

# Combustion Properties of Amino-Substituted Guanidinium 4,4',5,5'-Tetranitro-2,2'-biimidazolate(N4BIM) Salts

Bryce C. Tappan<sup>\*,[a]</sup> and David E. Chavez<sup>\*,[a]</sup>

**Abstract:** This paper describes the combustion properties of the amino-substituted guanidinium 4,4',5,5'-tetranitro-2,2'-biimidazolate (N4BIM) series, including the bis-mono, di and triaminoguanidinium salts. These salts are of interest as propellant ingredient additives, and in particular, the bis-tri-

aminoguanidinium salt of N4BIM displays excellent burn rate and combustion behavior. Our combustion studies have shown that TAGN4-BIM displays a fast burning rate and has the lowest pressure dependence exponent yet measured for a triaminoguanidinium salt.

**Keywords:** Propellants • Burn rate • High nitrogen • Aminoguanidinium • Tetranitrobiimidazole

## 1 Introduction

Over the past few years, 4,4',5,5' tetranitrobiimidazole and its corresponding derivatives have received increased attention in the energetic materials community [1,2]. We and others have investigated the bis amino-guanidinium-4,4',5,5'-tetranitro-2,2'-biimidazolate (N4BIM) salts as ingredients in gas generating, propellant and explosive applications. In this study we present the effect of the mono-, di- and triaminoguanidinium substitution on the combustion behavior of N4BIM divalent backbone. Because the molecules are relatively dense (1.73–1.76 g cm<sup>-3</sup>), and have a high ratio of fuel to oxygen in the molecule, they are of particular interest for propellant applications, where excess hydrogen in the decomposition products is desired. Examples include low-temperature gun propellants, air-breathing rocket systems, and enhanced blast explosives, with the triaminoguanidinium salt being of the greatest interest.

## 2 Results and Discussion

### 2.1 Burning Rate Behavior

We have previously investigated the combustion behavior of several high nitrogen materials [3]. In many of these studies we have investigated the triaminoguanidinium salts of high nitrogen energetic anions. However, we have not investigated the combustion behavior of the mono- or diaminoguanidinium derivatives. We sought to determine the influence of these cations on the combustion behavior compared to the triaminoguanidinium salt. In this study we focused on the bis monoaminoguanidinium (**1**), the bis diaminoguanidinium (**2**), and the bis triaminoguanidinium (**3**) salts of 4,4',5,5' tetranitro-2,2'-biimidazolate anion (Figure 1). Compounds **1–3** were prepared according to the

literature methods [1a]. The materials were pressed into cylindrical pellets at 88–92 % of theoretical maximum density. Combustion of the pellets was initiated with a CO<sub>2</sub> laser and filmed to observe the burn front of the pellet in a vessel under various overpressures of argon gas.

Figure 2 displays the combustion of **1** from 2.4 to 8.6 MPa. The figure shows a transition from a more opaque combustion product profile, to a phase where the combustion products become transparent at higher pressures. Figure 3 displays the combustion of **2** at 8.6 MPa between 0.22 s and 0.63 s. The still shots show the combustion burn front is relatively planar throughout the burn.

Comparison of the burning rate data for **1–3** shows that the addition of each additional amino functionality has a marked effect on the combustion behavior of each molecule. Figure 4 displays the burning rates of **1–3** vs. pressure (1–8.6 MPa). The burning rate is the lowest for **1** and steadily increases with the addition of each amino group. Examination of the burning rate pressure exponent reveals that it decreases regularly while burning rate increases with addition of each additional amino functionality (Table 1). The burning rate pressure exponent for **3** is the lowest pressure exponent for any triaminoguanidinium high nitrogen salt we have measured to date.

In our analysis of these results, two obvious factors stand out; the energy of the molecule is increased as the amino functionality increases, and the gas production increases per unit volume, as the density of **1–3** is essentially con-

[a] B. C. Tappan, D. E. Chavez  
Los Alamos National Laboratory  
MS C920  
Los Alamos, NM 87545, USA  
\*e-mail: btappan@lanl.gov  
dechavez@lanl.gov

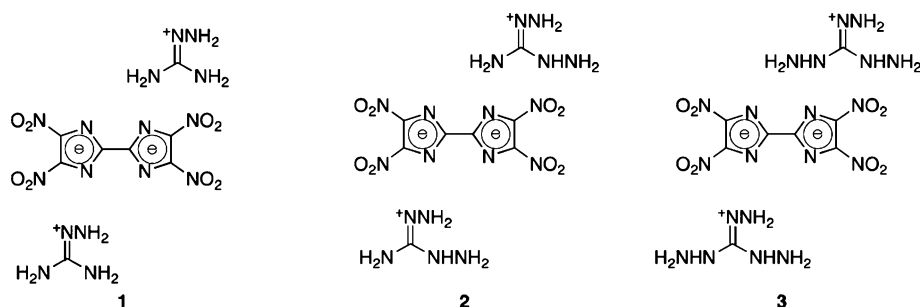


Figure 1. Chemical structure of 1, 2, and 3.



Figure 2. Combustion of MAGN4BIM from 2.4 to 8.6 MPa.

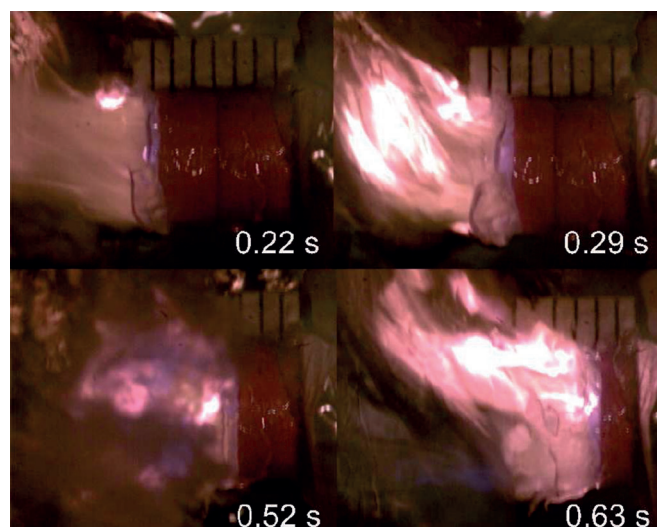


Figure 3. Laser induced combustion of 2 at 8.6 MPa from 0.22 s to 0.63 s.

stant, while the molecular weight is increased (Table 2). These factors are likely the reason for the overall rate increase with increasing amino functionality, but the change

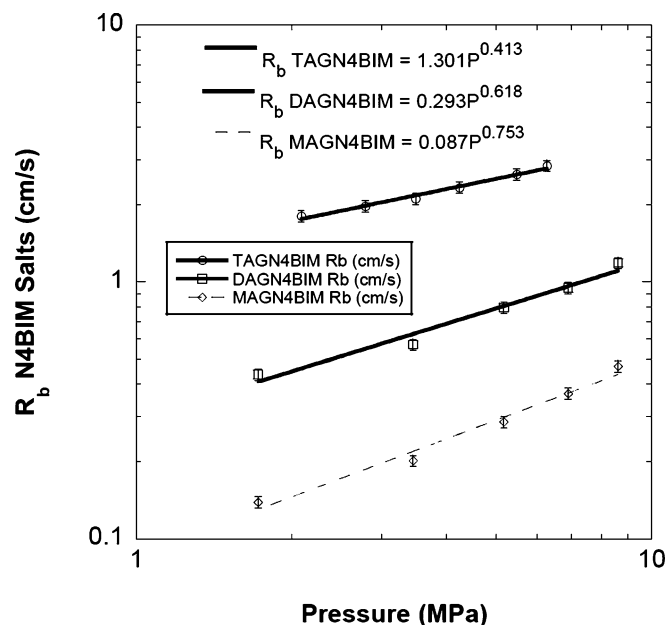


Figure 4. Burning rates vs. pressure for 1–3 up to 8.6 MPa.

Table 1. Burning rate parameters for 1–3.

Material	Pre exponent	Exponent	R <sub>b</sub> [cm s <sup>-1</sup> ] @ 6.9 MPa
1	0.087	0.753	0.37
2	0.293	0.618	0.95
3 <sup>a)</sup>	1.301	0.413	2.89

a) From Ref. [1a].

in the exponents are likely due to more complex mechanistic differences in the molecules. Rocket parameter calculations were also performed using the Cheetah thermochemical code [4]. The specific impulse and the chamber temperature were calculated for 1–3 and the data are displayed in Table 2. Here it is also seen that each additional amino group leads to an increase in both specific impulse and chamber temperature. The observed trend is both obvious and expected given the both the higher energy and gas production as the amino functionality is increased in the molecule.

**Table 2.** Calculated rocket parameters for 1–3.

Material	$I_{sp}$ [s]	Chamber temp. [K]	Density [ $\text{g cm}^{-3}$ ]	$H_f$ [ $\text{kJ mol}^{-1}$ ]
1	194	1463	1.75 <sup>a)</sup>	–133
2	206	1664	1.76 <sup>a)</sup>	176
3	214	1807	1.73 <sup>b)</sup>	413

a) Ref. [2b], 173 K. b) Ref. [1a], room temperature.

### 3 Experimental Section

Cylindrical pellets with 6.4 mm in diameter and ca. 9 mm long of **1** and two pellets of **2**, 6.4 mm in diameter and ca. 4.5 mm long were burned in a 2 L stainless steel vessel under pressurized argon of 0.2–8.6 MPa. The volume of the combustion chamber was sufficiently large that the decomposition gases had 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, and the same vacuum grease was used to attach the two DAGN4BIM together. The vessel was equipped with a ZnSe window such that samples could be ignited via a 0.10 s, 60 W pulse from a 10.6  $\mu\text{m}$  CO<sub>2</sub> laser from Coherent. The combustion event was filmed between 200 fps and 400 fps with a Phantom MIRO3 from Vision Research. The pressure was monitored with an Omega Model PX605-10KGI static pressure transducer. Optical records were analyzed using Phantom Cine Viewer v2.5.744.0 software from Vision Research to obtain the burning rate data.

### 4 Conclusions

The combustion behaviors of mono-, di-, and triamino guanidinium salts of 4,4',5,5'-tetrinitro-2,2'-biimidazolate (**1**, **2**, and **3** respectively) were studied. It was discovered that each addition of the amino group functionality to the guanidinium cation lead to a corresponding decrease in the burning rate pressure exponent as well as an increase in the burning rate between 1 and 10 MPa. The burning rate pressure exponent of **3** is the lowest of any triaminoguanidinium salt we have studied to date. Additionally, the calculated specific impulse values and rocket chamber temperatures increase, as expected, with the addition of each amino group. Further studies are necessary to determine whether this trend can be applied to the amino guanidinium salts of other high nitrogen energetic anions. While these salts offer only modest performance as monopropel-

lants, the highly variable combustion properties with variation of amino functionality could offer the ability to tune propellant behavior when **1–3** are used as energetic additives to formulations.

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