

REPLACING TNT: THE QUEST FOR A NEW MELT CASTABLE EXPLOSIVE

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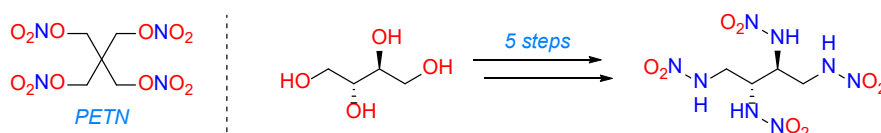
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INTRODUCTION

Trinitrotoluene (TNT) has been produced industrially for use as an explosive for military, mining, and demolition purposes since the beginning of the 1900s and is still used today. The continuous utility is in large part because TNT is melt castable, meaning it can be melted (80 °C) with steam and then poured into a desired shape.¹ In addition TNT has a high decomposition temperature (295 °C) and low sensitivities to friction and impact, meaning it is relatively safe to handle.¹ With TNT's low cost it is used as a starting material to make other high value explosives such as hexanitrostilbene and triaminotrinitrobenzene. Still, TNT is not free of issues. Relative to other secondary explosives (those with low impact and friction sensitivity but high detonation velocity V_{det}), TNT is low performing due to its modest $V_{det}= 6950 \text{ m s}^{-1}$. Therefore, it is often used as a mixture with hexogen (RDX) with a $V_{det}= 8750 \text{ m s}^{-1}$ to increase its performance.² In the early days of manufacturing TNT, workers became violently ill owing to TNT poisoning causing liver failure or anemia.³ TNT is also toxic to aquatic wildlife and is classified as a pollutant by the EPA.⁴ Finally, TNT and RDX are classified as class C carcinogens, and it is recommended that new alternatives are sought to replace these secondary explosives.³ In order for a new explosive to fill the role of TNT it must be melt castable, have a simple synthesis, and minimize environmental impact by reducing acidic waste and be less toxic.

NITRATE ESTERS

Pentaerythritol and erythritol are both readily available tetraols, allowing for easy manipulation into nitrate esters, thereby increasing the nitrogen content. This modification can be seen in the legacy secondary explosive, pentaerythritol tetranitrate (PETN), which is more shock sensitive than other explosives in this class. Recently, erythritol has been functionalized in five steps (**Scheme 1**) to afford tetranitramine with reduced sensitivity compared to PETN.⁵

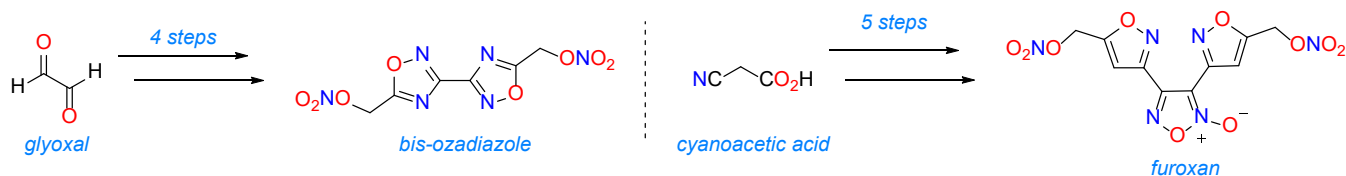


Scheme 1. Structure of PETN and elaboration of erythritol in five steps.

HETEROCYCLES

Heterocycle based energetic materials often have high densities owing to π stacking, particularly in symmetrical compounds.⁶ Having a high density is desired as it is correlated with possessing a higher V_{det} . In addition, it is easy to increase the oxygen balance of these scaffolds simply by nitrating them. Care

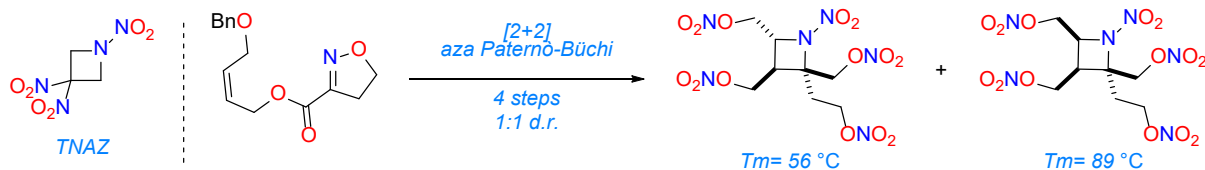
must be taken to avoid making the π interactions too strong, as this will increase the melting point outside of the range of a melt castable explosive. Recently both oxadiazoles and furoxans have received significant attention from scientists at Los Alamos National Lab and Aberdeen Proving Ground. Several oxadiazole and furoxan (**Scheme 2**) scaffolds have been prepared from glyoxal and cyanoacetic acid, respectively, with increased oxygen balance, density, and detonation velocities compared to TNT.^{6, 7}



Scheme 2. Elaboration of glyoxal and cyanoacetic acid into energetic heterocycles.

STRAINED RINGS

Cyclic compounds such as cyclobutane and azetidine add ring strain to increase the performance of an energetic material. In the 1990s 1,3,3-trinitroazetidine (TNAZ) was investigated as a prime candidate to replace TNT.⁸ It has not been used owing to its difficult synthesis and its high vapor pressure when molten. Since the development of TNAZ there has been little exploration of azetidine based energetic materials, but an aza-Paternò-Büchi developed by Schindler (**Scheme 3**) has enabled renewed interest.⁹ Using the aforementioned method several azetidine nitrate esters were prepared in just four steps.



Scheme 3. Structure of TNAZ and the aza-Paternò-Büchi developed by Schindler.⁹

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