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Synthesis and Energetic Properties of TAGDNAT: A New High-Nitrogen Material

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ABSTRACT: This paper describes the synthesis and characterization of Bis triaminoguanidinium 3,3'-dinitro-5,5'-azo-1,2,4-triazolate(TAGDNAT), a novel high-nitrogen molecule that derives it's energy release from both a high heat of formation and intramolecular oxidation reactions. TAGDNAT shows promise as a propellant or explosive ingredient not only due to it's high nitrogen content (66.35 wt%) but additionally due to it's high hydrogen content (4.34 wt%). This new molecule has been characterized with respect to its morphology, sensitivity properties, explosive and combustion performance. The heat of formation of TAGDNAT was also experimentally determined. The results of these studies show that TAGDNAT has one of the fastest low-pressure burning rates (at 1000 PSI) we have yet measured, 6.79 cm/s at 100 p.s.i. (39% faster than triaminoguanidinium azotetrazolate

(TAGzT), a comparable high-nitrogen/high-hydrogen material). Furthermore, its pressure sensitivity is 0.507, a 33% reduction compared to TAGzT.

Introduction

High-nitrogen materials continue to be the focus of energetic materials research scientists across the globe [1-6]. This is due in large part to the unique energetic materials properties that these materials possess [7-9]. An example of one of these unique properties is seen burn-rate modifying properties of the bis-triaminoguanidinium azotetrazolate (TAGzT) when incorporated into nitramine-based propellant systems. It has been shown that replacement of a portion of RDX with TAGzT in a some types of gun propellant systems leads to a dramatic increase in the overall burn rate of the propellant [10]. Several studies aimed at studying the combustion characteristics of TAGzT and its mixtures with RDX have been reported and insight into the burn-rate modification mechanisms are being elucidated [11].

Although, the burn-rate modifying ability of TAGzT is a very useful property, the ability to design an optimized burn-rate modifier from first principles is at best in its infancy. Important questions must be answered to achieve this goal. As part of our effort to support the development of burn-rate modification in general, we have been studying numerous triamino-guanidinium salts of a variety of heterocyclic anions looking for structure-function relationships with respect to burn rate modification. This paper describes the synthesis and characterization of TAGDNAT, a promising new high-nitrogen material and potential propellant burn-rate modifier.

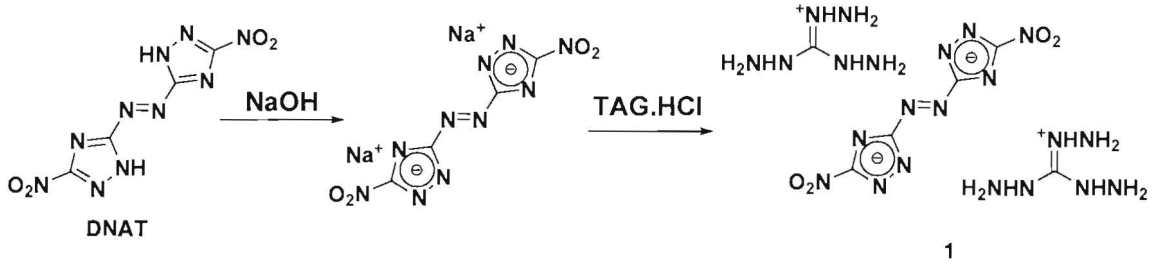
Results and Discussion

Synthesis and Characterization

TAGDNAT was prepared easily from 3,3'-dinitro-5,5'-azo-1,2,4-triazole (DNAT) [12-13] through neutralization by treatment with sodium hydroxide, followed by cation methathesis with triaminoguanidinium hydrochloride (Scheme 1). The reaction was performed in water and the product

was isolated in excellent yield as a yellow crystalline solid. The material was found to have a thermal decomposition onset temperature of 205 °C, using a 10 °C/ min heating ramp rate. The energy released upon decomposition was 1681 J/g. The heat of formation of TAGDNAT was measured using combustion calorimetry. A Parr 6300 calorimeter was employed and the heat of combustion was measured for the pure material in triplicate. Based on the vaules for the heat of combustion for TAGDNAT, a heat of formation of 711.28 kJ/mol was determined. The heat of formation of DNAT was reported to be 406 kJ/mol [13].

Scheme 1. Preparation of TAGDNAT.



The morphology of TAGDNAT was investigated by SEM. The TAGDNAT particles are rhomboid in shape and with particle dimensions of roughly 100 X 100 micron and 20-30 microns in thickness (Figure 1). This is in contrast to TAGzT which precipitates out as needles with a large aspect ratio, and introduces difficulties in formulation. TAGDNAT was studied by X-ray crystallographic analysis. An X-ray quality crystal was grown from water and the crystal structure is displayed in Figure 2. The molecule crystallized in the monoclinic crystal system with a density of 1.68 g/cm^3[14]. The density of TAGzT, for comparison is only 1.61 /cm^3[15-16].

The sensitivity properties of TAGDNAT were measured and are displayed in Table 1. The data are compared to TAGzT and PETN as references. TAGDNAT is slightly more thermally stable than TAGzT, and has improved sensitivity properties with respect to impact spark and friction.

Table 1. Explosive Sensitivity Data for **1**

Material	H_{50} (cm)	DSC (°C)	Friction (kg)	Spark (J)
1	38	202	16	0.125
TAGzT	25	195	10	0.0625
PETN	12	161	6.6	0.0625

Figure 1. Scanning electron microscopy images of TAGDNAT. The crystals have an aspect ratio of 1:2.

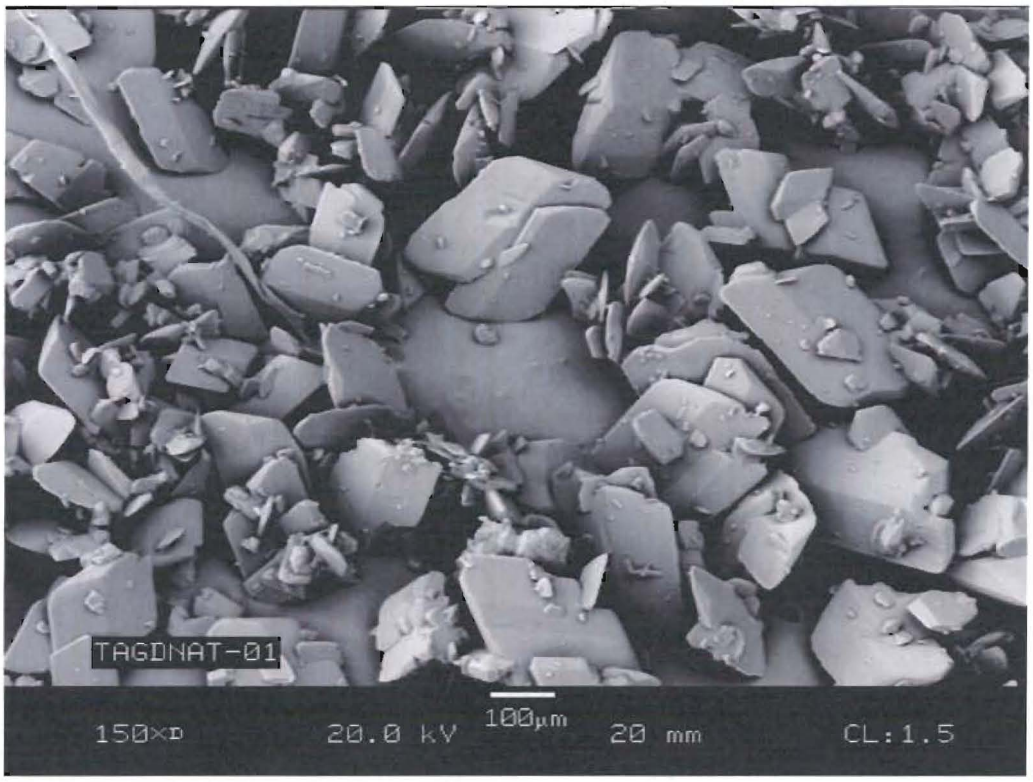
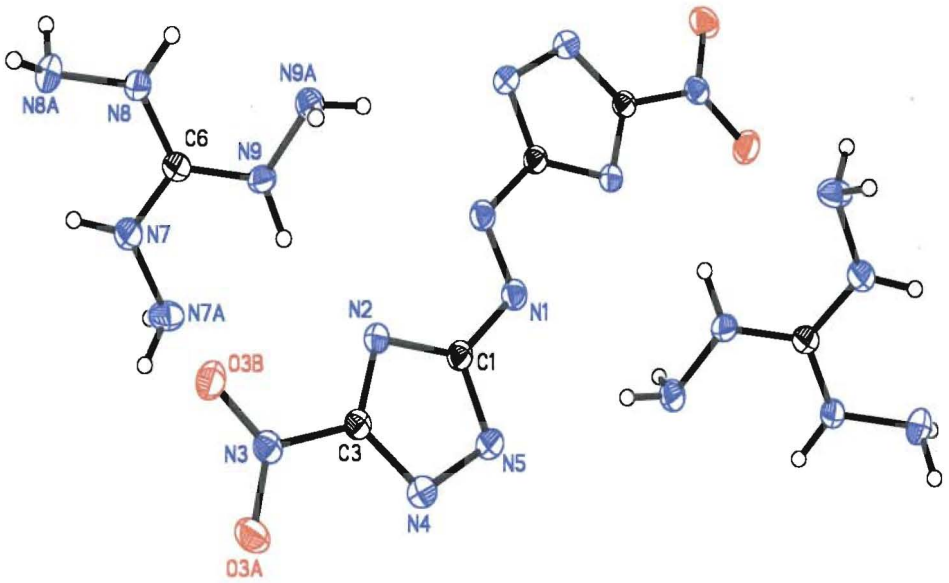


Figure 2. 50% thermal ellipsoids plot of Triaminoguanidinium 3,3-dinitroazotriazolate (TAGDNAT). Only one of the triaminoguanidinium molecules and ½ of the 3,3-dinitroazotriazolate is crystallographically unique.



Explosive Performance

The explosive performance of TAGDNAT was investigated using the rate-stick/plate-dent experiment. TAGDNAT was formulated with 5% KEL-F binder and pressed into cylindrical pellets (0.5 in. x 0.5 in.) of 94% theoretical maximum density. The measured detonation velocity and estimated detonation pressure are shown in Table 2 along with the predicted values calculated using the Cheetah 5.0 code [17]. We have also tried to obtain the same experimental data for TAGzT, however we have found that this material does not detonate using the same cylinder size, nor does it detonate at cylinders of 1 in. x 1 in. We have provided the predicted values for TAGzT using the Cheetah 5.0 code, which differ from the previously reported calculated values were using TIGER code. [15]

Table 2. Explosive Performance Properties for **1** and **2**.

	1 (exp)	**1** (calc)	TAGzT (exp)	TAGzT (calc)
D_v (km/s)[ρ, g/cm^3]	7.6 [1.58]	8.2 [1.58]	N/A	8.9 [1.60]calc.
P_{CJ} (kbar)[ρ, g/cm^3]	230	229	N/A	266 calc.

Burning Rate

Cylindrical pellets 6.3 mm in diameter and 6.4 mm long of the neat TAGDNAT and DNAT were burned in a 2L stainless steel vessel under pressurized argon of 2 - 70 atm. The volume is sufficiently large that the decomposition gases have little effect on the pressure. To prevent the flame front from spreading down the pellet sides, burning of the pellet sides was inhibited with a thin film of silicone vacuum grease. The pellets were ignited by means of a resistively heated nickel chromium wire. The combustion event was filmed between 50 fps and 1000 fps using a Red Lake MotionScope PCI 8000S high-speed-video system and a Phantom MIRO3 from Vision Research. The pressure was monitored with an Omega Model PX605-10KGI static pressure transducer. Optical records were analyzed using commercially available computer graphics software to obtain the burning rate data. Typical images are shown in Fig. 2.

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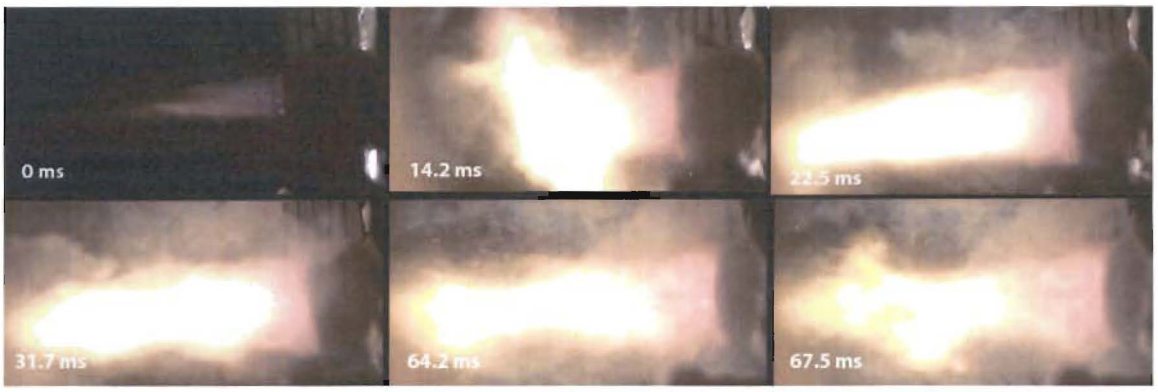

. **Figure 3.** Typical images from the burning of TAGDNAT at 68 atm.

In Fig. 4 we see the measured burning rates of TAGDNAT and DNAT as compared to the previously measured rates of TAGzT and HMX. [18-20] Most notably, the TAGDNAT shows a burning rate that exceeds that of TAGzT, with a lower pressure sensitivity. In fact, except at the lowest of pressures, TAGDNAT displays a rate that is even faster than DAATO3.5, when analyzed on a mass burning rate basis[19]. This is because despite the higher density of DAATO3.5 (1.90 g/cm^3), the morphology of the crystals only allow for a pressing density of 65% of theoretical density. Figure 4 shows the mass burning rate of TAGDNAT compared with that of DAATO3.5.

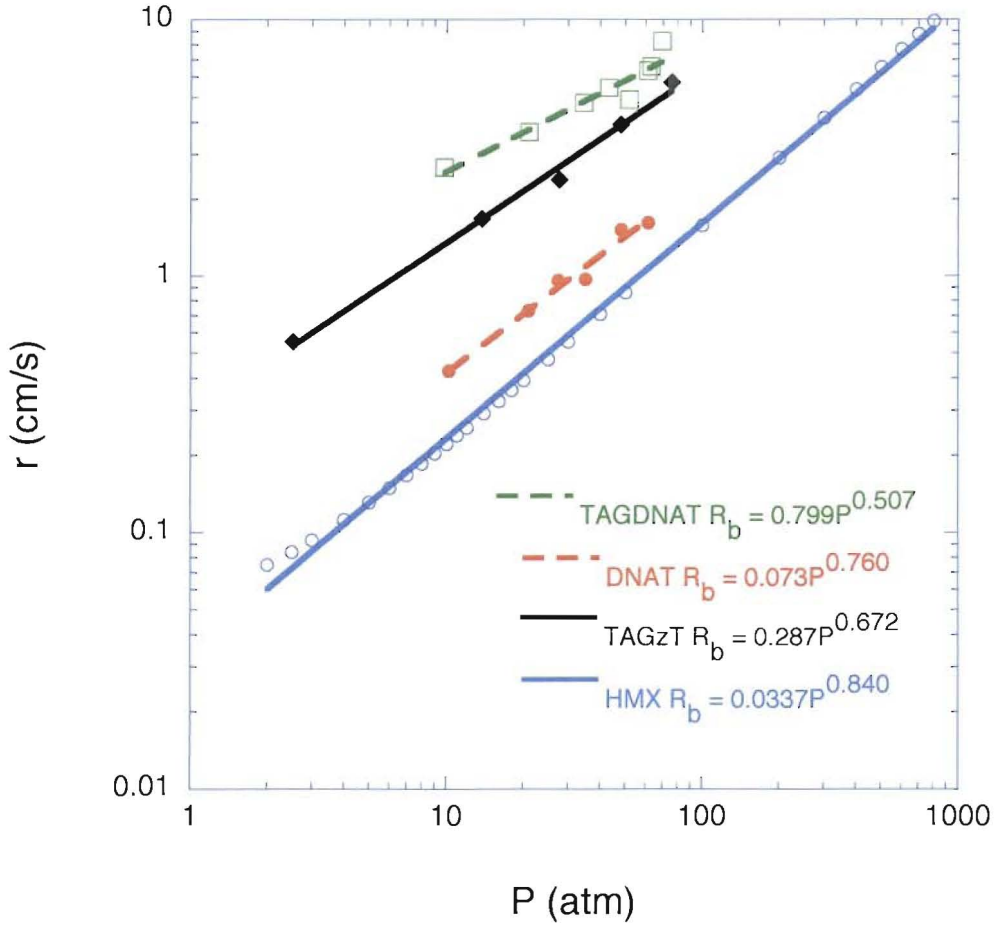

Figure 4. Burning rates of TAGDNAT and DNAT compared with TAGzT and HMX.

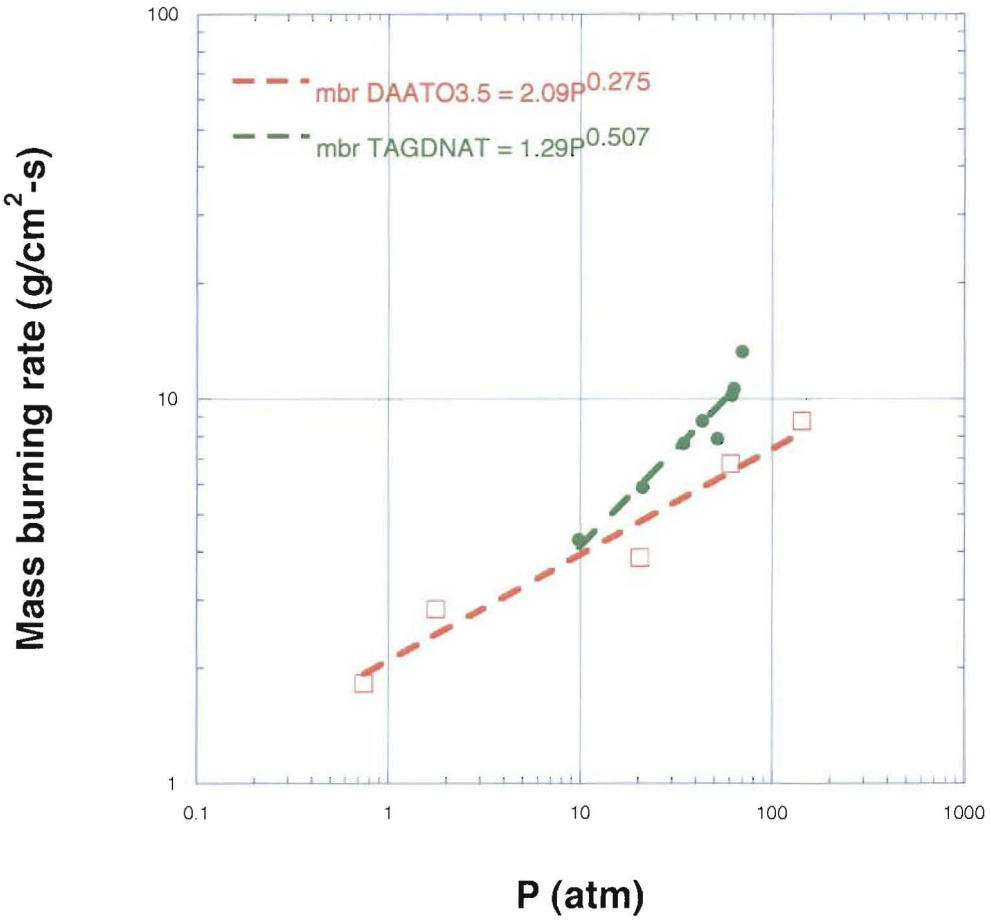

Figure 5. Mass burning rates of TAGDNAT and DAATO3.5.

Conclusions

TAGDNAT is a new high-nitrogen material that shows promise as a potential propellant burn-rate modifier with useful properties. We have shown that TAGDNAT compares favorably with TAGzT in many aspects. For example, TAGDNAT has a higher density, is less sensitive to impact, spark and friction, and has a particle morphology that use much more useful in applications that require extrusion. We have also shown that TAGDNAT has a lower burn rate exponent compared to TAGzT and burns much faster in the pressure regime studied. In fact, TAGDNAT has one of the fastest burn rates measured for a neat material. These properties make TAGDNAT an interesting candidate for

applications in areas such as propellants and gas generants. Further work is ongoing to characterize the burn-rate modification behavior of TAGDNAT.

Experimental

Caution! Although no problems have occurred during the synthesis and handling of 1, the material is an explosive. Laboratories and personnel should be properly grounded and safety equipment such as Kevlar gloves, blast shields and ear plugs are necessary, especially when working on large scales.

Bis-Triaminoguanidinium 3,3'-dinitro-5,5'-azo-1,2,4-triazolate (1)

3,3'-Dinitro-5,5'-azo-1,2,4-triazole[12] (15.24 g, 60 mmol) was added to water (300 mL). The mixture was then treated with a solution of NaOH (1N, 120 mL) heated to 80 °C and a yellow solution was obtained. Triaminoguanidinium hydrochloride (16.86 g, 120 mmol) was added and after a few minutes, a crystalline precipitate began to form. The reaction was allowed to cool to ambient temperature and then to 5 °C with an ice bath. The product was then filtered, washed with ice-cold water and air dried to provide **1**, 23.5 g (85%). m. p. 205 °C. . IR (KBr): ν = 3632, 3589, 3388, 3211, 1684, 1628, 1530, 1485, 1407, 1374, 1314, 1130, 1109, 981, 952, 866, 840, 797, 760, 660, 609, 525cm^{-1}; ^{1}H NMR (400 MHz, deuteriomethylsulfoxide) δ = 4.5 (bs, 6H), 8.6 (bs, 3H); ^{13}C NMR (100 MHz, deuteriomethylsulfoxide) δ = 159.06, 165.28, 170.79; Elemental analysis calc'd for $C_6H_{18}N_{22}O_4$: C, 15.59; H, 3.92; N, 66.65; found: C, 15.63; H, 3.94; N, 66.62.

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performing the rate stick/plate dent experiments.

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