

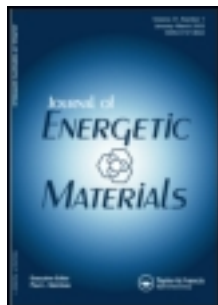
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An improved synthesis of 5-amino-3-nitro-1H-1,2,4-triazole (ANTA), a useful intermediate for the preparation of insensitive high explosives

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**AN IMPROVED SYNTHESIS OF 5-AMINO-3-NITRO-1*H*-1,2,4-
TRIAZOLE (ANTA), A USEFUL INTERMEDIATE FOR THE
PREPARATION OF INSENSITIVE HIGH EXPLOSIVES**

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ABSTRACT

Treatment of the ammonium salt of 3,5-dinitro-1*H*-1,2,4-triazole (ADNT) with hydrazine hydrate gives 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) in greater than 90% yields. In addition to its potential use as an insensitive high explosive, ANTA has been shown to be a useful intermediate for the preparation of other explosives.

INTRODUCTION

The search for new insensitive high explosives (IHE) is of continuing interest at Los Alamos. In 1982, we initiated a study of 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA)¹ and found it to be a potentially useful IHE with impact

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sensitivity and calculated performance comparable to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (TABLE 1). The impact sensitivity for new materials may be estimated from homologous series oxygen balance relationships.² The aminotrinitrobenzene series and 1,2,4-triazole series regressions are shown in FIGURE 1. This regression for the 1,2,4-triazole series predicts a Type 12 impact sensitivity for ANTA that is similar to that for TATB, i.e. it should be considerably greater than 320 cm.

The sodium salt (1) of ANTA has been treated with commercially available 4,6-dichloro-5-nitropyrimidine (2) in ethanol by French workers to yield a new IHE, which they have evaluated extensively.³ The structure of the product was recently established by x-ray crystallography of its solvates with N,N-dimethylformamide⁴ and 1-methyl-2-pyrrolidinone⁵ to be 4,6-bis(5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)-5-nitropyrimidine (3) instead of the isomeric 4,6-bis(5-nitro-1*H*-1,2,4-triazol-3-ylamino)-5-nitropyrimidine (4), as originally proposed by these workers (SCHEME 1).

The only previous report of the synthesis of ANTA is a four-step process starting initially with 3-amino-1*H*-1,2,4-triazole.⁶ In our hands this procedure gave only 5-10% overall yields of ANTA. Thus, in order for ANTA or its derivatives to be viable candidates for explosives applications, an improved method for its synthesis had to be developed.

TABLE 1

A Comparison of the Physical and Explosive Properties of ANTA and TATB.

	ANTA	TATB
Molecular Formula	$C_2H_3N_5O_2$	$C_6H_6N_6O_6$
Crystal Density (g/cm^3)	1.82	1.94
Melting point ($^{\circ}C$)	244	>325
Thermal stability ($^{\circ}C$)	>240	>350
Vacuum stability (ml/g/48 h, $120^{\circ}C$)	0.3	0.2
Impact sensitivity (cm), Type 12	>320	>320
Spark sensitivity (J), 3-mil foil	>1.0	4.25
Heat of formation (kcal/mol)	21.0 ± 2.5	-36.85
Detonation Velocity (km/s)	8.46 (calc.)	7.98 (calc.)
C-J Pressure (kbar)	314 (calc.)	315 (calc.)

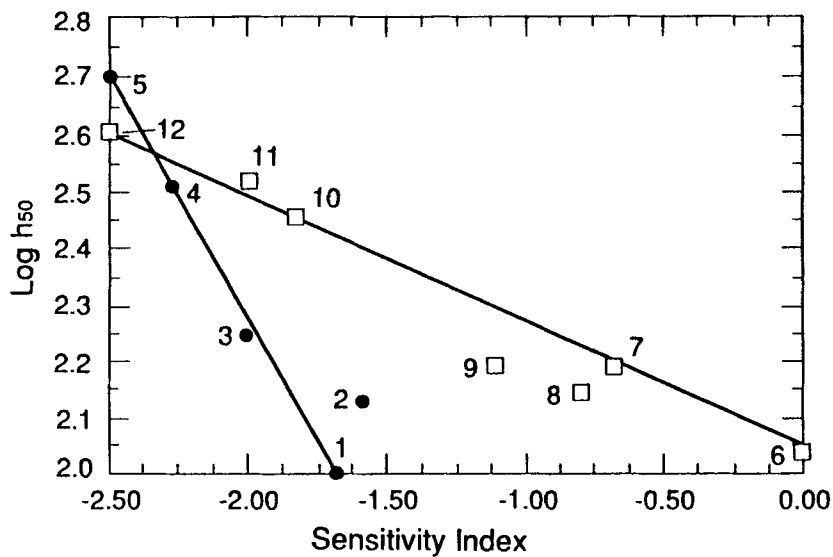
TABLE 2

Physical and Explosive Properties of
4,6-Bis(5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)-5-nitropyrimidine (3)

Molecular Formula	$C_8H_5N_{13}O_6$
Density (g/cm^3)	1.84 (gas pycnometry)
Impact Sensitivity (Type 12) (cm)	>320
Spark Sensitivity (3-mil foil) (J)	>1.0
Heat of Formation (kcal/mol)	103 ± 5
Detonation Velocity (km/s)	8.12 (calc.)
C-J Pressure (kbar)	297 (calc.)

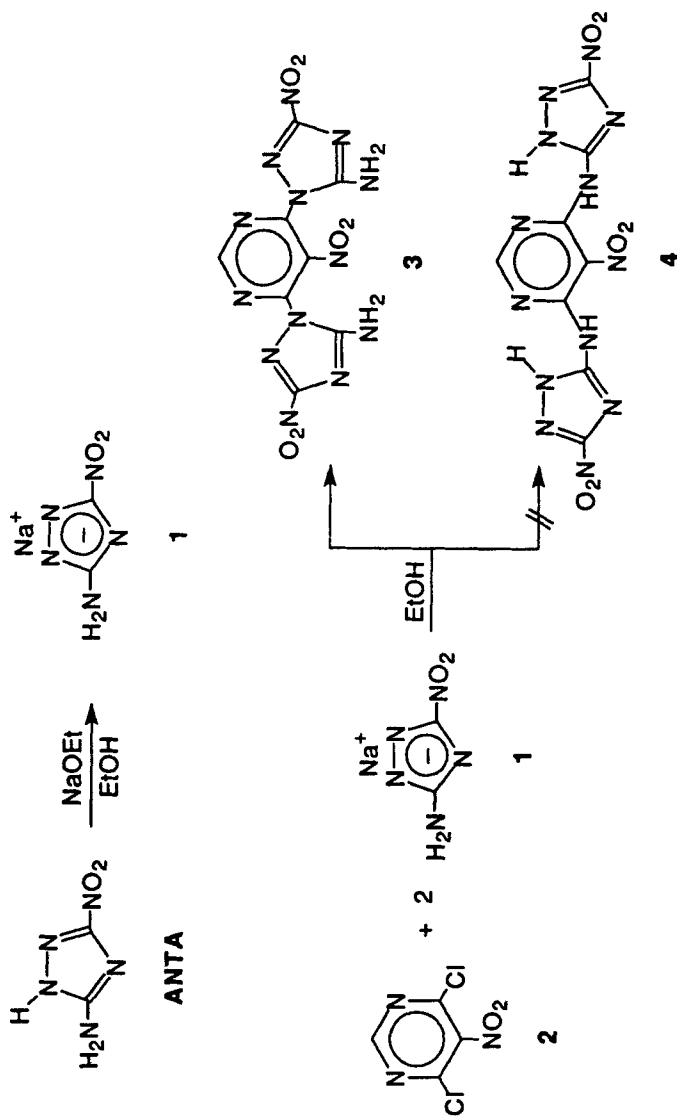
FIGURE 1

Scattergram of Sensitivity Index vs. Log h₅₀



- | | |
|--------------------------|--|
| 1. 1,3,5-Trinitrobenzene | 7. 4-Methyl-3,5-Dinitro-1,2,4-Triazole |
| 2. DIPAM | 8. N,N'-Dipicryl-5,5'-Dinitro-3,3'-Bi-1,2,4-Triazole |
| 3. 2,4,6-Trinitroaniline | 9. 5,5'-Dinitro-3,3'-Bi-1,2,4-Triazole |
| 4. DATB | 10. NTO |
| 5. TATB | 11. 3-Nitro-1,2,4-Triazole |
| 6. ADNT | 12. ANTA |

SCHEME 1



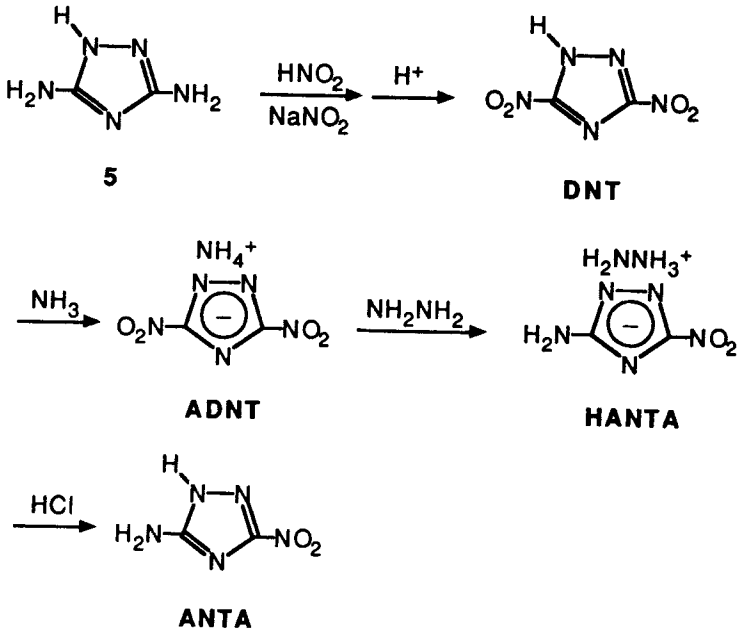
RESULTS

Our approach to the synthesis of ANTA was to selectively reduce 3,5-dinitro-1*H*-1,2,4-triazole (DNT), which is conveniently prepared from commercially available 3,5-diamino-1*H*-1,2,4-triazole (**5**) and isolated as the ammonium salt (ADNT).⁷ Sodium sulfide, which has been reported to selectively reduce aromatic nitro compounds to amines,^{8,9} was an effective reducing agent, but the yields of ANTA obtained from this process were less than 60% and the purification of the product was tedious. However, selective reduction of ADNT with hydrazine hydrate¹⁰ gave the hydrazinium salt of ANTA (HANTA), which was acidified *in situ* to consistently give greater than 90% yields of pure ANTA (SCHEME 2).¹¹

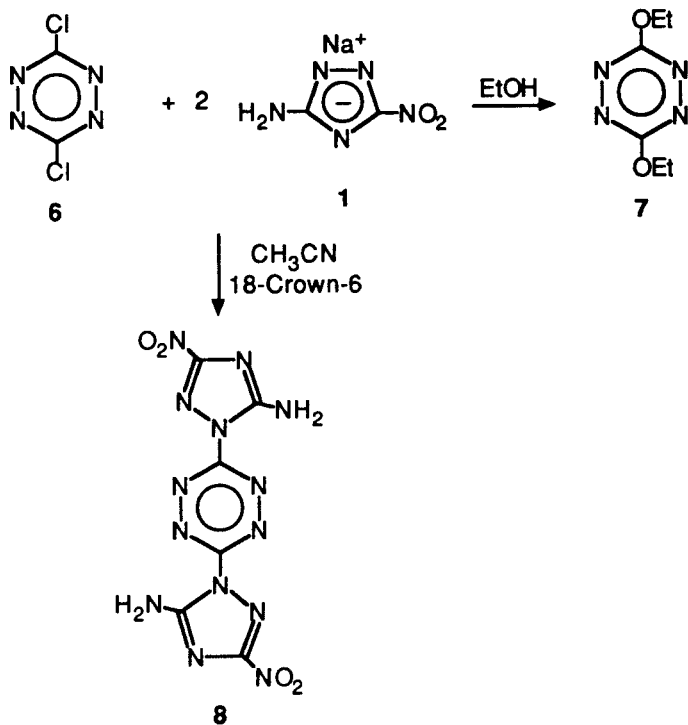
We repeated the the French procedure and determined some physical and explosive properties for **3** (TABLE 2). The detonation velocity of 8.12 km/s, which we calculated with the BKW method using our measured values for density and heat of formation, is significantly lower than that reported (8.6 km/s).

Analogous treatment of 3,6-dichloro-1,2,4,5-tetrazine (**6**)¹² with **1** in ethanol produced 3,6-diethoxy-1,2,4,5-tetrazine (**7**) as the only product; however, the reaction in acetonitrile gave 3,6-bis(5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**8**) in 60% yield (SCHEME 3). With a catalytic amount of 18-crown-6 present, the yield of **8** was improved to 77%. Preliminary impact sensitivity tests indicate that **8** is too sensitive to be considered for IHE applications, so a complete characterization of **8** was not performed.

SCHEME 2



Scheme 3



Similarly, **1** reacted with cyanuric chloride (**9**) in the presence of a catalytic amount of dibenzo-18-crown-6 in acetonitrile to produce 2,4,6-tris(5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)-1,3,5-triazine (**10**) in good yield (SCHEME 4). Only two of the chloro groups of **9** were replaced in the absence of dibenzo-18-crown-6. We are currently evaluating the explosive properties of **10**. Thus, we have demonstrated the utility of ANTA as a synthon for new explosives. The structural assignments of **8** and **10** are based upon analogy with the known structure **3**.

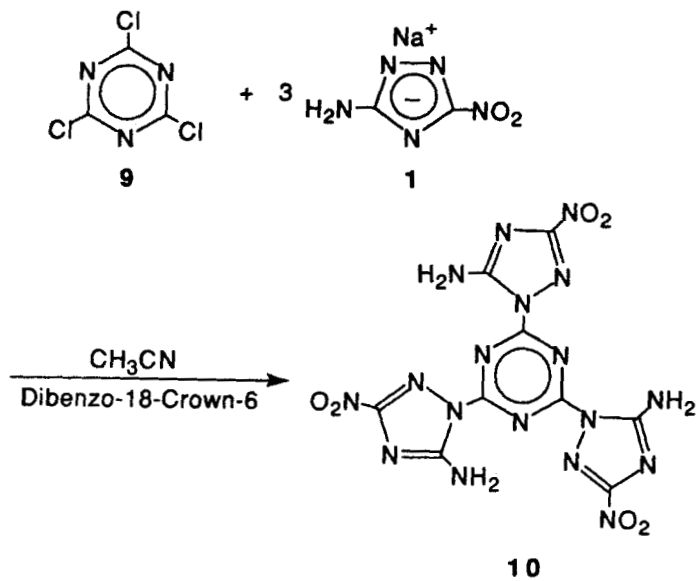
EXPERIMENTAL

All NMR spectra were obtained on a JEOL GSX-270 spectrometer. Chemical shifts are relative to internal tetramethylsilane = 0 for the ¹H- and ¹³C-NMR spectra and to external nitromethane = 0 for the ¹⁵N-NMR spectra. Microanalyses were performed at Los Alamos National Laboratory by M. J. Naranjo. All melting points were determined at 2°/minute with a Mettler FP1 apparatus and are corrected.

5-Amino-3-nitro-1*H*-1,2,4-triazole (ANTA) and its Sodium Salt (**1**).

To a stirred solution of hydrazine hydrate (33 ml, 0.66 mol) was added ammonium 3,5-dinitrotriazolate (ADNT)⁷ (25 g, 0.14 mol) at 25°C. After the ADNT had completely dissolved, the temperature was raised to 80°C and held at this temperature for 2 h. The solution was cooled to room temperature, diluted to approximately 50 ml with water, and adjusted to pH 4 with 10% hydrochloric acid. The precipitated solid was collected by filtration and dried under high vacuum to

SCHEME 4



yield 17.0 g (93%) of pure ANTA, mp 244°C [lit.⁶ mp 240°C]; ¹³C-NMR (methyl sulfoxide): δ 157.5, 160.9; ¹⁵N-NMR (methyl sulfoxide): δ -327.2, -199.8, -178.9, -107.2, -23.6.

Anal. Calcd. for C₂H₃N₅O₂: C, 18.61; H, 2.34; N, 54.26. Found: C, 18.70; H, 2.25; N, 54.63.

The sodium salt of ANTA (**1**) was prepared by adding ANTA (1.29 g, 0.01 mol) to a freshly prepared solution of sodium ethoxide (0.01 mol) in ethanol (30 ml). After heating under reflux for 2 h, the salt was removed by filtration, washed with ethanol, and dried to give 1.48 g (98%) of **1**.

4,6-Bis(5-amino-3-nitro-1H-1,2,4-triazol-1-yl)-5-nitropyrimidine (**3**).

To a freshly prepared solution of sodium ethoxide (5 mmol) in ethanol (20 ml) was added ANTA (0.66 g, 5 mmol). After heating the mixture under reflux for 2 h, 4,6-dichloro-5-nitropyrimidine (**2**) (0.49 g, 2.5 mmol) was added and the resulting mixture was refluxed an additional 3 h. The solid was removed by filtration, washed sequentially with water, methanol, and chloroform, and dried under vacuum to yield 0.68 g (80%) of **3**. The compound does not melt, but begins to decompose at 300°C according to differential thermal analysis; ¹H-NMR (methyl sulfoxide-d₆): δ 8.70 (s, 4H), 9.11 (s, 1H); ¹³C-NMR (1-methyl-2-pyrrolidinone): δ 148.9, 156.8, 158.6, 159.9, 161.5; ¹³C-NMR (methanesulfonic acid): δ 122.1, 148.1, 148.3, 151.6, 156.7; ¹⁵N-NMR (methanesulfonic acid): δ -245.4, -203.5, -124.6, -119.6, -43.5, -30.2.

Anal. Calcd. for C₈H₅N₁₃O₆: C, 25.34; H, 1.33; N, 48.02. Found: C, 25.54; H, 1.28; N, 47.70.

3,6-Bis(5-amino-3-nitro-1H-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (8).

To a slurry of **1** (0.68 g, 5 mmol) and 18-crown-6 (0.02 g, 0.075 mmol) in anhydrous acetonitrile (15 ml) was added a solution of 3,6-dichloro-1,2,4,5-tetrazine (**6**)¹² (0.34 g, 2.25 mmol) in anhydrous acetonitrile (2 ml). The mixture was heated under reflux for 4 h, cooled to room temperature, and centrifuged until the supernatant liquid was clear. The liquid was decanted and the solid was washed successively with water and methanol. With each wash, the solid was separated from the solvent by centrifugation followed by decantation. The resulting solid was dried under high vacuum to yield 0.58 g (77%) of **8**. The product does not melt, but begins to decompose at 260°C according to differential thermal analysis; ¹³C-NMR (methanesulfonic acid): δ 150.0, 151.6, 159.1; ¹⁵N-NMR (methanesulfonic acid): δ -297.8, -244.9, -205.0, -116.3, -42.8, -16.0.

Anal. Calcd. for C₆H₄N₁₄O₄: C, 21.44; H, 1.20; N, 58.33. Found: C, 21.29; H, 1.14; N, 57.80.

2,4,6-Tris(5-amino-3-nitro-1H-1,2,4-triazol-1-yl)-1,3,5-triazine (10).

A mixture of **1** (0.73 g, 5.3 mmol), cyanuric chloride (**9**) (0.27 g, 1.5 mmol), and dibenzo-18-crown-6 (0.01 g, 0.03 mmol) in anhydrous acetonitrile (25 ml) was heated under reflux for 5 h. After the mixture had cooled to room temperature, it was centrifuged until the supernatant liquid was clear. The liquid was decanted and the solid was washed successively with water, methanol, toluene, and acetone. With each wash, the solid was separated from the solvent by centrifugation followed by decantation. The resulting solid was dried at 100°C under vacuum to yield 0.56 g (81%) of **10**. The product does not melt, but begins

to decompose at 260°C according to differential thermal analysis; ¹³C-NMR (methanesulfonic acid): δ 150.8, 153.6, 163.7; ¹⁵N-NMR (methanesulfonic acid): δ -294.4, -244.5, -198.4, -167.2, -116.9, -43.75.

Anal. Calcd. for C₉H₆N₁₈O₆: C, 23.38; H, 1.31; N, 54.54. Found: C, 23.30; H, 1.27; N, 54.39.

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