

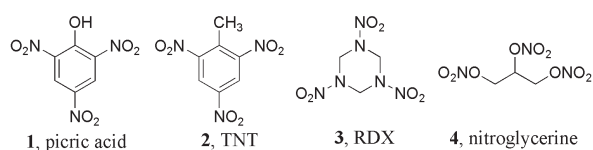
# More Bang for your Buck: An Introduction to CHNO Explosives

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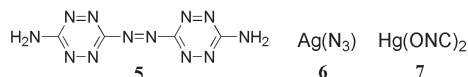
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## Introduction

Explosives, explosions and violent reactions have fascinated chemists for centuries. The current development of explosives is the culmination of extensive efforts to understand the chemistry of energetic molecules and the reactions that they undergo. There are various types of explosives with CHNO molecules, the most abundant class, e.g. **1-4**. These structurally related compounds all have an oxygen-containing group and release their energy through the violent combustion of the carbon and hydrogen atoms of the skeleton.



Many other molecules react sufficiently violently to cause explosions, although they are much less commonly used on a large scale. Important classes of such explosive compounds include organic molecules almost exclusively carrying nitrogen, e.g. tetrazine **5**.<sup>1</sup> Such molecules have extremely high energies of formation and this is released when they react. Inorganic complexes with energetic counter ions, such as silver azide (**6**) and mercury fulminate (**7**) are also commonly used as explosives, particularly in detonators due to their sensitivity.



Explosives can be roughly divided into three classes:<sup>2</sup>

1. *Propellants* are materials with a slow rate of reaction that is not dependent on atmospheric oxygen for combustion. Such mixtures are used in rockets and fire-works.
2. *High explosives*, which make up the bulk of common explosives. They react energetically, but are relatively insensitive to detonation.
3. *Initiators* are unstable and easily detonated. In common explosives small amounts are used to instigate a primary shockwave to start the explosive reaction.

The combustion reactions of explosives fall into two types dependent on the speed of reaction each giving different effects. *Deflagration* is a process analogous to burning, in which energy is released relatively slowly by thermal conduction and radiation. Deflagration occurs in propellants where the explosive is consumed over a comparatively long period of time. *Detonation* processes have an associated shock wave which travels above the sonic velocity of the material. High temperatures and pressures exist within this shock wave, giving rise to faster and more vigorous reactions than are possible in deflagrating explosives.

Explosive detonations have various properties that differentiate them from chemical reactions that occur in a less violent manner. The energy of an explosion is released in an extremely short period of time. In detonation, a shockwave passes through the explosive extremely quickly;<sup>3</sup> typical detonation velocities vary from 6000–8500 ms<sup>-1</sup>. The travelling shockwave represents a huge step jump in temperature and pressure, an increase so large that the material behind the advancing detonation front reacts, immediately propelling it forward. Under these conditions, the explosive material is almost exclusively transformed into hot and voluminous gases. Orthogonal to the direction of the detonation front, a rarefaction wave is released as a shock front, removing energy from the detonation wave, releasing pressure and removing the detonation products. The combination of the large amounts of gas released, the high temperatures, and the shockwave causes much of the damage associated with an explosion.

Reactions in explosives under detonation occur faster than diffusion of external reactants into the detonating material. Therefore, for the reaction to be complete, sufficient reactants must be available within the explosive mixture. In CHNO explosives, the combustion of the carbon and hydrogen is the main reaction and it requires oxygen. If there is sufficient oxygen to react with the combustible material within the explosive, it is said to be *oxygen balanced*. If the explosive is deficient in oxygen, the products will contain unreacted or partially reacted carbon and hydrogen. An explosive with an excess of oxygen will be able to oxidize material other than carbon and hydrogen, leading to the formation of toxic side products, typically nitrogen oxides. The oxygen balance of a particular explosive can be expressed as the weight percent of oxygen released after all combustible material is consumed. Ammonium nitrate releases about 20% of its weight as free oxygen and can be combined with a fuel source, such as diesel oil to give the oxygen balanced binary explosive ANFO (ammonium nitrate fuel oil). The goal of modern high explosives research is to attain oxygen balance at the molecular level. Industrial explosives are designed to have slightly more oxygen than necessary in order to reduce emissions.

It can be shown, using fluid dynamics, that the change in pressure in an explosion is proportional to the density of the explosive, multiplied by the detonation velocity and the velocity of the products of the detonation.<sup>4</sup> The detonation velocity is the sum of the velocity of the products of detonation and the speed of sound in the explosive, which is higher in more dense materials. Therefore, charges of higher density will have a greater effect per unit volume due to faster detonation velocity and higher final pressures. Brisance is the destructive fragmentation effect of an explosion on material in its immediate

vicinity. Brisance is increased by the speed of the detonation wave and the pressure of the explosive products; as shown above, both are dependant on the density of the explosive.<sup>5</sup> The relative effectiveness of an explosive is often measured in comparison to **2** (TNT) as a moderately powerful explosive of moderate brisance ( $\rho$  1.65 g/cm<sup>3</sup>).

## History of Explosives

The early history of explosives almost exclusively involves the development of gunpowder. This consists of a mixture of saltpetre (potassium or sodium nitrate) as the oxidising agent, with carbon and sulfur as fuels. Saltpetre is formed by the decay of proteins and can be recovered from ores. Sulfur is found in high concentrations at sites of volcanic activity, and the heating of wood in an oxygen-free environment forms charcoal. Explosive mixtures were often formed by accident. A notable example occurred *ca.* 220 BC when a group of Chinese chemists mixed saltpetre, charcoal and sulfur together in an attempt to extract gold from an ore – it caused a large explosion.<sup>6</sup>

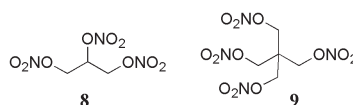
Initial gunpowder formulations were of limited effectiveness due to impurities in the available saltpetre. However, in the 13<sup>th</sup> century, Roger Bacon successfully purified saltpetre by recrystallizing it from water.<sup>7</sup> From then on the strength of gunpowder grew with the increasing purity of the components until the late 18<sup>th</sup> century when it reached its peak. In order to attain peak effectiveness, the components of gunpowder need to be mixed adequately to ensure intimate contact between the oxidising agent and the fuel. At the molecular level this is done by increasing the number of oxygen atoms per molecule and it is most easily achieved by the attachment of nitro groups to organic molecules. One of the earliest organics to be treated in this way was glycerine, first nitrated by the Italian chemist Sobrero who halted his efforts upon discovery of its explosive nature. Alfred Nobel, a student contemporary of Sobrero, and his father Immanuel developed the industrial nitration of glycerine by using a mixture of concentrated nitric and sulfuric acids. However, numerous early industrial accidents occurred due to explosions and, in 1864, one such detonation destroyed the first Nobel factory and killed Alfred's brother.<sup>8</sup> The use of nitroglycerine was greatly improved from Nobel's discovery that mixing it with filler mitigates accidental detonation, and then with the development by Alfred Nobel of a reliable mercury fulminate detonator.<sup>3</sup>

The CHNO explosives attain their oxygen balance on the molecular scale from the addition of nitro groups. They can be broadly divided into three different classes, dependent on the site of attachment. The strength of the bond to the nitro group determines the ease of detonation. The weaker the bond, the easier it is to initiate the detonation process. Bond strengths decrease from nitrated carbon (C-NO<sub>2</sub>) > nitramine (CN-NO<sub>2</sub>) > nitrate ester (C-ONO<sub>2</sub>) with bond strengths of ~300, ~200 and ~170 kJ/mol, respectively.<sup>9</sup> When a CHNO explosive detonates, the weakest bond is broken and this must release enough energy to break the next weakest, and so on until all are consumed by combustion and the energy released in the form of hot gases.

## Nitrate Esters

Nitrate esters were the first synthetic explosives to be produced on a large scale, with the nitroglycerine of Alfred Nobel. They are formed by the reaction of a nitronium ion (NO<sub>2</sub><sup>+</sup>) with a pendant alcohol group to give a nitrate ester (-ONO<sub>2</sub>). As a general rule, the more nitrate ester groups that an explosive contains, the more powerful the detonation will be, and the more sensitive the explosive. Nitroglycerine (**8**), the prototypical nitrate ester explosive, is produced by mixing concentrated nitric acid and fuming sulfuric acid with glycerine. Generally, the method can be used to produce nitrate esters from alcohols. They are powerful, but sensitive to detonation and often chemically unstable. Nitrate **8** is particularly prone to accidental detonation when solid (m.p. 12.5 °C),<sup>3</sup> or impure. Dynamite is a mixture of nitroglycerine with diatomaceous earth, which reduces the shock sensitivity and provides for safe transport.

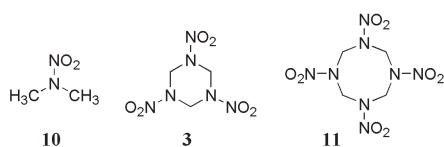
Nitrate esters are no longer used on a large scale either in civilian or military applications, but they are occasionally added to other explosives as sensitizers. It is interesting to note that nitrated compounds often have medicinal properties, for instance nitroglycerine has been used as a treatment for angina. In the body, nitrate esters are broken down by enzymatic reduction to nitric oxide (NO), a biochemical signalling molecule.<sup>10</sup>



Pentaerythritol tetranitrate (PETN, **9**) is the most common of the nitrate ester explosives still in use. It has an intermediate sensitivity that places it between initiating explosives, such as azides and fulminates, and bulk explosives. It is commonly mixed with other secondary explosives to sensitize them to ignition, and it is the base material of primacord<sup>®</sup> fuses, surrounded by a protective polymer layer. PETN (**9**) is produced by nitration using the ICI method that has removed the need for sulfuric acid in the synthesis.<sup>6</sup> It has considerable strength as an explosive, due to its high detonation velocity (8274 m/s) and high density (1.77 g/cm<sup>3</sup>). PETN (**9**) has a slight negative oxygen balance (-10%) upon detonation and leaves behind a little detonation residue, giving mostly CO<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O and CO.<sup>11</sup>

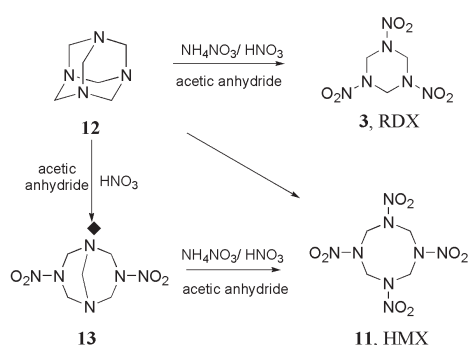
## Nitramine Explosives

The first nitramine to be synthesised at the turn of the 20<sup>th</sup> century was RDX (**3**), but for use as a medicine. Development of nitramines proceeded in the 1920's with various derivatives being produced. Nitramines are some of the most powerful explosives in use today, while also being stable and insensitive to accidental detonation.<sup>12</sup> The nitramine group (N-NO<sub>2</sub>) is formed by nitration of an amine with the nitronium ion. Non-cyclic nitramines, such as dimethylnitramine (**10**), are only weak explosives while cyclic nitramines, such as RDX (**3**) and HMX (**11**), are more powerful. RDX has a specific energy of ~1400 kJ/kg, which corresponds to 1.5 that of TNT.<sup>3</sup>



Nitramine explosives are insensitive to accidental detonation. Indeed **3** and **11** can be heated safely to their melting point. They are insensitive to impact with **3** (RDX) being about half as sensitive as PETN (**9**) that has comparable explosive strength. Cyclic nitramines are dense solids (1.82 g/cm<sup>3</sup>), giving them fast detonation speeds; RDX has a detonation velocity of about 8400 m/s, compared with 6900 m/s for TNT.<sup>3</sup> Nitramines are mixed with polymers to form plastic explosives, with the widely known military explosive Composition-4 (C-4; **12**) being a mixture of RDX and polyisobutylene.

The commercial scale synthesis of **3** is shown in Scheme 1. It is performed over a single step by mixing hexamethylenetetramine (**12**) with ammonium nitrate and nitric acid in acetic anhydride. When originally undertaken, some HMX (**3**) was isolated as a minor product. The nitration of the bicyclononane **13**, under conditions similar to the production of **3**, gives HMX (**11**) exclusively. This precursor was formed from **12** with nitric acid and acetic anhydride.



Scheme 1. Industrial synthesis of **3** and **11**.

Given the relationship between density and explosive power, it is important to fully characterise all the possible polymorphs of an explosive to ensure that the highest possible density is reached. Nitrate **3** (HMX) has four polymorphs that are formed by heating below the melting point followed by slow cooling.<sup>13</sup> Two of these are shown in Fig. 1, and differ in the conformation of the eight-membered ring and the orientation of the nitro groups. The  $\beta$ -polymorph of **3** is formed by heating to 116 °C; it is the most stable polymorph and, paradoxically, the most powerful having with the highest density ( $\rho$  1.90 g/cm<sup>3</sup>). The  $\delta$ -polymorph of **3**, formed by heating to 193 °C, is the least dense ( $\rho$  1.58 g/cm<sup>3</sup>) and most sensitive, being about seven times more sensitive to detonation than the  $\beta$  analogue.

Studies of the reaction products of explosions are important in the design of new explosives.<sup>12</sup> However, they suffer from the significant problem of needing analysis of product distributions over the course of extremely fast and violent reactions. This can be simplified by focusing upon the products of the initiation process. In these initial stages of an explosion, sufficient heat must be generated to begin detonation. Studies of the thermolysis of explosives

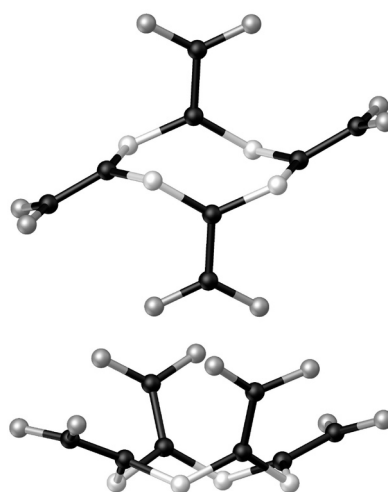
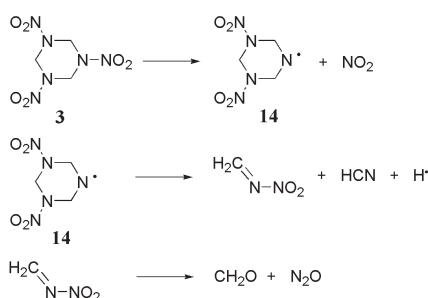


Fig. 1. The structures of the  $\beta$ - (upper) and  $\delta$ -polymorph (lower) of HMX (**3**); hydrogen atoms are omitted for clarity.

simply involve heating an explosive at various temperatures and following this by analysis of the product distribution. Studies on **3** (RDX) have shown that it requires approximately 160–200 kJ/mol to detonate. This is consistent with the initial reaction being the homolysis of the N-N nitramine (N-NO<sub>2</sub>) bond.<sup>14</sup> These bonds in **3** and **11** are much weaker than those in non-cyclic nitramines such as dimethylnitramine (**10**), possibly explaining why these molecules are more explosive. The detonation chemistry of nitramines is shown in Scheme 2 and begins with homolysis of the N-NO<sub>2</sub> bond to produce amine radical **14** and nitrogen dioxide. Radical **14** then induces ring fragmentation to form (eventually) nitrous oxide and formaldehyde. All the fragments react further in the extreme conditions to give the overall product distribution, which consists mainly of nitrous oxide and molecular nitrogen with some carbon dioxide, carbon monoxide, residual solid and water.<sup>15</sup>

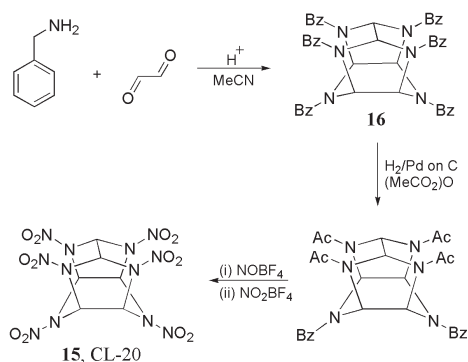


Scheme 2. Initial reactions in the detonation of RDX (**3**).

One of the most powerful military explosives currently being trialled is the caged nitramine – hexanitro-**15** (CL-20) (Scheme 3).<sup>16</sup> Caged molecules have high energies of formation that are released during detonation, and high densities, leading to violent explosions. CL-20 is less sensitive to heat than either **3** or **11**, and, like the latter, it can exist in various polymorphic forms, the most stable having a density<sup>17</sup> of 2.04 g/cm<sup>3</sup>.

The synthesis of **15** is remarkably simple and high-yielding. Benzylamine reacts with glyoxal (ethane-1,2-dione) under acid catalysis and in acetonitrile to produce the hexabenzyl analogue **16** of CL-20 (**15**). Reductive acylation replaces four of the benzyl groups of **16** with acetates

(Scheme 3). This is then sequentially reacted with the strong nitrating agents nitrosotetrafluoroborate and nitro-tetrafluoroborate to give **15** in ~40% yield.<sup>16</sup>

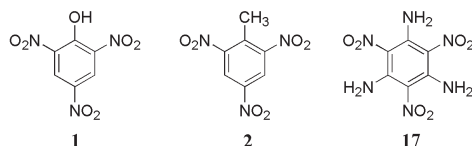


Scheme 3.

Studies on the initiation of CL-20 (**15**) show that, as for **3**, the first reaction is the homolysis of the nitramine bond. However, once this has occurred, the amine radical is stabilized by intermolecular reactions with other caged molecules, accounting for the stability of **15**. In an explosion, nitrogen dioxide is released before intramolecular reactions occur, thereby producing different products to RDX (**3**) or HMX (**11**). Despite having a slightly deficient oxygen balance, this gives reaction products higher in NO<sub>2</sub> and NO than from **3** or **11**.<sup>13,19</sup>

## C-Nitro Explosives

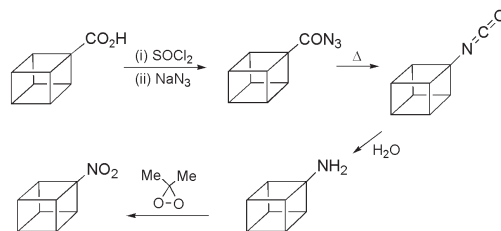
The most well known class of explosives is the nitrated aromatics, with the most widely recognized being 2,4,6-trinitrotoluene (TNT, **2**). TNT was developed as an explosive in the late 19<sup>th</sup> century<sup>3</sup> as a safe alternative to picric acid (**1**), a common early propellant and explosive. Wet picric acid is less sensitive to detonation, but is extremely corrosive towards metals and the metal salts formed are dangerously sensitive to accidental detonation. Until the development of the petroleum industry in the early 20<sup>th</sup> century, TNT could not be made in large quantities due to a lack of toluene. It is a popular explosive, easy to mix with other explosives, and insensitive to accidental detonation, while being quite powerful.



Nitrated aromatics are quite easy to synthesize and nitration is a common reaction in undergraduate laboratories. The sensitivity to detonation for these explosives is due to the high strength of the C-NO<sub>2</sub> bond (*ca.* 300 kJ/mol). As noted above, **2** has a relatively slow detonation speed compared to more modern explosives. Its relative strength is also slightly lower due to a negative oxygen balance (-73%) that leaves reaction products not been fully oxidised. These include a large amount of CO and even some H<sub>2</sub>.<sup>20</sup> Further developments of nitrated aromatics have included the use of other nitrogen functional groups. A modern explosive used for its extreme insensitivity to accidental detonation is 1,3,5-triamino-2,4,6-trinitrotoluene (TATB, **17**). This has been used in specialist applications

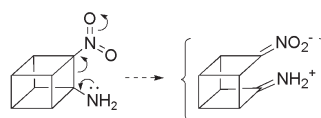
where early detonation can prove disastrous, such as in the trigger of nuclear weapons. This robust solid has a melting point above 600 °C, and is one of the densest nitrated aromatics known ( $\rho$  1.94 g/cm<sup>3</sup>), which makes it one of the more powerful. With more nitrogen per molecule than TNT it also produces more complex nitrogen, containing residues (such as HCN and HNCO) when it explodes.<sup>21</sup>

The search for denser and even more powerful explosives has followed development of other explosives, *e.g.* **15**, into the use of caged molecules. Cubane is extremely energetic, having an enthalpy of formation of *ca.* 630 kJ/mol and, while being kinetically stable, its decomposition occurs only above 220 °C. Cubane is also one of the densest hydrocarbons known<sup>22</sup> with a density of 1.29 g/cm<sup>3</sup>, making nitrated cubanes a goal for new explosives research. Octanitrocubane is predicted to be even denser ( $\rho_{\text{calc}}$  2.1 g/cm<sup>3</sup>) and this would make it one of the densest CHNO explosives known. It is predicted to release 20–30% more energy than CL-20 (**15**) in an explosion. Octanitrocubane has a zero oxygen balance and, in an explosion, should give only molecular nitrogen and carbon dioxide, depending upon the mechanism of fragmentation on explosion. Simple nitrocubanes can be synthesized from the corresponding carboxylic acids using standard procedures,<sup>23</sup> as shown in Scheme 4 for the mono-nitro derivative. A cubane-1-carboxylic acid is converted to its azide, which upon heating undergoes a Curtius rearrangement to give the corresponding isocyanide. This, in turn, is then hydrolysed to an amine and oxidation with dimethyldioxirane generates the nitro moiety.<sup>24</sup>



Scheme 4. Synthesis of nitrocubane.

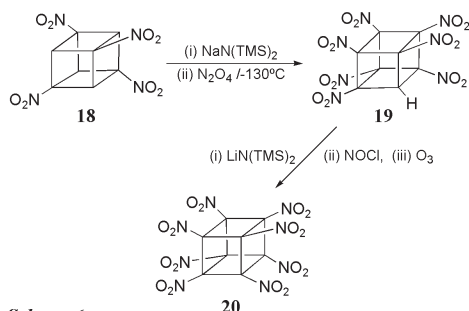
Attempts to synthesise cubanes with adjacent nitro groups using these methods have failed because the products fragment as illustrated in Scheme 5. When an electron-donating amine group is adjacent to an electron-withdrawing nitro group the strain of the cubane skeleton causes the molecule to fragment.<sup>25</sup> This seemed to put the synthesis of more nitrated cubanes in doubt, until it was recognised that the protons of 1,3,5,7-tetranitrocubane are acidic, with a pK<sub>a</sub> equivalent to the  $\alpha$ -proton of a carbonyl group.<sup>26</sup>



Scheme 5.

Treatment of tetranitrocubane **18** with a strong base, such as tetramethylsulfamide, can form the sodium salt that can then be nitrated with dinitrogen tetroxide at the interface of a melting tetrahydrofuran solution of the salt. Indeed, if this is done with four molar equivalents of base, heptanitrocubane **19** is produced (Scheme 6), but this does

not react further to give octanitrocubane (**20**) under these conditions. However, if the lithium or sodium salt of **19** is treated with nitrosyl chloride, followed by oxidation using ozone in cold dichloromethane, **20** is formed, probably by way of (nitroso)heptanitrocubane.



Scheme 6.

Although produced only on a small scale, a single suitable crystal of **20** was grown and the X-ray structure is shown in Fig. 2,<sup>27</sup> but the density was lower than expected ( $\rho$  1.98 g/cm<sup>3</sup>). Since calculations of the densities of these compounds have been found accurate in the past, it is possible that, as for with HMX (**11**) and CL-20 (**15**), other polymorphs of **20** may exist. Currently, heptanitrocubane is of most interest as it is significantly easier to synthesize, and the isolated polymorph more dense ( $\rho$  2.028 g/cm<sup>3</sup>).<sup>9</sup>

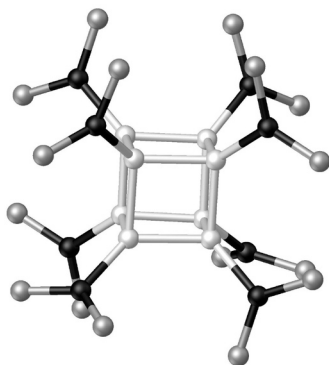


Fig. 2. The structure of octanitrocubane (**20**).

## Conclusion

Explosives have been an important part of the development of society over the last two centuries. The CHNO explosives are the most common class of explosive molecules, with the desire to combine high explosive force with low sensitivity to accidental detonation driving future development. The power of explosives is dependant on attaining the highest density through choice of compound and polymorph. Investigations of the detonation chemistry are also crucial to gaining a complete understanding of the properties of an explosive. Caged molecules, such as CL-20 (**15**) and octanitrocubane (**20**), with their high densities and large energies of formation are at the forefront of current explosives research.

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