

Casting TNT as an explosive

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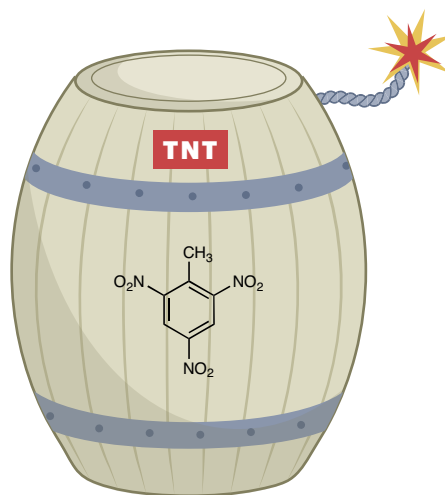
Few explosives are better-known to non-chemists than trinitrotoluene (TNT). Thomas M. Klapötke reflects on the enduring appeal of TNT and whether its starring role as an explosive is nearing its end.

There are arguably few explosives that are more recognizable to the general public than TNT. Although trinitrotoluene is not a household name, its abbreviation TNT is. Who can forget its role in cartoons, especially when Coyote tries to defeat Roadrunner with boxes labelled TNT in some hair-brained scheme?¹ Possibly only gunpowder, dynamite and nitroglycerine have the same recognition amongst the general public as being synonymous with the term explosive.

It is 160 years since the discovery of TNT in 1863 by Julius Wilbrand², who reacted toluene with a nitric acid–sulfuric acid mixture at elevated temperature. However, it was not until nearly 30 years later in 1891 when industrial-scale production of TNT commenced³. Nowadays, the annual industrial production of TNT by Europe's biggest producer NITRO-CHEM (based in Poland) has increased to 5,000 tonnes per year. Even so, it is still predominantly used by the military.

TNT – or 2-methyl-1,3,5-trinitrobenzene to use its IUPAC name – is an example of a secondary explosive³. Explosive compounds can be subdivided into the classes of primary explosives (highly friction- and impact-sensitive, lower detonation velocity) or secondary explosives (less sensitive but higher detonation velocity)^{3,4}. The detonation velocity – a measure of how quickly a shock wave travels through an explosive – of TNT is only mediocre (7.026 m s^{-1}) (ref. 5), and has long been surpassed by much more powerful secondary explosives such as hexogen (RDX) ($8,833 \text{ m s}^{-1}$; ref. 5), β -octogen (β -HMX) ($9,110 \text{ m s}^{-1}$; ref. 4) or ϵ -hexanitrohexaazaisowurtzitane (ϵ -CL-20) ($9,570 \text{ m s}^{-1}$; ref. 5).

Despite its lower performance, TNT is still widely used today, largely thanks to its low melting point ($80 \text{ }^\circ\text{C}$) and much higher decomposition temperature ($295 \text{ }^\circ\text{C}$), which make it an excellent melt-cast explosive³. Melt-cast explosives are a sub-class of secondary explosives that can be melted at moderate



temperatures ($80\text{--}100 \text{ }^\circ\text{C}$) and poured into a form to cool and solidify without decomposition or detonation occurring³. Such a process is not possible with many of the aforementioned pure compounds, due to their high melting points or low decomposition temperatures, giving TNT an inherent advantage over the competition. However, melt-cast explosive mixtures such as Comp. B (39.5% TNT, 59.5% RDX, -1% wax) are widely used, in which solid RDX is added to molten TNT³. Even without best-in-class metrics, TNT's utility propels its use into worldwide recognition.

However, the long reign of TNT as the melt-cast explosive par excellence may be reaching its end. Increasingly, the environmental impacts of not only TNT and its metabolites, but also of nitrated by-products in its production, have been a cause for concern⁶. It has been shown that TNT manufacturing plants have produced high concentrations of soil contaminants that can leach into groundwater⁶. Despite these concerns, the current shortage of TNT in the USA and many European countries, in particular as a result of the Russia–Ukraine conflict, underscores the need for alternatives.

One candidate vying to replace TNT is 2,4-dinitroanisole (DNAN or DNAs). DNAN's melting point of $92\text{--}96 \text{ }^\circ\text{C}$, decomposition temperature of $226 \text{ }^\circ\text{C}$ and low sensitivity to external stimuli make it useful as a melt-cast explosive in low-sensitivity melt-cast formulations³. Although DNAN is being used as a TNT replacement in melt-cast formulations, its

similarity to TNT – both are nitrated benzene rings with either a methyl (TNT) or methoxy group (DNAN) attached – means that its toxicity is similar, and yet its explosive performance (detonation velocity = $5,960 \text{ m s}^{-1}$; ref. 5) is far below modern standards.

Jesse Sabatini, David Chavez and co-authors⁷ recently discovered one of the most promising possible TNT replacements, namely 5,5'-bis-(1,2,4-oxadiazole)-3,3'-bismethylene dinitrate (BODN). In contrast to both TNT and DNAN, which exemplify the traditional approach of nitrating a carbon-backbone, BODN consists of oxadiazole rings and nitrate ester functional groups. Other modern approaches to synthesizing secondary explosives involve cage compounds with so-called explosophore groups attached, or nitrogen-rich compounds such as tetrazole-based or triazole-based molecules³.

The field remains wide open for a successor to TNT, but before TNT becomes consigned to the history books, any challenger must fulfil stringent specifications: detonation velocity above $7,600 \text{ m s}^{-1}$, density above 1.76 g cm^{-3} , melting point in the region of $80\text{--}100 \text{ }^\circ\text{C}$, but decomposing not below $180 \text{ }^\circ\text{C}$, low sensitivity to impact ($>10 \text{ J}$), friction ($>120 \text{ N}$) and electrostatic discharge ($>700 \text{ mJ}$), as well as – crucially – an economic industrial-scale synthesis and much lower toxicity, mutagenicity and cytotoxicity than that of TNT³. Until then, TNT will continue its explosive reign.

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Competing interests

The author declares no competing interests.