ml aliquot was then added to 10 ml of 0.5 M potassium iodide containing starch as an indicator and the liberated iodine titrated with 0.5 M sodium thiosulfate. Concentrations of 0.25 M to 0.35 M hypofluorous acid were typically generated. With continued cooling and stirring was added 1/10 of an equivalent of substrate to be oxidized, either 3,6-diamino-1,2,4,5-tetrazine (20) or 3,6-diamino-1,2,4,5-tetrazine-1-oxide (23). After 1 hour the suspension was analyzed by TLC on silica utilizing t-butyl methyl ether as developing solvent ( $R_f=0.5$  for (25),  $R_f=0.33$  for (24)). The approximate yields were determined by visual analysis of the developed TLC plates and are reported in the text. The

suspension was then filtered to remove any insoluble 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (**1**) and the filtrate concentrated under reduced pressure. The residue was separated by column chromatography on silica utilizing 80% ethyl acetate/20% hexanes as eluant. There were significant losses of both materials on the column. The density of compound (**24**) was determined to be 1.919 g/cm<sup>3</sup> by x-ray crystallography<sup>15</sup> and was identical to that previously reported.<sup>11</sup> The structure of (**25**) was proven and the density determined as 1.972 g/cm<sup>3</sup> by x-ray crystallography.<sup>15</sup> Compound (**25**) had the following physical properties: mp 168°C dec; <sup>1</sup>H NMR (deuterioacetonitrile)  $\delta$  7.56 (bs, 2H); <sup>13</sup>C NMR (deuterioacetonitrile)  $\delta$  154.5, the nitro-carbon was not seen even after extended time; IR (KBr) 3436, 3322, 3283, 1658, 1552, 1518, 1438, 1309, 1171, 1135 cm<sup>-1</sup>.

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