

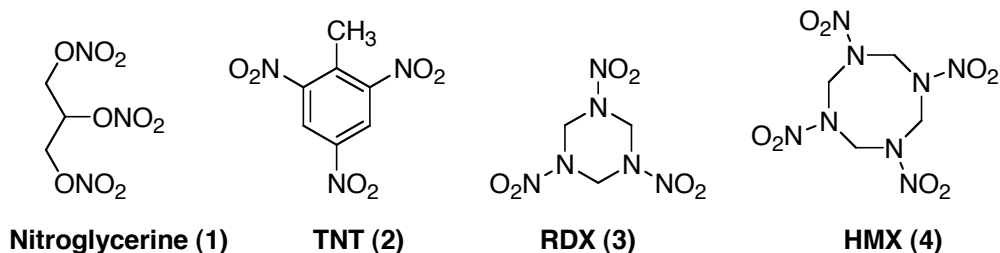
## Design and Synthesis of Explosives: Polynitrocubanes and High Nitrogen Content Heterocycles

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### Introduction

In the ninth century, Chinese alchemists discovered black powder, a mixture of sulfur, charcoal, and saltpeter ( $\text{KNO}_3$ ), while trying to invent a formula for immortality.<sup>1</sup> Since then humans have been fascinated by explosives and have strived to develop more powerful formulations. In 1846, the Italian chemist Ascanio Sobrero, prepared nitroglycerine (**1**) by adding glycerine to concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . Nitroglycerine was not used as an explosive until 1863 when Alfred Nobel stabilized it by adding a nitrocellulose binder, a mixture he termed “dynamite” (from Greek: *dynamis* meaning power).<sup>2</sup> Dynamite and 2,4,6-trinitrotoluene (**2**) were the explosives of choice until the advent of the nitramine explosives RDX (**3**) and HMX (**4**) prior to the second World War. More than 60 years later, HMX (and its formulations) is still the workhorse for most military and heavy duty civilian applications.



### Background

The two most common methods used to quantitate the performance of explosives are the velocity of detonation (VOD) and the detonation pressure ( $P_D$ ). VOD is the rate at which the chemical reaction propagates through the solid explosive or the velocity of the shockwave produced by an explosion.  $P_D$  is a measure of the increase in pressure followed by detonation of an explosive.<sup>3</sup>

Despite the development of high explosives such as HMX, active efforts have continued within the military and scientific communities to produce better explosives to complement emerging weapons and space technologies. Chemists have begun to take a molecular approach to improve explosive performance. In an explosion, a relatively stable molecule reacts to produce a large volume of gaseous products and heat. If more moles of gas can be produced from an explosive, it will deliver superior performance in terms of detonation pressure. Oxygen balance, which is a ratio of the amount of oxygen in the explosive to the amount of oxygen needed for complete combustion, is also an important property of explosives, because it dictates the extent of the combustion reaction and the composition of the products. A perfectly oxygen-balanced explosive is capable of complete combustion in the absence of air. The heat of formation ( $\Delta H_f$ ) of an explosive is also important: the more positive  $\Delta H_f$ , the more energy released upon combustion. Finally, the most important factor in determining explosive

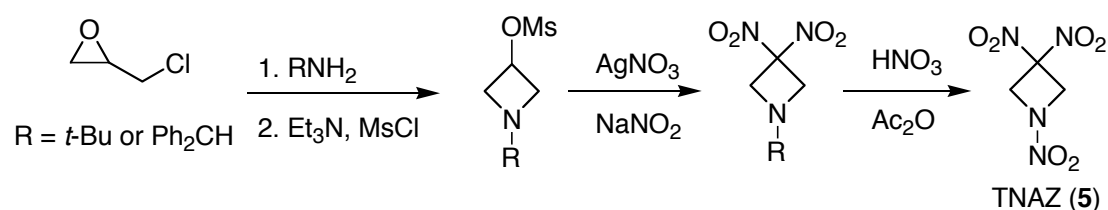
performance is the density. The VOD is related to the square of the density, and  $P_D$  is directly related to density.<sup>4</sup> Prediction of explosive performance and sensitivity prior to synthesis is a widely used strategy. Computer programs (Cheetah<sup>5</sup>, LOTUSES<sup>6</sup>) are available to calculate the density,  $\Delta H_f$ , VOD and  $P_D$  from the molecular formula. More advanced methods to predict the complicated decomposition pathways and products of an explosion at high temperature and pressure are still being developed.<sup>7,8</sup>

### Strained Cyclic Nitramine Explosives

The incorporation of strained cyclic and cage structures into a molecule is an effective method for increasing the performance of an explosive. Cyclic structures typically have higher densities than those of conventional explosives because they are more compact. The strain energy associated with some cage structures also leads to an increase in the  $\Delta H_f$ , which in turn increases explosive performance.

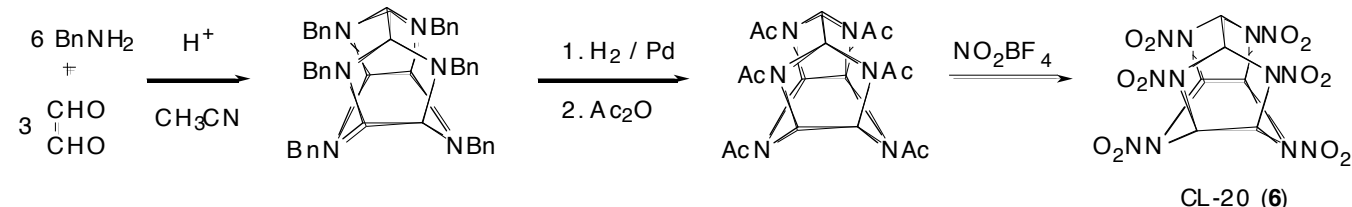
The small molecule explosive 1,3,3-trinitroazetidine (TNAZ, **5**) was prepared by Gil-

**Scheme 1:**



ardi *et al* according to Scheme 1.<sup>9</sup> The ring strain associated with the azetidine provides additional energy release upon ring opening.<sup>8</sup> TNAZ is an attractive explosive because it is dense (1.84 g/cm<sup>3</sup>), thermally stable until 240°C, half as shock sensitive as HMX, compatible with many materials (*e.g.* aluminum, brass, glass, steel), and melt castable, rendering it easier to engineer for applications.<sup>10</sup> The major disadvantages associated with TNAZ are its volatility and cost. It is currently being produced on pilot-plant scale for testing.

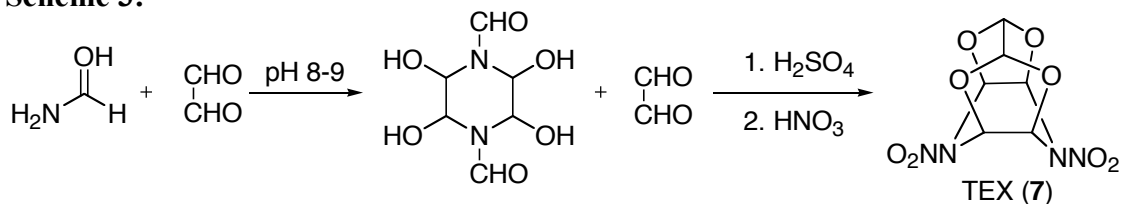
**Scheme 2:**



Researchers at the Naval Weapons Center at China Lake synthesized the highly strained hexaazaisowurtzitane nitramine cage structure, CL-20 (Scheme 2, **6**), by condensing benzylamine with glyoxal.<sup>11</sup> CL-20 is currently the most powerful non-nuclear explosive produced on large scale (450 kg). It has a very high density (2.04 g/cm<sup>3</sup>) and  $\Delta H_f$  (+98 kcal/mol), resulting in a VOD of 9380 m/s and is stable until 228°C. CL-20 burns cleaner than traditional nitramines and is 14% more powerful than HMX.<sup>11</sup>

Boyer and co-workers reported the synthesis of nitramine **7** (TEX)

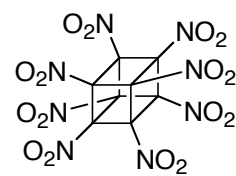
**Scheme 3:**



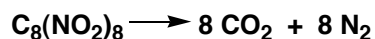
by base-catalyzed condensation of glyoxal with formamide.<sup>12</sup> With a density of 1.99 g/cm<sup>3</sup> and a VOD of 8665 m/s and  $P_D = 370$  kbar, TEX is a powerful explosive. It is also less shock and friction sensitive than HMX or RDX and is thermally stable until 240°C. TEX is currently produced on pilot plant scale and is being pursued as an insensitive explosive.<sup>11</sup>

### Polynitrocubanes

In 1981, it was suggested that octanitrocubane (ONC, **8**) might be a promising explosive.<sup>13</sup> ONC has a perfect oxygen balance, meaning that under ideal combustion conditions the only products would be CO<sub>2</sub> and N<sub>2</sub> gases, and based on its high predicted density (1.9 – 2.2 g/cm<sup>3</sup>) and  $\Delta H_f$  (+81 - +144 kcal/mol), a 15-30% performance enhancement over HMX was predicted.

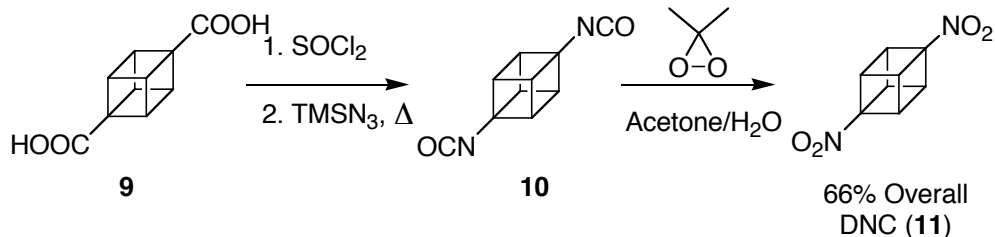


**Octanitrocubane (8)**



Cubane, is itself a unique molecule with some extraordinary physical and chemical properties. The C-C bond angles in cubane are 90°, highly distorted from the ideal 109.5° for a sp<sup>3</sup> carbon. This distortion manifests itself in a high strain energy (166 – 188 kcal/mol) and heat of formation (+144 – 166 kcal/mol).<sup>14</sup> In 1964 Eaton and Cole reported the first synthesis of cubane-1,4-dicarboxylic acid (**9**) via a Favorskii rearrangement of an  $\alpha$ -halo ketone.<sup>15</sup> Cubane is one of the densest hydrocarbons known (1.29 g/cm<sup>3</sup>) and is thermally stable up to 220 °C. This may seem surprising considering the incredible amount of strain within the molecule, but it is kinetically stable because it lacks favorable decomposition pathways.<sup>16</sup>

**Scheme 4:**

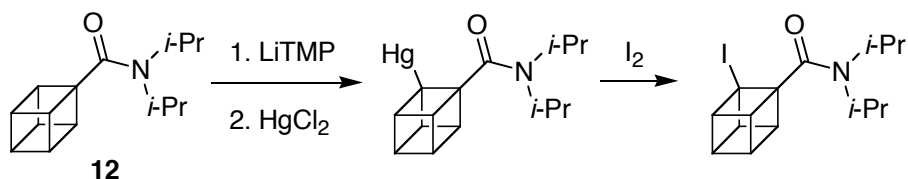


Nitrations of unsaturated molecules have been known for over a century, but the direct nitration of a saturated hydrocarbon has proved problematic. The first synthesis of a polynitrocubane, 1,4-dinitrocubane (DNC, **11**), was indirect and inefficient (18%),<sup>17</sup> but an improved route proceeded from diacid **9** (Scheme 4). The acid chloride was converted to the highly explosive acyl azide intermediate, which underwent a

Curtius rearrangement to the isocyanate (**10**). Subsequent oxidation with dimethyldioxirane gave 1,4-dinitrocubane (**11**) in a greater 66% overall yield.<sup>18</sup>

More direct methods involving nitration of the cubane skeleton were sought. The directed metalation of cubane reported in 1985 was the first amide-directed

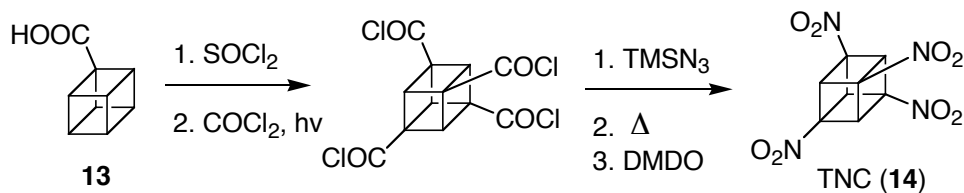
**Scheme 5:**



metalation of a saturated molecule.<sup>19</sup> Amide **12** was added to excess lithium tetramethylpiperazide (LiTMP) to afford the “ortho” lithiated species. The use of HgCl<sub>2</sub> to trap the anion helped drive the reaction forward (Scheme 5). It seems that DNC would be easily accessible via electrophilic nitration at the ortho position followed by conversion of the amide to the nitro group according to the aforementioned procedure. However, when electron-withdrawing and donating groups were placed adjacent to each other (as in 1-amino-2-nitrocubane), the cubane skeleton decomposed under a “push-pull” mechanism.<sup>20</sup> Meta-metalation of the cubane skeleton was not possible, so the synthesis of a polynitrocubane with adjacent nitro groups was not reported for several years.

The synthesis of 1,3,5,7-Tetranitrocubane (TNC, **14**), was reported in 1993.<sup>21</sup> The synthesis was complicated and lengthy because fragmentation had to be avoided. In 1997 a new procedure was reported in which cubanecarboxylic acid (**13**) was chlorocarbonylated using the photochemical Kharasch-Brown reaction (Scheme 6).<sup>22,23</sup> UV irradiation followed by recrystallization from Et<sub>2</sub>O, gave the 1,3,5,7 isomer in 95%

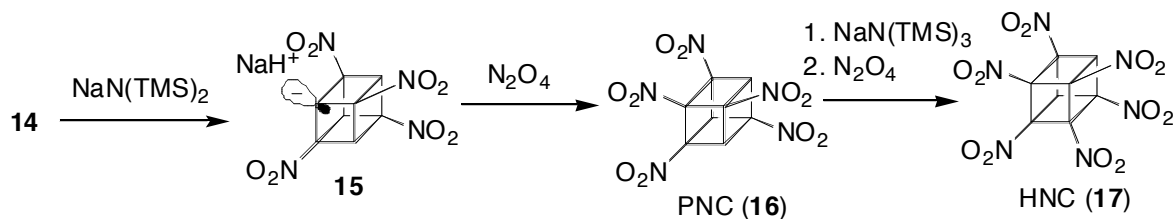
**Scheme 6:**



Scheme 6:  
purity which was converted to TNC by the Curtius rearrangement-isocyanate oxidation method described earlier.<sup>18</sup>

The most useful property of TNC is its acidity. With a pK<sub>a</sub> of ~21, TNC is 10<sup>20</sup> times more acidic than cubane. Thus, TNC could be deprotonated with NaN(SiMe<sub>3</sub>)<sub>2</sub> to form cubyl anion **15**, which reacted with N<sub>2</sub>O<sub>4</sub> under a modified procedure giving pentanitrocubane (PNC, **16**).<sup>21</sup> PNC was the first nitrated cubane with adjacent nitro groups and thus provided evidence that DNC might eventually be made. Reaction of PNC with NaN(SiMe<sub>3</sub>)<sub>2</sub> gave the corresponding cubyl anion and subsequent nitration using N<sub>2</sub>O<sub>4</sub> gave hexanitrocubane (HNC, **17**).

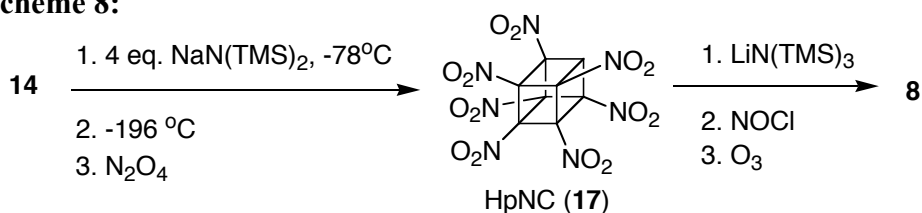
**Scheme 7:**



The synthesis of heptanitrocubane (HpNC, 17) was similar to that of HNC and PNC, except more base (4 equiv.) was used to form the cubyl anion of TNC, prior to nitration. On gram scale, the crude product, obtained in 74% yield, contained more than 95% HpNC. This reaction is remarkably fast, but a large number of steps are involved in adding the three nitro groups to TNC to form HpNC.

Unfortunately, no ONC was formed even when increased amounts of base and  $\text{N}_2\text{O}_4$  were used, leading to speculation that it could

**Scheme 8:**



not be made. However, HpNC was deprotonated with  $\text{NaN}(\text{TMS})_2$  and addition of iodine or methyl triflate afforded the respective iodinated and methylated products, thus proving that HpNC could be deprotonated and that there was room for an extra substituent on the molecule. Nevertheless nitration of the HpNC anion with several electrophilic nitrating agents was unsuccessful. It had been speculated that nitration of the cubane anions occurred due to oxidation of the anion to the radical by the nitrating agent, followed by combination of the two radicals. The authors thought that the HpNC anion was so stabilized by the seven nitro groups that the oxidation was not possible. Thus, they used excess nitrosyl chloride ( $\text{NOCl}$ ) and subsequent ozonation to reach ONC in 55% yield, 19 years after its conception.<sup>25</sup>

Both HpNC and ONC are stable solids, which survive blows from a hammer on the bench top. Crystals of both polynitrocubanes were analyzed, giving the data shown in Table 1.<sup>26,27</sup>

As can be seen in Table 1, both HpNC and ONC have excellent explosive properties. There is some thought that HpNC would make the superior explosive due to its simpler synthesis, higher density

**Table 1:** Various properties of HpNC and ONC

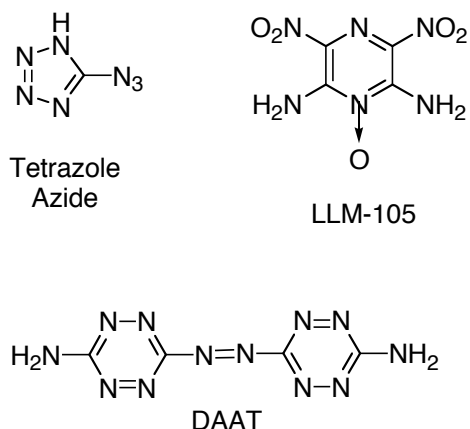
Property	HpNC (17)	ONC (5)
Density ( $\text{g}/\text{cm}^3$ )	2.028	1.979
Oxygen Balance	-5.9%	0%
Calc'd $\Delta H_f^{24}$ (kcal/mol)	154	163
Decomposition Temperature ( $^\circ\text{C}$ )	>200	>200
Energy Release (kcal/mol)	-	830
Volume Expansion	-	1150 fold
Detonation Velocity ( km/s )	-	10.1
Detonation Pressure ( kbar )	-	500

and imperfect oxygen balance. Although ONC is perfectly oxygen balanced and does not need any atmospheric oxygen to combust, this may be a disadvantage because the products are higher molecular mass gases (*i.e.* CO<sub>2</sub> vs. CO and H<sub>2</sub>O), which means fewer moles are produced. HpNC on the other hand is thought to produce lighter, and therefore more moles of, gaseous products.<sup>28</sup> The density of ONC was determined by examining the crystal structure and was lower than predicted. The authors postulated that a higher density may be accessible by isolating a different polymorph of ONC with closer packing. HpNC is denser than ONC because it has one proton in place of a nitro group allowing the HpNC molecules to interact by hydrogen bonding, in which a nitro group from one molecule approaches the methine carbon on another molecule. Despite its long development and excellent explosive properties, ONC is currently too expensive to be produced in quantities useful for practical applications. The commercially available starting material for the ONC synthesis, dimethyl cubane-1,4-dicarboxylate, costs \$40,000/kg. For this reason, an alternative, more efficient synthesis is needed.

### High Nitrogen Content Explosives

Another popular area of explosives research is the synthesis of compounds with high nitrogen content. These molecules typically have high density and large  $\Delta H_f$ . The  $\Delta H_f$  is attributed to the large number of N-N and N=N bonds. The bond energy of an N-N bond (38 kcal/mol) or an N=N bond (100 kcal/mol) is significantly less than that of the triple bond in N<sub>2</sub> (228 kcal/mol), which results in a large energy release upon combustion.<sup>29</sup> The major product of the explosion is N<sub>2</sub>, which is more environmentally friendly and leaves less of a smoke trail behind a missile, making it more difficult to detect.

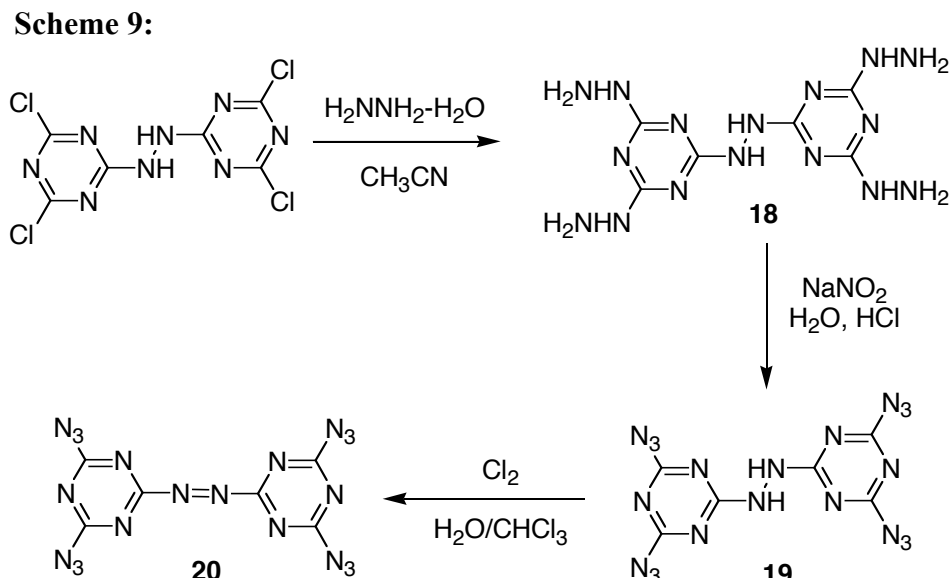
Several high nitrogen heterocycles (*e.g.*, tetrazoles, tetrazines, pyrazine N-oxides) have been recently synthesized as high energy materials (Figure 1),<sup>30,31,32</sup> the most interesting of which was reported by chemists at the U.S. Naval Research and Los Alamos National Laboratories.<sup>33</sup> Azo-1,3,5-triazine **20** was prepared according to Scheme 9. The triazine core was functionalized with azido groups to increase its nitrogen content and density (1.724 g/cm<sup>3</sup>) and to raise its melting point, rendering it more thermally stable. The molecular formula of **20** is C<sub>6</sub>N<sub>20</sub>, corresponding to nearly 80% nitrogen content by mass.



**Figure 1:** Recently synthesized high nitrogen content heterocycles

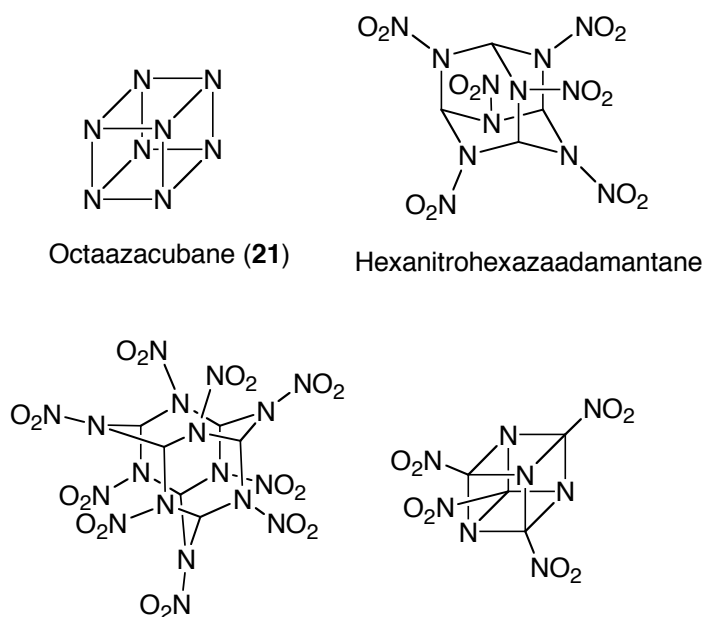
Azo compound **20** also has the highest heat of formation ever observed for an energetic material at +518 kcal/mol. Conversion of the hydrazino groups in **18** increases the  $\Delta H_f$  by 321 kcal/mol and the conversion of **19** to **20** adds an additional 100 kcal/mol.

Much attention has been focused on producing solid all-nitrogen materials at room temperature. Ionic solids containing the  $N_5^+$  cation have been synthesized (e.g.,  $AsF_6N_5$ ),<sup>29</sup> but attempts to synthesize  $N_3N_5$  have been unsuccessful. If this ionic solid is synthesized, it will likely be followed by other forms of solid all-nitrogen compounds, such as octaazacubane (**21**).



## Conclusions and Future Directions

During the 20<sup>th</sup> century, the field of explosives underwent significant advances from using materials such as TNT and dynamite to rationally designed molecules like ONC and CL-20. Although the latter are not yet used in practical applications, the development of new synthetic methods might make them more economical. The developing field of high nitrogen-content materials as explosives and propellants, is also very promising. It appears that we are reaching the limit for properties of energetic materials, but as our ambitions for space exploration and improved weapons technologies advance, so will the substances used to fuel them. Using imagination and modern predictive technologies, chemists have already begun thinking of future candidates for energetic materials (Figure 2)<sup>28</sup> that would offer higher strain energy and oxygen balance and most importantly a worthy synthetic challenge.



**Figure 2:** Future explosive targets

Using imagination and modern predictive technologies, chemists have already begun thinking of future candidates for energetic materials (Figure 2)<sup>28</sup> that would offer higher strain energy and oxygen balance and most importantly a worthy synthetic challenge.

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