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PREPARATION OF 1-SUBSTITUTED-3,3-DINITROAZETIDINES

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ABSTRACT

DNAZ (3,3-dinitroazetidine), **1**, readily undergoes nucleophilic addition reactions with electron deficient haloaromatics, cyanogen bromide, *S*-methyl-*N*-nitroisothiourea and dichloroglyoxime to afford novel, energetic 1-substituted-3,3-dinitroazetidines. *N*-Nitrosation of DNAZ readily occurs, and Mannich condensations of DNAZ with poly-nitroalcohols are also described. The synthesis and properties of the energetic materials derived from these reactions will be discussed.

INTRODUCTION

Recently, we reported the first synthesis of DNAZ (3,3-dinitroazetidine), **1**. DNAZ was prepared from 1-*t*-butyl-3,3-dinitroazetidine, **2**, in a three step procedure (eq 1) beginning with the treatment of **2** with benzyl chloroformate to afford carbobenzyloxy protected 3,3-dinitroazetidine, **3**.[2]

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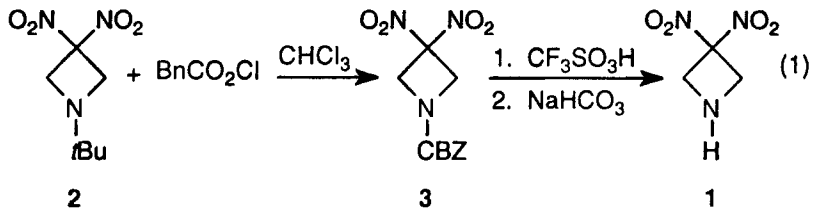
Subsequent removal of the carbobenzyloxy protecting group provided **1**. A more efficient synthesis utilizing methyl chloroformate was later



2 **3** **1**

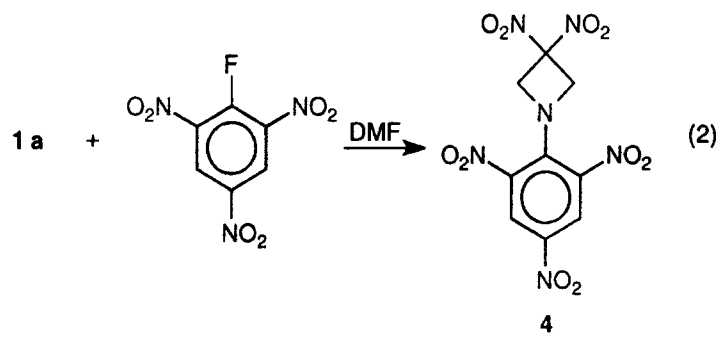
developed.[3] The pK_b of DNAZ was determined by aqueous titration to be 6.5, and as an extension of this work, the energetic salts of DNAZ were prepared and characterized[4] from the metathesis reaction of DNAZ-trifluoromethanesulfonate, **1a**, with the ammonium salt of the appropriate acid.[2] Some of the energetic salts prepared were: DNAZ-nitrate, **1b**; DNAZ-dinitramide, **1c**; DNAZ-perchlorate, **1d**; and DNAZ-hydrochloride, **1e**.

One of the goals of the current research effort was to prepare, characterize and evaluate eutectic candidates with TNAZ (1,3,3-trinitro-azetidine) in order to mediate some of the less desirable characteristics of TNAZ. With this goal in mind and as the next progression in the study of DNAZ, we wanted to prepare energetic compounds that were derivatives of DNAZ by exploiting the nucleophilicity of the nitrogen in the azetidine ring. We now wish to report the results of this investigation.

RESULTS

In comparison to other 2° amines, azetidines undergo all of the usual reactions of 2° amines, but the unique cyclic structure of the azetidine ring has been shown to exhibit enhanced nucleophilicity.[5] Many different *N*-alkylations have been achieved with azetidines. For example, in the reaction of azetidines with phenyl acetates[6] and activated halobenzenes,[7] the enhanced nucleophilicity was attributed to a less crowded transition state.[8] Azetidines also undergo regiospecific nucleophilic aromatic substitution with haloquinolones.[9]

We have also found DNAZ to be a powerful nucleophile for nucleophilic aromatic substitutions of activated aromatics. DNAZ readily reacts with electron deficient rings such as picryl fluoride to afford the monosubstituted-trinitrobenzene, **4**, in 78% yield (eq 2). In a similar



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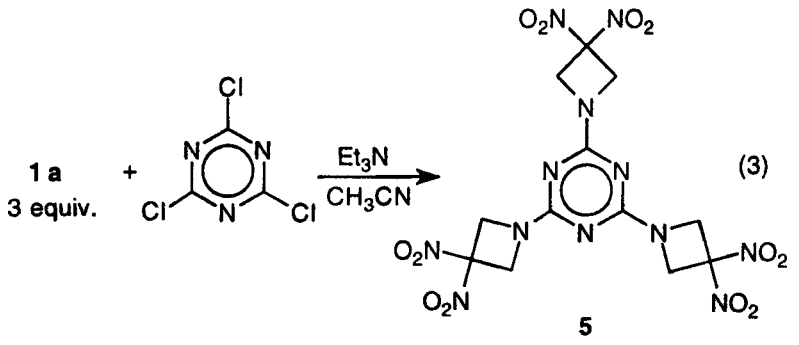
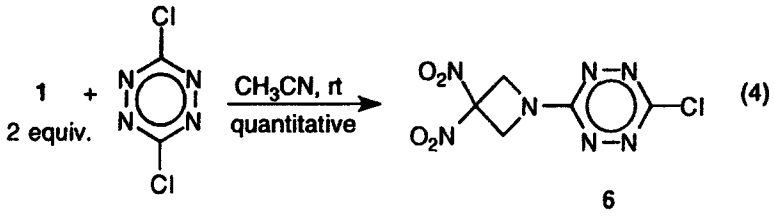
fashion, three equivalents of **1a** react with cyanuric chloride (eq 3) to replace all available chlorides providing **5** in 63% yield. Some of the physical and explosive properties of **4** and **5** are given (Table 1).



In another nucleophilic aromatic substitution reaction, the parent azetidine has been reported to react with 3,6-*bis*-methylthio-1,2,4,5-tetrazine to afford a mixture of 3-(1-azetidinyl)-6-methylthio-1,2,4,5-tetrazine (6%) and 3,6-*bis*-(1-azetidinyl)-1,2,4,5-tetrazine (75%).[10] We also investigated nucleophilic aromatic substitution of DNAZ with 3,6-dichloro-1,2,4,5-tetrazine. In contrast to the reaction of the parent azetidine with 3,6-*bis*-methylthio-1,2,4,5-tetrazine, DNAZ displaced only one chloride of 3,6-dichloro-1,2,4,5-tetrazine, furnishing in almost quanitative yield 3-chloro-6-(3,3-dinitro-1-azetidinyl)-1,2,4,5-tetrazine, **6**, (eq 4). Only a small amount of the second chloride was displaced under slightly different reaction conditions by refluxing in acetonitrile in the presence of triethylamine to afford the *bis*-substituted tetrazine, **7** in 15%



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yield (eq 5). This was the only reaction where a difference between the parent azetidine and DNAZ was observed. Some of the physical properties of **7** are also reported (Table 1).

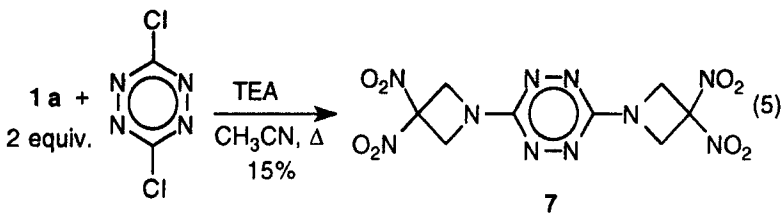

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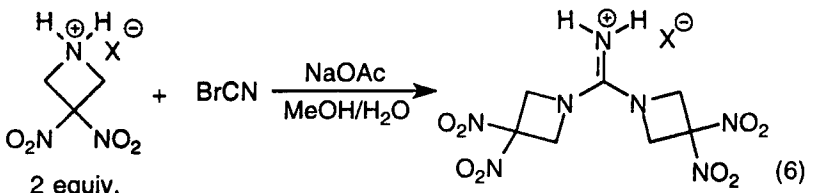
Table 1. Physical and Explosive Properties of DNAZ-Substituted Aromatic Rings

Compound	4	5	7
DTA Exotherm [°C]	251	249	230
Drop Weight Impact Height Type 12 [cm]	39	178	45
Density [g/cm^3] (calcd.)[11]	1.78	1.74	1.75

We were also interested in preparing guanidine-DNAZ based energetic materials. Guanidines are frequently prepared through the reaction of amines with cyanogen bromide. As anticipated, cyanogen

bromide reacts readily with energetic DNAZ salts, **1b-d**, to yield guanidine salts, **8b-d**, in fair to good yields (eq 6). In an effort to increase the performance properties, dehydration of **8b** to afford the nitroimine was attempted. Unfortunately, **8b** resisted all attempts to dehydration.



(6)

1b, X = $NO_3^{\ominus}$
1c, X = $N(NO_2)_2^{\ominus}$
1d, X = $ClO_4^{\ominus}$

8b, X = $NO_3^{\ominus}$
8c, X = $N(NO_2)_2^{\ominus}$
8d, X = $ClO_4^{\ominus}$

Another guanidine-DNAZ derivative, **9**, was prepared by the acylation of *S*-methyl-*N*-nitroisothiourea[12] with DNAZ (eq 7) to yield **9** in 66% yield. The melting point of **9**, 133 °C, makes this DNAZ derivative a viable candidate for forming a eutectic with TNAZ, and future studies will investigate this possibility. Some of the physical and explosive properties of **8b-d** and **9** are tabulated (Table 2).

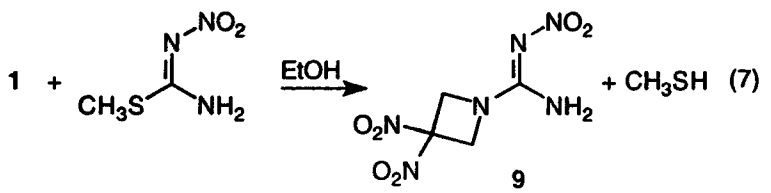


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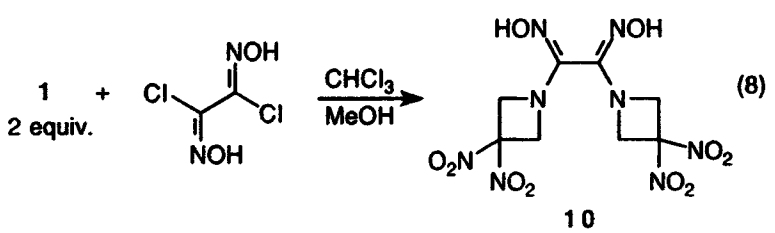
Table 2. Physical and Explosive Properties of DNAZ-Guanidine Substituted Derivatives

Compound	8b	8c	8d	9
Melting Point [°C]	-	-	-	133
DTA Exotherm [°C]	212	204	237	225
ΔH_f[kcal/mol]	-	-	-	+8
Density [g/cm^3]	1.74[13]	1.73[14]	1.85[13]	1.75[14]
Drop Weight Impact Height Type 12 [cm]	38	22	21	40

In a similar type of reaction, two equivalents of DNAZ reacted with dichloroglyoxime to afford the *bis*(DNAZ-substituted) glyoxime, **10**, in 72% yield (eq 8). Ring closure reactions of **10** to afford the furazan were attempted. Dehydration of **10** with sodium hydroxide in propylene glycol provided no organic product, and the utilization of acetic anhydride as a cyclizing agent only afforded *bis*-O-acyl derivative of **10**. Oxidative ring closure to prepare the furoxan by treatment of **10** with potassium ferricyanide only returned the starting material.



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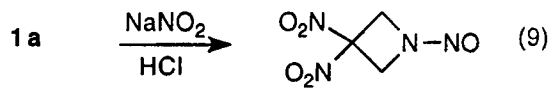
Besides nucleophilic addition reactions, the parent azetidine is readily *N*-nitrosated to provide another example of a nitrogen transformation of azetidine.[15] We have also found that DNAZ undergoes *N*-nitrosation to provide the simplest energetic derivative of DNAZ, 1-nitroso-3,3-dinitroazetidine, **11**, in excellent yield (eq 9).



(9)

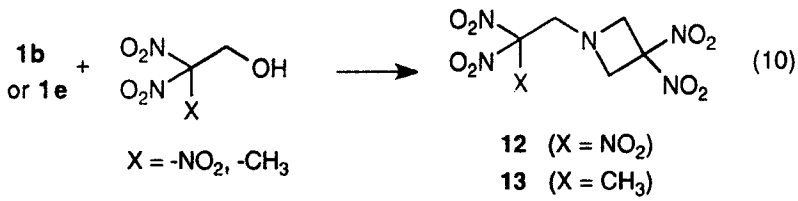
11

The structure of **11** is the most similar to TNAZ, and as anticipated, the eutectic mixture of **11** and TNAZ had a reduced vapor pressure compared to that of pure TNAZ.[16] The eutectic composition was determined to be 54 mole% TNAZ with a melting point of 82.6 °C, making it very similar to the melting point of TNT[17]. Some of the physical explosive properties of **11**, TNAZ and the **11**/TNAZ eutectic mixture are given (Table 3).

The Mannich condensation of β-nitro-alcohols has been extensively investigated, and this reaction has facilitated the preparation of a variety of nitro-aliphatic amines.[18,19,20] DNAZ reacts readily with 2,2,2-trinitroethanol and 2,2-dinitropropanol to afford the corresponding Mannich bases, **12** and **13** (eq 10). Unfortunately, when 2,2-dinitropropanol was utilized, a significant side product produced is the aminal of

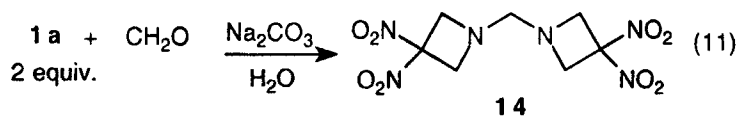
Table 3. Physical and Explosive Properties of 11, TNAZ and Nitroso-DNAZ/TNAZ Eutectic Mixture

Compound	11	TNAZ[21]	Eutectic
Melting Point [°C]	104	101	83
DTA Exotherm [°C]	213	233	-
ΔH_f[kcal/mol]	+22	+2	-
Density [g/cm^3]	1.75[14]	1.84	-
Drop Weight Impact Height Type 12 [cm]	20	22	22
Detonation Velocity [km/s] (calcd.)[22]	8.4	9.0	8.9
Detonation Pressure [kbar] (calcd.)[22]	321	364	353



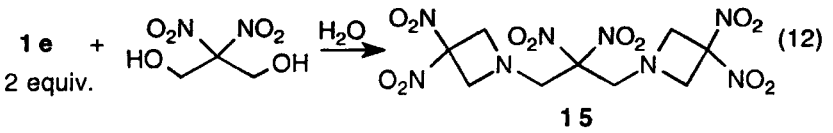
(10)

DNAZ, **14**, formed by the addition of two equivalents of DNAZ to formaldehyde. The two compounds, **13** and **14**, could be readily separated by radial chromatography, but **14** was more easily prepared from the reaction of **1a** and formalin in near quantitative yield (eq 11).



(11)

A double Mannich condensation occurs when 2,2-dinitropropane-1,3-diol (ADIOL) is reacted with two equivalents of DNAZ giving the *bis*-addition product, **15** in 24% yield (eq 12). With a favorable melting point of 148 °C, **15** will also be investigated for forming a eutectic with TNAZ. Some of the physical and explosive properties of **12-15** are tabulated (Table 4).



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In summary, DNAZ has been found to be a very effective energetic nucleophile that undergoes addition with a wide variety of electrophiles. Those DNAZ-derivatives with favorable physical and performance properties will be further investigated as potential eutectic candidates with TNAZ.

Table 4. Physical and Explosive Properties of DNAZ-Mannich Bases

Compound	12	13	14	15
Melting Point [°C]	94	60	91	148
DTA Exotherm [°C]	164	194	164	163
Density [g/cm^3] [11]	1.80	1.65	1.67	1.70
Drop Weight Impact Height Type 12 [cm]	17	-	43.2	34

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 relative to internal Me_4Si. 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 and/or iodine. Radial chromatography was performed on a radial chromatograph (Harrison) using a 4-mm plate of silica gel. All melting points were determined at 2°C/min with a Mettler FP1 apparatus and are corrected.

1-Picryl-3,3-dinitro-1-azetidine, 4. Picryl fluoride (0.462 g, 2.0 mmol) was added to **1a** (0.522 g, 2.0 mmol), in DMF (10 mL). Protected from water, the reaction mixture was heated on a steam cone for 7 h. The reaction mixture was drowned in water, resulting in the formation of a yellow precipitate. The yellow solid was collected by filtration and allowed to air-dry, and the crude product was purified by washing with methyl-*t*-butyl ether to afford a yellow product (0.56 g, 78%): mp 223-225 °C; ^{1}H NMR (DMSO-d_6) δ 4.93 (s, 4H), 8.94 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 63.6, 105.5, 126.1, 134.5, 137.4, 142.7; IR (KBr) 3100, 3032, 3015, 1615, 1572, 1527, 1490, 1441, 1429, 1363, 1329, 1302, 1269,

1099, 920, 838, 749, 737 cm^{-1}. *Anal.* Calcd. for $C_9H_6N_6O_{10}$: C, 30.18; H, 1.69; N, 23.46. Found: C, 30.20; H, 1.74; N, 23.50.

2,4,6-*tris*[(3,3-Dinitro)-1-azetidinyl]-1,3,5-triazine, 5. Triethylamine (2.1 g, 20.8 mmol) and cyanuric chloride (0.62 g, 3.37 mmol) were added to a solution of **1a** (3.0 g, 10.1 mmol) in acetonitrile (30 mL). The mixture was stirred at rt for 1 h and then brought to reflux for 4 h. After cooling to rt, the reaction mixture was poured into water and allowed to stand overnight to agglomerate. The solid was collected by filtration, and recrystallization from EtOAc/hexanes provided a beige solid (1.10 g, 63%): mp. 249 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 4.92 (s, 12H); ^{13}C NMR (DMSO-d_6) δ 58.3, 107.7, 166.0; IR (KBr) 2963, 1574, 1539, 1481, 1440, 1367, 1333, 1306, 844, 813, 733 cm^{-1}.

3-Chloro-6-[(3,3-dinitro)-1-azetidinyl]-1,2,4,5-tetrazine, 6. 3,6-Dichloro-1,2,4,5-tetrazine (0.151 g, 1.0 mmol) was dissolved in acetonitrile, and **1** (0.294 g, 2.0 mmol) was added. The mixture was allowed to stir for 1 h at rt, during which time **1e** precipitated from solution. The mixture was filtered, and the solvent was evaporated to provide a crystalline, orange product (0.265 g, 98%): mp. 177-179 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 5.25 (s, 4H); ^{13}C NMR (DMSO-d_6) δ 59.7, 108.1, 161.6, 163.2; IR (KBr) 3003, 2953, 1591, 1533, 1458, 1447, 1371, 1338, 1306, 1216, 1137, 1052, 945, 929 cm^{-1}.

3,6-*bis*[(3,3-Dinitro)-1-azetidinyl)-1,2,4,5-tetrazine, 7. Triethylamine (0.70 g, 6.90 mmol) was added to a stirred solution of **1a** (1.0 g, 3.37 mmol) in acetonitrile (10 mL), and this addition was followed by the slow addition of 3,6-dichloro-1,2,4,5-tetrazine (0.166 g, 1.10 mmol). The reaction mixture was slowly brought to reflux over 2 h and then allowed to reflux for another 4 h. After cooling to rt, the reaction mixture was poured into water and allowed to stand overnight to agglomerate. The red precipitate was collected by filtration, air dried, and recrystallized from EtOAc/hexanes, affording a red solid (0.60 g, 15%): mp. 230 °C (dec.); ^{1}H NMR (DMSO-d_6) δ 5.13 (s, 8H); ^{13}C NMR (DMSO-d_6) δ 59.4, 108.2, 162.4; IR (KBr) 3009, 2964, 1586, 1564, 1484, 1445, 1369, 1335, 1302, 1057, 945, 839 cm^{-1}.

General Procedure for Preparation of 8b-d. Cyanogen bromide (0.758 g, 7.2 mmol) was added to a solution of sodium acetate (1.29 g, 15.7 mmol) in a methanol (30 mL) and water (9 mL) mixture, and **1b-d** (15.7 mmol) was added. After stirring at rt for 48 h, the mixture was refluxed for 7 h. (The reaction with **1c** was protected from light during this time.) After cooling to rt, the resultant precipitate was collected by filtration, washed with a minimum of cold water, and air dried.

1,1'-Carboimidoyl-*bis*-[(3,3-dinitro)-1-azetidine] nitrate, 8b: (1.56 g, 57%): mp. 212 °C dec.; ^{1}H NMR (DMSO-d_6) δ 5.17 (s, 8H),

8.61 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 60.0, 105.9, 157.3; IR (KBr) 3354, 3086, 3029, 2965, 1672, 1575, 1374, 1322, 1280 cm^{-1}. *Anal.* Calcd. for $C_7H_{10}N_8O_{11}$: C, 22.00; H, 2.64; N, 29.32. Found: C, 22.17; H, 2.46; N, 28.95.

1,1'-Carboimidoyl-*bis*-[(3,3-dinitro)-1-azetidine] dinitramide, 8c: (1.58 g, 52%): mp. 204 °C dec.; ^1H NMR (DMSO-d_6) δ 5.16 (s, 8H), 8.56 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 60.0, 105.9, 157.4; IR (KBr) 3377, 3340, 3276, 3230, 3180, 3015, 2961, 1669, 1575, 1516, 1313, 1186, 1026 cm^{-1}. *Anal.* Calcd. for $C_7H_{10}N_{10}O_{12}$: C, 19.73; H, 2.36; N, 32.86. Found: C, 19.96; H, 2.39; N, 32.82.

1,1'-Carboimidoyl-*bis*-[(3,3-dinitro)-1-azetidine] perchlorate, 8d: (2.49 g, 83%): mp. 237 °C dec.; ^1H NMR (DMSO-d_6) δ 5.15 (s, 8H), 8.54 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 60.0, 105.9, 157.3; IR (KBr) 3460, 3381, 3293, 3023, 2970, 1660, 1624, 1578, 1447, 1437, 1375, 1337, 1313, 1095 cm^{-1}. *Anal.* Calcd. for $C_7H_{10}N_7O_{12}Cl$: C, 20.04; H, 2.40; N, 23.36. Found: C, 20.36; H, 2.10; N, 23.27.

1-*N*-Nitroamino-1'-carboimidoyl(3,3-dinitro)-1-azetidine), 9. *S*-Methyl-*N*-nitroisothiourea[12] (2.54 g, 18.8 mmol) was added to a solution of **1** (2.76 g, 18.8 mmol) in absolute EtOH (5 mL), and the reaction mixture was stirred in a water bath at 45 °C for 24 h. The resulting precipitate was collected by filtration, and the crude filter cake

was washed with EtOH. After air drying, a white powder (2.9 g, 66%) was collected: mp. 133 °C; ^{1}H NMR (DMSO-d_6) δ 4.88 (s, 4H), 8.71 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 59.0, 106.6, 159.3; IR (KBr) 3418, 3032, 3382, 3315, 1631, 1577, 1500, 1453, 1372, 1328, 1223, 1061, 845, 783 cm^{-1}. *Anal.* Calcd. for $C_4H_6N_6O_6$: C, 20.52; H, 2.58; N, 35.90. Found: C, 20.89; H, 2.73; N, 35.85.

***N,N'*-Dihydroxy-*bis*-[(3,3-dinitro)-1-azetidine]ethane-diimidamide, 10.** Dichloroglyoxime (0.486 g, 3.1 mmol) was added to a solution of **1** (0.937 g, 6.4 mmol) dissolved in a $CHCl_3$ (25 mL) and MeOH (5 mL) mixture. The reaction mixture was allowed to stir at rt for 2 h. EtOAc (70 mL) was added, and the organic phase was washed with water (2 x 25 mL) and brine (25 mL), dried over $MgSO_4$, and evaporated to yield a yellow solid (0.84g, 72%). The crude product was dissolved in EtOAc and passed through a small pad of silica gel and evaporated. A pale yellow solid was obtained (0.82g, 70%): mp. 92 °C (dec.); ^{1}H NMR (acetone-d_6) δ 5.15 (s, 8H), 9.58 (br s, 2H); ^{13}C NMR (acetone-d_6) δ 63.3, 110.5, 144.1; IR (KBr) 3535, 3273, 2960, 1626, 1572, 1441, 1326, 956, 851 cm^{-1}. *Anal.* Calcd. for $C_8H_{10}N_8O_{10}$: C, 25.41; H, 2.66; N, 29.63. Found: C, 25.92; H, 2.80; N, 29.20.

1-Nitroso-3,3-dinitroazetidine, 11. **1a**, (4.455 g, 15.0 mmol) was dissolved in cold water (6 mL), and concentrated hydrochloric acid

(2 mL) was added. The slurry was stirred in an ice bath while sodium nitrite (1.05 g, 15.2 mmol) dissolved in water (6 mL) was added slowly over 10 min. The reaction mixture was allowed to stir 1h at 0 °C. A light yellow precipitate formed and was collected by filtration. The crude product was washed with water and allowed to air dry to yield a white solid (2.42 g, 92 %). Recrystallization from EtOAc/hexanes afforded the pure product: mp 103-105 °C; ^{1}H NMR ($CDCl_3$) δ 4.94 (s, 2H), 5.75 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 61.0, 62.6, 106.0; IR (KBr) 3038, 3014, 2982, 2963, 2906, 1568, 1420, 1335, 1203, 867, 843, 812 cm^{-1}. *Anal.* Calcd. for $C_3H_4N_4O_5$: C, 20.46; H, 2.29; N, 31.82. Found: C, 20.67; H, 2.24; N, 31.41.

1-(2,2,2-Trinitroethyl)-3,3-dinitroazetidine, 12. 2,2,2-Trinitroethanol (0.905 g, 5.0 mmol) was added to a solution of 3,3-dinitroazetidinium hydrochloride, **1e**, (0.918 g, 5.0 mmol) dissolved in cold water (30 mL). Sodium hydroxide (5.0 mL, 1.0 M) was slowly added over a few minutes. The solution turned yellow, and a white precipitate had formed. The suspension was stirred an additional hour and then filtered. The solid was washed with water and air dried to yield a white solid (0.80g, 52%): mp 94-95 °C; ^{1}H NMR ($CDCl_3$) δ 4.28 (s, 2H), 4.53 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 60.4, 63.7, 107.3, 125.8; IR (KBr) 2899, 1602, 1441, 1416, 1373, 1334, 1306, 1243, 996, 867, 806, 780 cm^{-1}. *Anal.* Calcd. for

$C_5H_6N_8O_{10}$: C, 19.36; H, 1.75; N, 27.10. Found: C, 19.92; H, 1.86; N, 27.29.

1-(2,2-Dinitropropyl)-3,3-dinitroazetidine, 13. Sodium carbonate (0.122 g, 1.2 mmol) and **1b** (0.215 g, 1.0 mmol) were added to a solution of 2,2-dinitropropanol (0.151 g, 1.0 mmol) dissolved in acetonitrile (10 mL). The reaction mixture turned yellow and was allowed to stir for 48h at rt. Water (25 mL) was added, and the reaction mixture was washed with EtOAc (3 x 40 mL). The combined organic phases were dried over $MgSO_4$ and evaporated to yield a yellow solid (0.22 g) that was a mixture of **13** (59%) and **14** (41%). The two components were separated by radial chromatography (EtOAc/hexanes, 1:4 to 1:1). **13**: mp 60-62 °C. ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 3.73 (s, 2H), 4.37 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 20.6, 61.9, 63.2, 107.7, 117.2; IR (KBr) 3432, 2925, 1577, 1563, 1464, 1384; 1332, 1230, 1023, 807, 845 cm^{-1}. *Anal.* Calcd. for $C_6H_9N_5O_8$: C, 25.81; H, 3.25; N, 25.09. Found: C, 26.13; H, 3.25; N, 24.84.

1,1'-Methylene-*bis*-(3,3-dinitro-1-azetidine), 14. Sodium carbonate (0.870 g; 8.2 mmol) was added to a solution of **1a** (2.44 g, 8.2 mmol) dissolved in water (15 mL). The mixture was stirred at rt for 15 min, then formalin (37%, 0.33g, 4.1 mmol) was added. The mixture was allowed to stir overnight at rt. A beige precipitate was formed, and EtOAc was added to the reaction mixture. The two layers were separated, and

the aqueous phase was washed with EtOAc (3 x 50 mL). The combined organic phases were dried over $MgSO_4$ and evaporated to dryness to afford an off-white solid (1.21 g, 98%). Recrystallization from EtOAc/hexanes afforded an off-white solid (0.92 g, 74%): mp 91-92 °C. ^1H NMR ($CDCl_3$) δ 3.56 (s, 2H), 4.21 (s, 8H); ^{13}C NMR ($CDCl_3$) δ 60.3, 78.3, 108.7; IR (KBr) 3436, 2847, 1569, 1438, 1334, 1242, 1226, 1056, 867, 844, 781 cm^{-1}. *Anal.* Calcd. for $C_7H_{10}N_6O_8$: C, 27.46; H, 3.29; N, 27.45. Found: C, 27.50; H, 3.46; N, 27.09.

1,3-*bis*-(3,3-Dinitro-1-azetidinyl)-2,2-dinitropropane, 15. 2,2-Dinitro-1,3-propanediol (ADIOL) (1.66 g, 10.0 mmol) was added to a solution of 3,3-dinitroazetidinium hydrochloride, **1e**, (3.67g, 20.0 mmol) dissolved in cold water (30 mL). After the suspension was heated to 70 °C for 5h, it was allowed to cool overnight. The flocculent white precipitate was collected by filtration, and the crude product was washed with water and allowed to air-dry to yield a white solid (1.02 g, 24%): mp 148-149 °C; ^1H NMR (acetone-d_6) δ 4.00 (s, 4H), 4.47 (s, 8H); ^{13}C NMR (acetone-d_6) δ 58.5, 62.3, 107.7, 118.0; IR (KBr) 2990, 2943, 1576, 1462, 1444, 1425, 1379, 1339, 1308, 1232, 1212, 990, 866, 843, 799, 744, 725 cm^{-1}. *Anal.* Calcd. for $C_9H_{12}N_8O_{12}$: C, 25.48; H, 2.85; N, 26.41. Found: C, 25.29; H, 2.78; N, 26.17.

References

[1]Author to whom correspondence should be addressed.

[2]M. A. Hiskey, M. D. Coburn, M. A. Mitchell, and B. C. Benicewicz, J. Heterocyclic Chem., *29*, 1855 (1992).

[3]M. A. Hiskey, M. D. Coburn, Los Alamos Report LA-12587-MS (1993).

[4]M. A. Hiskey, M. M. Stinecipher, and J. E. Brown, J. Energetic Materials, *11*, 157 (1993).

[5]J. A. Moore, R. S. Ayers, in "Small Ring Heterocycles," part 2; A. Hassner, ed., John Wiley, New York, 1983, pp. 1-217.

[6]L. R. Fedor, T. C. Bruice, K. L. Kirk, J. Meinwald, J. Am. Chem. Soc., *88*, 108 (1966).

[7]L. W. Deady, G. J. Leary, R. D. Topsom, J. Vaughan, J. Org. Chem., *28*, 511 (1963).

[8]A. Fischer, R. E. Hutchinson, R. D. Topsom, G. J. Wright, J. Chem. Soc. (B), 544 (1969).

[9]J. Frigola, A. Tormes, J. A. Castrillo, J. Mas, D. Vano, J. M. Berrocal, C. Calvet, L. Salgado, J. Redondo, S. Garcia-Granda, E. Valenti, J. R. Quintana, J. Med. Chem. *37*, 4195 (1994).

[10] H. Fischer, T. Mueller, I. Umminger, F. A. Neugebauer, H. Chandra, M. C. R. Symons, J. Chem. Soc. Perkin Trans. II, 413 (1988).

[11]J. R. Stine, Los Alamos Report LA-8920 (1981).

[12]L. Fishbein and J. A. Gallaghan, J. Am. Chem. Soc., *76*, 1877 (1954).

[13]Density determined by flotation.

[14]Density determined by R. D. Gilardi, Unpublished Results, Naval Research Laboratory, Washington D. C.

[15]C. L. Bumgardner, K. S. McCallum, J. P. Freeman, J. Am. Chem. Soc. *83*, 4417 (1961).

[16]R. Behrens, Jr., "Vapor Pressures of TNAZ, Nitroso-DNAZ and TNAZ/Nitroso-DNAZ Mixtures," Sandia National Laboratories, Livermore, CA, March 1995.

[17]H. H. Cady, Unpublished Results, Los Alamos National Laboratory, Los Alamos, NM.

[18]M. B. Frankel and K. Klager, J. Chem. Eng. Data, *7*, 412 (1962).

[19]F. Feuer, G. G. Bachman, and W. May, J. Am. Chem. Soc., *76*, 5124 (1954).

[20]M. B. Frankel and K. Klager, J. Am. Chem. Soc., *79*, 2953 (1957).

[21]T. G. Archibald, R. Gilardi, K. Baum, and C. George, J. Org. Chem., *55*, 2920 (1990).

[22]L. E. Fried, Cheetah Computer Program, Lawrence Livermore National Laboratory, 1995.