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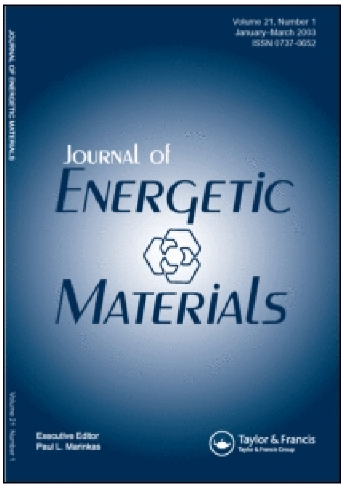

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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Darren L. Naud; Michael A. Hiskey; Herbert H. Harry

Online publication date: 29 October 2010

To cite this Article Naud, Darren L. , Hiskey, Michael A. and Harry, Herbert H.(2003) 'Synthesis and Explosive Properties of 5,5'-Dinitro-3,3'-azo-1 H -1,2,4-triazole (DNAT)', Journal of Energetic Materials, 21: 1, 57 — 62
To link to this Article: DOI: 10.1080/07370650305584
URL: http://dx.doi.org/10.1080/07370650305584

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Energetic Materials, 21: 57–62, 2003
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0737-0652/03 $12.00 + .00
DOI: 10.1080/07370650390195799

Synthesis and Explosive Properties of 5,5′-Dinitro-3,3′-azo-1*H*-1,2,4-triazole (DNAT)

DARREN L. NAUD
MICHAEL A. HISKEY
HERBERT H. HARRY

Los Alamos National Laboratory
High Explosives Science and Technology
Los Alamos, NM, USA

The synthesis of 5,5′-dinitro-3,3′-azo-1H-1,2,4-triazole (DNAT) by the oxidative coupling of 5-amino-3-nitro-1H-1,2,4-triazole is described. The thermal properties of DNAT were investigated by differential scanning calorimetry and thermogravimetric analysis. The sensitivity and explosive properties are also reported.

Keywords: 5,5′-dinitro-3,3′-azo-1H-1,2,4-triazole, 5-amino-3-nitro-1H-1,2,4-triazole

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Introduction

At Los Alamos National Laboratory the synthesis of compounds high in nitrogen content has been the focus of our efforts for the past decade. Of the many newly synthesized compounds that we have previously reported, two explosives of significant importance contain the azo functionality, namely, 4,4′-diamino-3,3′-azofurazan (DAAzF) [1] and 3,3′-azobis(6-amino-s-tetrazine) (DAAT) [2]. Both compounds have remarkably high heats of formation (DAAzF = 128 kcal/mol; DAAT = 206 kcal/mol) that can be significantly attributed to the

Address correspondence to D. Naud, Los Alamos National Laboratory, High Explosives Science and Technology, MS-C920, Los Alamos, NM 87545. E-mail: naud@lanl.gov

azo functionality. Because a large positive heat of formation is a desirable feature of explosive molecules, we have continued searching for other suitable azo explosives. This paper describes the synthesis and explosive properties of another azo-containing explosive, 5,5′-dinitro-3,3′-azo-1*H*-1,2,4-triazole (DNAT).

Results

The compound 5,5′-dinitro-3,3′-azo-1*H*-1,2,4-triazole (DNAT) has been previously investigated, but yields were low and product purity was poor, and further investigation was therefore hampered [3]. In the above study, DNAT was produced by the oxidation of the potassium salt of 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) with potassium permanganate followed by treatment with acid. Lee et al. describe the synthesis of the precursor, ANTA [4]. Oxidizing ANTA with ammonium persulfate in an aqueous medium yielded mixtures of DNAT and the azoxy form of DNAT. Better yields and purity, however, are obtained when permanganic acid formed in situ is used to generate DNAT (Figure 1). One minor product of the reaction is 5-chloro-5′-nitro-3,3′-azo-1*H*-1,2,4-triazole, which was confirmed by X-ray crystography [5]. Presumably, this compound is formed by nucleophilic substitution of one nitro group of DNAT by a chloride ion. This type of displacement has been observed to occur under similar conditions [6].

The density of DNAT was measured to be 1.88 g/cm^3 by gas pycnometry, which is relatively high when compared to other explosives. Unfortunately, anhydrous DNAT powder produced by drying the hydrated form of DNAT cannot be pressed into pellets with densities greater than approximately 90% of theoretical maximum

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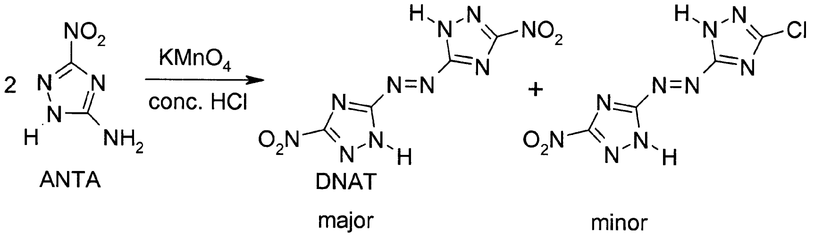

Figure 1. Oxidative coupling of ANTA by permanganic acid produces the explosive DNAT as the major product.

density. In the attempt to produce a powder with larger-sized particles, anhydrous DNAT was recrystallized from acetonitrile by using a Soxhlet apparatus. However, the resulting powder pressed to only slightly higher densities (91.7% theoretical maximum density).

The heat of formation of DNAT was measured to be + 97.4 ± 0.3 kcal/mol by combustion calorimetry; when normalized on a per atom basis, a value of 4.87 kcal/mol-atom is realized. Lee et al. previously reported a heat of formation of + 78 kcal/mol [3]. Although DNAT has a lower heat of formation when compared to the other two azo explosives, DAAT (206 kcal/mol or 10.3 kcal/mol-atom) and DAAzF (128 kcal/mol or 7.11 kcal/mol-atom), DNAT has a better oxygen balance and therefore can produce more combustive energy.

The impact sensitivity of DNAT was measured to be 50 cm (2.5 kg, Type 12), whereas an HMX standard gave 25 cm under similar conditions. DNAT exhibited some slight sensitivity to friction (BAM apparatus), giving one positive result at 25 kg, but also giving negative results at maximum loadings of 36 kg. In addition, the explosive was shown to have no sensitivity to spark (0.36 J).

Two detonation experiments were performed on DNAT. In each experiment the DNAT was formulated with 2.5 wt% Estane binder and 2.5 wt% BDNPA/F plasticizer. In the first experiment a poly-rho test was performed at a diameter of 0.5 inches and in the density range 1.42 and 1.66 g/cm^3. This test can be described as an explosive rate stick composed of pellets with increasing density. Between each pellet was a Mylar foil switch that was used to detect the arrival of the detonation front. A booster train composed of four of the lowest density DNAT pellets initiated the rate stick at the low density end while the times for the detonation front to travel the distance of each pellet were recorded by an oscilloscope. In essence, the poly-rho test is a single-shot experiment that yields detonation velocity as a function of explosive density. The results of this test are shown in Figure 2.

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In the second test the detonation velocity of DNAT was measured as a rate stick composed of a stack of 0.5 inch diameter and 0.5 inch tall pellets. The pellets were pressed to approximately 1.67 g/cm^3 or 90.3% theoretical maximum density, which was the highest that could be achieved with our press. Using a data-collection technique similar to that used for the poly-rho experiment, the detonation velocities of five pellets of the rate stick were measured to be approximately 7.95 km/s. The same rate stick experiment gave plate dent data, which came to 287 kbar. Using these velocity measurements obtained from the rate stick experiments and from the poly-rho, a fitted line was

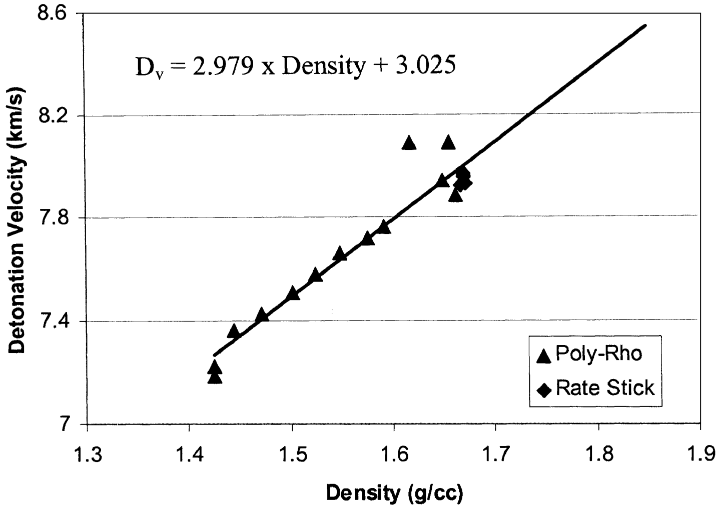

Figure 2. Detonation velocity (Dv) data obtained from poly-rho and rate stick experiments. The fitted line is extrapolated to the theoretical maximum density of the formulated explosive.

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calculated and drawn in Figure 2. The line extrapolates to the theoretical maximum density of the formulated explosive, which is approximately 1.85 g/cm^3. The detonation velocity at that density is 8.5 km/s.

Synthesis

To 1.4 L of concentrated hydrochloric acid was slowly added 80 g (0.62 mol) of 5-amino-3-nitro-1*H*-1,2,4-triazole (ANTA) with stirring. The suspension was warmed to 45 °C to dissolve the ANTA into the acid solution. To this mixture was added a warm solution (approximately 50 °C) composed of 700 mL of water and 68.6 g of potassium permanganate (0.43 mol) over the course of 10 min. Because the reaction is slightly exothermic, the mixture's temperature was maintained at 50 °C by the addition of ice.

After stirring for 4 hr and cooling to room temperature, the solution was refrigerated overnight and filtered cold on a fritted funnel. The crude product was dissolved in 1.5 L of boiling water and filtered hot to remove insoluble impurities. The solution was chilled overnight and the product collected by filtration. Drying the product for 8 hr at 105 °C provided 47.6 g (60% yield, based on pure DNAT) of anhydrous DNAT containing a few percent of 5-chloro-5′-nitro-3,3′-azo-1*H*-1,2,4-triazole. To this crude product was added 50 mL of ethanol and triturated with heating for 15 min; thereafter the mixture was cooled in an ice bath.

The thick mixture was filtered to remove as much ethanol as possible and later washed with chilled ethanol (ca. 200 mL). The yellow cake was dried in an oven at 105 °C for 8 hr. The yield of pure DNAT was 42.3 g or 54%. The structure of DNAT as a DMSO di-solvate had been previously confirmed by X-ray crystallography [5]. In that work the position of the ring proton was determined to be on the second nitrogen position adjacent to the carbon bearing the azo linkage.

^{13}C NMR (DMSO-d_6) 163.10, 162.80. Elemental Analysis, calculated for $C_4H_2N_{10}O_4$: C, 18.91; H, 0.79; N, 55.12. Found: C, 18.56; H, 0.99; N, 55.66.

The impurity, 5-chloro-5′-nitro-3,3′-azo-1,2,4-triazole, was isolated by fractional crystallization from ethanol. ^{13}C NMR (DMSO-d_6) 164.66, 162.00, 160.81, 147.58. Elemental Analysis, calculated for $C_4H_2N_9O_2Cl$: C, 19.72; H, 0.83; N, 51.76. Found: C, 19.66; H, 1.03; N, 52.17.

The yield and purity of DNAT produced by the above method appear to be somewhat dependent on the experimental conditions. Several experiments were performed to determine the affect on product yield by varying the rate of addition of the permanganate solution to the reaction mixture. When the permanganate was added over the course of 30 min, the yield of crude DNAT (i.e., after recrystallization from 1.5 L water) decreased to 51%; when the addition was performed over 70 min, the yield of crude DNAT decreased still further to 38%. Furthermore, the purities of the crude products, as determined by ^{13}C NMR, worsened.

Best results were obtained by repeating the same reaction but reducing the amount of concentrated HCl from 1.4 L to 1.0 L and performing the addition of permanganate solution in 10 min. This gave the highest yield of 70.6% after recrystallization from 1.5 L water. Attempts to synthesize DNAT by substituting hydrochloric acid with sulfuric acid produced no product, thus indicating the oxidation chemistry is somewhat complex and may require chloride ion in addition to the permanganate ion.

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