

Synthesis and Characterization of 1,2,3,4-Cyclobutanetetranitramine Derivatives

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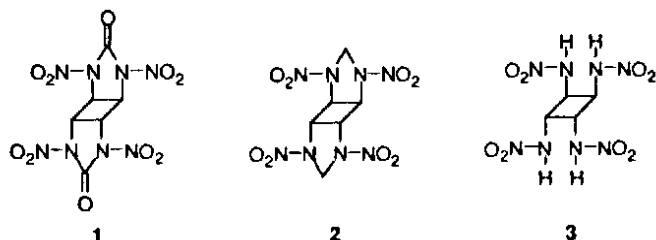
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A series of new nitramines have been synthesized. All of the new compounds possess four nitramine moieties arranged about a cyclobutane ring in a $1\alpha,2\alpha,3\beta,4\beta$ (cis,trans,cis) configuration. One of the new materials, **1**, is unusually thermally and hydrolytically stable but sensitive to impact. 1,2,3,4-Cyclobutanetetranitramine (**3**) is reported for the first time.

Introduction

As part of our continuing effort to prepare new energetic materials with performance properties comparable or superior to hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) but with less sensitivity toward certain stimuli, a series of derivatives of 1,2,3,4-cyclobutanetetranitramine was investigated. On the basis of calculated density and performance (Table 1) using standard methodologies,^{1,2} structures **1-3** were chosen as target com-



pounds. These theoretical predictions did not take into account the strain energy of the cyclobutane ring (26 kcal/mol), however, suggesting that the actual performance of these compounds could exceed the predictions. The syntheses of these new nitramines are described here.

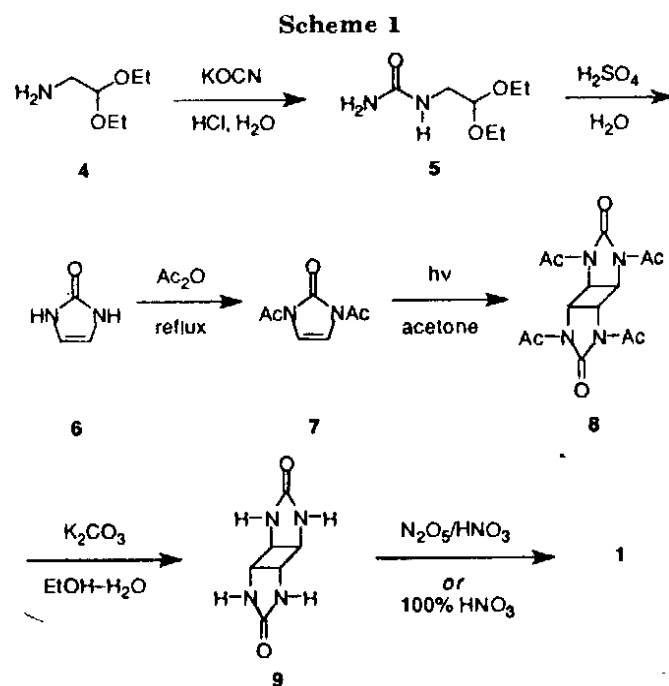
Results and Discussion

The synthesis of nitramine **1** (specifically, a nitrourea) is outlined in Scheme 1. Treatment of aminoacetaldehyde diethyl acetal (**4**) with potassium cyanate in aqueous HCl yields ureidoacetaldehyde diethyl acetal (**5**), a white crystalline solid, which is dehydratively ring-closed to imidazolinone **6** in mild acid solution.³ Acetylation of **6** is easily accomplished in refluxing acetic anhydride to form the diacetyl derivative **7**. Irradiation of bisacetamide **7** dissolved in acetone with either a 200- or 550-W medium-pressure Hanovia lamp produces photodimer **8**

Table 1. Predicted Explosive Properties of Nitramines 1-3 vs Reference Compounds

property	1	2	3	HMX (exptl) ^b	PETN ^c (exptl) ^b
density (g·cm ⁻³)	1.99	1.85	1.83	1.89	1.77
detonation pressure (kbar)	328	321	388	390	335
detonation velocity (mm/μs)	8.41	8.33	9.04	9.11	8.26

^a Pentaerythritol tetranitrate. ^b Dobratz, B. M.; Crawford, P. C. LLNL Explosives Handbook: Properties of Chemical Explosives and Explosive Simulants. Livermore, CA, Lawrence Livermore National Laboratory report UCRL-52997, Jan 1985. Available from the National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22161.



in approximately 20-30% yield.⁴ There is a competing polymerization during photolysis which reduces the efficiency of this reaction. Further improvements in the efficiency of the photolysis may be possible with different solvents, photosensitizers, temperature, light source, wavelengths, etc. The desired dimer **8** precipitates from solution in a pure form and is collected by filtration. The photodimerization produces exclusively the $1\alpha,2\alpha,3\beta,4\beta$ (cis,trans,cis) tetramine isomer as shown. Hydrolysis of the acetyl groups is carried out in refluxing aqueous

* Abstract published in *Advance ACS Abstracts*, November 15, 1996.
(1) Cichra, D. A.; Holden, J. R.; Dickinson, C. Estimation of Normal Densities of Explosive Compounds From Empirical Atomic Volumes. Silver Spring, MD, Naval Surface Weapons Center report TR79-273. Available from the National Technical Information Service, U.S. Department of Commerce, Springfield, VA 22161, Feb 1980.

(2) (a) Rothstein, L. R.; Petersen, R. *Propellants Explos.* 1979, 4, 56, 86. (b) Rothstein, L. R. *Propellants Explos.* 1981, 6, 91.

(3) (a) Duschinsky, R.; Dolan, L. A. *J. Am. Chem. Soc.* 1945, 68, 2350. (b) Haines, D. R.; Leonard, N. J.; Wiemer, D. F. *J. Org. Chem.* 1982, 47, 474.

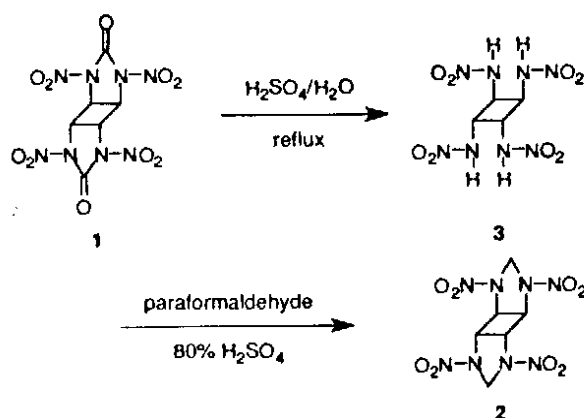
(4) Steffan, G.; Schenck, G. O. *Chem. Ber.* 1967, 100, 3961.

Table 2. Sensitivity Properties of 1 vs PETN

property	1	PETN
impact sensitivity, H_{50} , ^a cm	7.2–11	9–15
friction sensitivity (ABL), ^b $\log_{10}(\text{lb}f)$	≥ 2.9	2.0–2.1
electrostatic sensitivity, 0.25 J	10/10 no fire	10/10 no fire
TGA onset, ^c °C	216	$\sim 205^d$
DSC exotherm, ^e °C	232	197 ^f
average particle size, μm	22	

^a ERL impact tester, Type 12 tooling, 2.5-kg weight. ^b Allegany Ballistics Laboratory test (per MIL-STD-1751), threshold initiation value for 10/10 no-fires. ^c Thermogravimetric analysis, initial temperature of apparent weight change per ASTM E914. ^d Zeman, S. *Thermochim. Acta* 1993, 230, 191. ^e Extrapolated onset temperature by differential scanning calorimetry (2 °C/min) per ASTM E537. ^f Ando, T.; Fujimoto, Y.; Morisaki, S. *J. Hazard. Mater.* 1991, 28, 251. Heating rate 10 °C/min.

Scheme 2



ethanol containing potassium carbonate, forming the bisurea derivative 9. Nitration of 9 in either dinitrogen pentoxide/nitric acid solution or 100% nitric acid yields the desired nitramine 1. The final product must be washed thoroughly with water and dried. The concentrations of the nitrogen pentoxide/nitric acid solutions used in the nitration step ranged from 7 to 25% N_2O_5 . All nitration yields are high. If aqueous nitric acid is used, e.g., 70 or 90% HNO_3 , there is some hydrolysis of the final product. Some of the sensitivity properties of 1 are shown in Table 2.

Compound 1 is soluble in polar organic solvents such as DMF and DMSO. When solutions of 1 in either DMF or DMSO are treated with water, the nitramine precipitates immediately as a fine white solid. 1, a white solid, does not melt. At ~ 240 °C, the material decomposes into a dark solid with evolution of a red gas. This material is surprisingly stable thermally, chemically, and hydrolytically in comparison to similar materials such as dinitroglucuril (DINGU) and tetranitroglucuril (TNGU or Sorguy).^{5,6} 1 can be heated at reflux for several hours in dilute sulfuric acid solutions before any decomposition is detected.

Nitramines 2 and 3 are derived from 1. The synthesis of these materials is outlined in Scheme 2.

Nitrourea 1 is hydrolyzed to 1,2,3,4-cyclobutanetetranitramine (3) in dilute sulfuric acid at reflux, by methodology similar to that previously used to prepare *N,N'*-dinitro-1,2-ethanediamine (EDNA).⁷ After 6–8 h,

the white suspension slowly darkens in color and becomes a clear solution. Cooling, followed by concentration, causes 3 to precipitate out as a light brown solid. This primary nitramine is isomeric with HMX and should be handled with extreme caution. We predict this material to exhibit high impact and friction sensitivity, but impact and friction sensitivity measurements have not been made. Nitramine 3 does not melt. As the material is slowly heated, detonation occurs at ~ 156 °C. By differential scanning calorimetry (DSC), exothermic decomposition is under way at 140 °C. Interestingly, 1,2,3,4-cyclobutanetetranitramine has previously been abstracted three times by *Chemical Abstracts*.^{8–10} Each citation was erroneous, however, having understandably misinterpreted "cyclotetramethylenetetranitramine", a trivial name for HMX, to be 1,2,3,4-cyclobutanetetranitramine (3).

Treatment of 3 with paraformaldehyde in 80% aqueous H_2SO_4 produces the methylene-bridged nitramine 2, analogous to the formation of 1,3-dinitroimidazolidine from EDNA.¹¹ The molecular structure of 2 was confirmed by an X-ray structure determination.¹² The measured X-ray density of 2 is $1.82 \text{ g}\cdot\text{cm}^{-3}$. The impact sensitivity, H_{50} , of 2 is 19.1 cm (2.5-kg drop weight), and DSC shows an exotherm maximum at 248 °C.

With bisurea 9 readily available, we further explored the synthesis of other cyclobutanetetranitramines and nitrosamines. Alkylation and reduction of 9 are accomplished as shown in Scheme 3. Treatment of bisurea 9 with sodium hydride in THF produces the expected tetrasodium salt. Alkylation of the salt followed by reduction with lithium aluminum hydride (LAH) gives tertiary amines as potentially useful intermediates. Use of dimethyl sulfate as the alkylating agent produces the tetramethyl derivative 10, which was not isolated in a highly pure state but was suitable for subsequent nitrosolysis and nitrolysis. The preparation of homologous derivatives was attempted using ethyl iodide and isopropyl bromide, but the LAH reduction¹³ does not cleanly produce the expected tetraethyl and tetraisopropyl derivatives. In these two cases, there is an appreciable amount of unreacted urea that could not be removed from the desired products, which were not prepared pure. Overall yields of these homologues are low.

Tetramethyltetramine 10, when treated with dinitrogen tetroxide, produces the tetranitrosamine 11, as shown in Scheme 3. The structure of 11 was confirmed by X-ray crystallography.¹² Reactions of the tetraethyl and tetraisopropyl octahydro-3 α ,3 β ,6 α ,6 β -cyclobuta-[1,2-*d*:3,4-*d'*]diimidazole derivatives with dinitrogen tetroxide are believed to give the corresponding tetranitrosamines as well. However, the yields of these transformations were very low, and they were not pursued further. Attempts to oxidize or nitrolyze 11 to the

(8) Acharya, H. K.; Limaye, R. T. *Def. Sci. J.* 1964, 14, 325; *Chem. Abstr.* 1966, 64, 15755d.

(9) Fogel'zang, A. E.; Svetlov, B. S.; Adzhemyan, V. Ya.; Kolyasov, S. M.; Sergienko, O. I. *Dokl. Akad. Nauk SSSR* 1974, 216, 603; *Chem. Abstr.* 1974, 81, 123859.

(10) Bagnato, L.; Grasso, G. *J. Chromatogr.* 1986, 357, 440; *Chem. Abstr.* 1986, 104, 227215.

(11) Goodman, L. *J. Am. Chem. Soc.* 1953, 75, 3019.

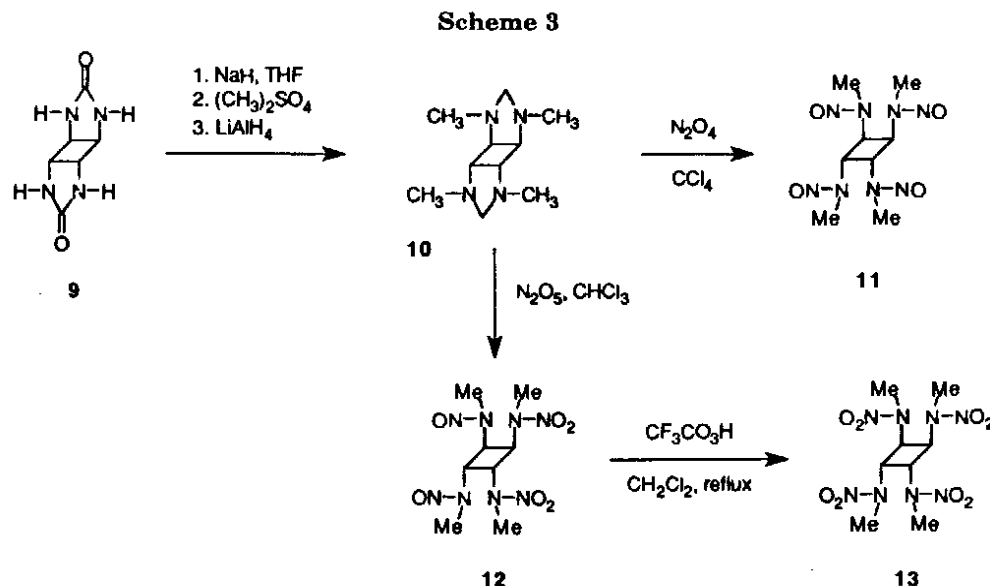
(12) ORTEP diagrams are included in the Supporting Information for this article. The authors have deposited atomic coordinates for structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(13) Bates, H. A.; Condlis, N.; Stein, N. L. *J. Org. Chem.* 1986, 51, 2228.

(5) Meyer, R. *Explosives*, 3rd ed.; VCH Publishers: New York, 1987; p 103.

(6) Oyumi, Y.; Brill, T. B. *Propellants Explos. Pyrotech.* 1988, 13, 69.

(7) Bachmann, W. E.; Horton, W. J.; Jenner, E. L.; MacNaughton, N. W.; Maxwell, C. E., III *J. Am. Chem. Soc.* 1950, 72, 3132.



tetranitramine led to decomposition; no evidence of nitramine was detected.

By a similar reaction intended to be a nitrolysis of **10**, a dinitrodinitrosotetramine (**12**) is formed in a reaction with dinitrogen pentoxide in chloroform (Scheme 3). The reaction mixture is complex, and **12** is isolated after extensive purification. Other isomers were probably present but were not recovered. The structure of **12** was confirmed by X-ray crystallography.¹² Since **12** is formed in low yield, it may be the product of the reaction between **10** and a mixture of dinitrogen pentoxide and small amounts of dinitrogen tetroxide which may be present from some thermal decomposition of N_2O_5 in $CHCl_3$.¹⁴

Dinitrodinitrosotetramine **12** is oxidized to the tetranitramine **13** using trifluoroperoxyacetic acid in refluxing methylene chloride (Scheme 3). Nitramine **13** is thermally stable and somewhat energetic. No melting point is observed, but a detonation takes place at 256 °C.

In the course of attempts toward product **2**, a tetra-benzyl analogue of **10**, octahydro-1,3,4,6-tetrakis(phenylmethyl)-3 α ,3 β ,6 α β ,6 β α -cyclobuta[1,2-*d*:3,4-*d'*]diimidazole (**14**), was similarly prepared and structurally confirmed by X-ray crystallography,¹² but it proved not to be a useful intermediate.

Conclusions

A number of new energetic nitramines have been prepared. The common feature of each is a cyclobutane ring with the nitramine moieties arranged in a *cis,trans-cis* configuration. One of these compounds, **1**, has been found to be particularly energetic and may find use as a more hydrolytically and thermally stable alternative to PETN in certain applications, such as charges in exploding-bridgewire detonators.

Experimental Section

General Information. **WARNING:** Virtually all of the nitramine compounds prepared herein are potentially dangerous high explosives! In general, many nitramines should be treated as such and should be handled by appropriately qualified personnel. NMR spectra were measured at 80 MHz for 1H and 20 MHz for ^{13}C . Melting points were determined

in capillary tubes. Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN).

(2,2-Diethoxyethyl)urea (5).³ Aminoacetaldehyde diethyl acetal (**4**; 38 mL, 266 mmol) was mixed with ice/water (55 g). To this slurry was added 5 N HCl (52.6 mL) precooled to -40 °C followed immediately by a solution of potassium cyanate (32 g, 400 mmol) in water (70 mL). The resulting solution was heated at reflux for 90 min, cooled to room temperature, and then concentrated to approximately one-third of the original volume. A white precipitate (**5**) was collected by vacuum filtration and dried. The yield was 38 g (81%).

1,3-Dihydro-2H-imidazol-2-one (6).³ Ureidoacetaldehyde diethyl acetal (**5**; 38 g, 216 mmol) was slurried with 0.1 N sulfuric acid (29.6 mL) and water (6.0 mL). The mixture was warmed to 55 °C for 1 h followed by addition of 1 N sulfuric acid (6.0 mL) with heating continued for an additional 2 h. A strong smell of ethanol was evident; the clear colorless solution may develop a slight pink color. After cooling to ambient temperature, the clear solution was placed in a refrigerator overnight. The desired product, **6**, precipitated from solution as white crystals (8.0 g, 44%).

1,3-Diacetyl-1,3-dihydro-2H-imidazol-2-one (7).^{4,15} 2-Imidazolinone (**6**; 10.7 g, 127 mmol) was refluxed in acetic anhydride for 2 h. The solution was cooled to ambient temperature and the excess acetic anhydride and acetic acid were removed under reduced pressure, which gave ~18 g of an off-white solid (**7**), suitable for use directly in the next step. However, it can be purified by recrystallization from ethyl acetate, giving 11.8 g (68%) of pure **7**. 1H NMR (acetone- d_6) δ 2.57 (s), 7.06 (s).

1,3,4,6-Tetraacetyloctahydro-3 α ,3 β ,6 α β ,6 β α -cyclobuta[1,2-*d*:3,4-*d'*]diimidazole-2,5-dione (8).⁴ Bisacetamide **7** (100 g) was dissolved in acetone (4.5 L) and irradiated at room temperature with a 550-W medium-pressure Hanovia lamp in an immersion photolysis apparatus for a total of 8 days. (The reaction was stopped at 4 days to collect the first batch of product **8**, which precipitated from solution as a fine white solid. The filtered acetone solution was then irradiated for an additional 4 days.) A total of 23.3 g (23%) of product was collected. Yields can range up to 30%. This photolysis also works using a 200-W lamp although with slightly decreased yields. There is a competing polymerization reaction that keeps the yield of the desired dimerization reaction low.

Octahydro-3 α ,3 β ,6 α β ,6 β α -cyclobuta[1,2-*d*:3,4-*d'*]diimidazole-2,5-dione (9).⁴ Photodimer **8** (450 mg, 1.3 mmol) was suspended in a solution of 95% ethanol (15 mL) and water (5 mL) containing potassium carbonate (370 mg, 2.7 mmol) and heated at reflux for 4 h. The fine white solid (**9**) that precipitated from solution was filtered and dried; yield 188 mg (86%).

(14) Fischer, J. W. In *Nitro Compounds: Recent Advances in Synthesis and Chemistry*; Feuer, H.; Nielsen, A. T., Eds.; VCH Publishers: New York, 1990; p 267.

(15) Whitney, R. A. *Tetrahedron Lett.* 1981, 22, 2063.

Octahydro-1,3,4,6-tetranitro-3 α ,3 β ,6 α ,6 β -cyclobuta-[1,2-*d*:3,4-*d'*]diimidazole-2,5-dione (1). Bisurea **9** (250 mg, 1.5 mmol) was added in portions to a stirred solution of 25% dinitrogen pentoxide in nitric acid at 0 °C. The resulting white suspension was slowly allowed to warm to ambient temperature and then stirred overnight. Vacuum filtration of the white suspension, with thorough washing with water and drying, gave the desired nitramine **1** in 97% yield (0.50 g). This reaction works equally as well with lower concentration dinitrogen pentoxide solutions or even neat 100% nitric acid. High yields are still achieved when scaled up to 2–3 g of bisurea **9**: ¹H NMR (DMSO-*d*₆) δ 5.51 (s); ¹³C NMR (DMSO-*d*₆) δ 55.0, 141.2; IR (KBr) 3030, 3000, 1810, 1580, 1310, 1250, 1100 cm⁻¹. Anal. Calcd for C₆H₄N₈O₁₀: C, 20.70; H, 1.16; N, 32.19. Found: C, 20.40; H, 1.20; N, 32.39.

***N,N,N',N''*-Tetranitro-1 α ,2 α ,3 β ,4 β -cyclobutanetetramine (3).** Nitrourea **1** (2.8 g, 8 mmol) was suspended in water (50 mL) containing sulfuric acid (1 mL) and refluxed with vigorous stirring until the solid completely dissolved—approximately 4–6 h. The resulting light-brown solution was cooled and concentrated until a brown precipitate formed. The primary tetranitramine **3** was collected by vacuum filtration as a beige amorphous solid (0.87 g, 36%); detonates at 156 °C; ¹H NMR (DMSO-*d*₆) δ 4.80 (s, 4), 10.76 (s, 4); ¹³C NMR (DMSO-*d*₆) δ 52.9; IR (KBr): 3280, 3000, 1585, 1400, 1350 cm⁻¹.

Octahydro-1,3,4,6-tetranitro-3 α ,3 β ,6 α ,6 β -cyclobuta-[1,2-*d*:3,4-*d'*]diimidazole (2). Nitramine **3** (500 mg, 1.7 mmol) was added to a stirring solution of paraformaldehyde (120 mg, 4.0 mmol) in 80% sulfuric acid (5 mL) at -5 °C. The brown suspension was stirred for 45 min and then poured into ice/water (20 mL); the light-brown solid, nitramine **2** (174 mg, 32%), was collected and dried by vacuum filtration; mp 228 °C dec. A crystal suitable for X-ray structure determination¹² was grown from 100% nitric acid: ¹H NMR (DMSO-*d*₆) δ 5.44 (s, 4), 5.82 (slightly br s, 4); ¹³C NMR (DMSO-*d*₆) δ 62.4 (d), 67.8 (t); IR (KBr) 2970, 1520, 1390, 1295, 755, 575 cm⁻¹; MS (CI, methane) 321 (MH⁺).

***N,N,N',N''*-Tetramethyl-*N,N',N'',N'''*-tetranitroso-1 α ,2 α ,3 β ,4 β -cyclobutanetetramine (11).** Bisurea **9** (0.75 g, 4.5 mmol) was added in one portion to sodium hydride (0.52 g, 21 mmol) suspended in THF at ambient temperature. This mixture was stirred for 45 min followed by addition of dimethyl sulfate (2.03 mL, 21 mmol), and the resultant mixture was heated at reflux overnight. After cooling to room temperature, the cloudy white solution was filtered and solvent was removed under reduced pressure to yield the crude tetramethylbisurea (0.92 g) as a white solid; mp 242–250 °C dec. Purification was accomplished by recrystallization from hot acetone to give the desired intermediate, octahydro-1,3,4,6-tetramethyl-3 α ,3 β ,6 α ,6 β -cyclobuta-[1,2-*d*:3,4-*d'*]diimidazole-2,5-dione, as a white solid (0.43 g, 50%): ¹H NMR (DMSO-*d*₆) δ 2.71 (s, 12), 3.91 (s, 4); ¹³C NMR (DMSO-*d*₆) δ 28.1, 58.2, 159.7; IR (KBr): 2900, 1650, 1440, 1390, 1200, 920 cm⁻¹.

Lithium aluminum hydride (1.4 g, 37 mmol) was added to the above tetramethylbisurea (436 mg, 1.9 mmol) suspended in THF at ambient temperature followed by stirring for 3 days under nitrogen. The resulting suspension was carefully quenched by adding water (10 drops), 1 M NaOH (10 drops), and water (10 drops), drying (MgSO₄), and removing solvent under reduced pressure to give an oily solid. Sublimation of the crude product gave the desired intermediate, octahydro-

1,3,4,6-tetramethyl-3 α ,3 β ,6 α ,6 β -cyclobuta-[1,2-*d*:3,4-*d'*]diimidazole (**10**; 275 mg, 72%), suitable for use in subsequent reactions; sublimes 55 °C (0.1 Torr); ¹H NMR (DMSO-*d*₆) δ 2.29 (s, 12), δ 3.27 (s, 4), 3.38 (AB quartet, 4, *J* = 6.3 Hz); ¹³C NMR (acetone-*d*₆) δ 38.4, 64.6, 78.6; IR (KBr) 2920, 1460, 1440, 1360, 1215, 1145, 1095, 995 cm⁻¹.

Dinitrogen tetroxide (5 mL) was added in one portion to tetramethyltetramine **10** (100 mg, 0.5 mmol) in carbon tetrachloride (5 mL) at room temperature. The deep red solution was stirred overnight and then carefully poured into water (25 mL). This two-phase mixture was extracted with dichloromethane (3 \times 20 mL). The organic extracts were combined, washed with saturated sodium bicarbonate (20 mL) and brine (20 mL), and dried (MgSO₄); solvent was removed under reduced pressure, giving tetranitrosamine **11** (100 mg, 68%) as a yellow solid; mp 247–249 °C dec. The molecular structure of **11** was confirmed by an X-ray structure determination:¹² ¹H NMR (DMSO-*d*₆) δ 3.00 (s, 12), 6.19 (s, 4); ¹³C NMR (DMSO-*d*₆) δ 33.2 (q), 61.4 (d); IR (KBr) 3020, 1435, 1345, 1210, 1125, 1045 cm⁻¹.

***N,N,N',N''*-Tetramethyl-*N,N''*-dinitro-*N,N'*-dinitroso-1 α ,2 α ,3 β ,4 β -cyclobutanetetramine (12).** Dinitrogen pentoxide in chloroform (0.8 M, 5 mL) was added directly to tetramethyltetramine **10** (56 mg, 0.3 mmol) at 0 °C followed by stirring for 2.5 h. The reaction was quenched with saturated sodium bicarbonate (25 mL) and extracted with chloroform (25 mL). Washing the organic layer with brine (25 mL), drying (MgSO₄), and removal of solvent afforded a white solid (34 mg). Purification on silica gel, eluting with 75% ethyl acetate in hexane, followed by recrystallization from ethyl acetate gave the dinitrodinitrosotetramine **12** as a white crystalline solid (yield ~2 mg, 2%); mp 207–209 °C dec. The molecular structure of **12** was confirmed by an X-ray structure determination:¹² ¹H NMR (acetone-*d*₆) δ 3.10 (m, 6), 3.44 (m, 6), 5.7 (m, 4); IR (KBr): 3010, 2940, 1520, 1435, 1355, 1300, 1250 cm⁻¹; MS (CI, methane) 321 (MH⁺).

***N,N,N',N''*-Tetramethyl-*N,N',N'',N'''*-tetranitro-1 α ,2 α ,3 β ,4 β -cyclobutanetetramine (13).** Dinitrodinitrosotetramine **12** (78 mg, 0.24 mmol) was added to a solution of trifluoroperoxyacetic acid in dichloromethane (made *in situ* by addition of 1.5 mL of 90% hydrogen peroxide to 9.6 mL of trifluoroacetic anhydride in 15 mL of dichloromethane) at 0 °C. After 5 min, the solution was refluxed for 4 h. The reaction was then cooled, quenched with saturated sodium bicarbonate, and extracted with chloroform (2 \times 25 mL). Combining the organic layers, washing with water (25 mL) and brine (25 mL), drying (MgSO₄), and removal of solvent afforded the desired tetranitramine **13** (40 mg, 47%) as a white solid; mp 262 °C (detonates); ¹H NMR (acetone-*d*₆) δ 3.47 (s, 12), 5.78 (s, 4); ¹³C NMR (DMSO-*d*₆) δ 59.5, 88.4; IR (KBr) 2920, 1510, 1420, 1360, 1285 cm⁻¹.

Supporting Information Available: ORTEP presentations for **2**, **11**, **12**, and **14**, presentations of ¹H NMR spectra for **3** and **13**, and a ¹³C NMR spectrum for **13** (7 pages). This material is found in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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