

## SYNTHESIS – THE CORE COMPONENT OF ENERGETIC MATERIALS RESEARCH

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**Abstract:** The synthesis of new and novel energetic materials can be pursued with different interests. There is the pure academic interest, which consists, for example, of the complete characterization and analysis of already known compounds or the synthesis of exotic compounds with a nitrogen content above 90%. On the other hand, there is the industrial interest, which consists mainly in finding replacements for the currently used "state of the art" molecules that surpass them in their properties or at least do not have their disadvantages such as toxicity. In the synthesis of energetic compounds, various strategies can be used to achieve certain properties, such as increasing stability or energy content by addition of certain functional groups to the molecular backbone. When a new compound is prepared, which at best is a possible replacement, it is important to study the compound extensively. New materials are then chemically analyzed among other techniques by X-ray diffraction, NMR and vibrational spectroscopy. In addition, their physicochemical properties are determined in terms of impact sensitivity (IS), friction sensitivity (FS) and electrostatic discharge (ESD), as well as their thermal stability. In addition, the energetic properties are calculated using the EXPLO5 code and various tests such as SSRT (Small-scale Shock Reactivity Test) or Koenen tests are performed to get a sense for their energetic behavior.

**Keywords:** energetic materials, future energetics, nitrogen, performance, synthesis.

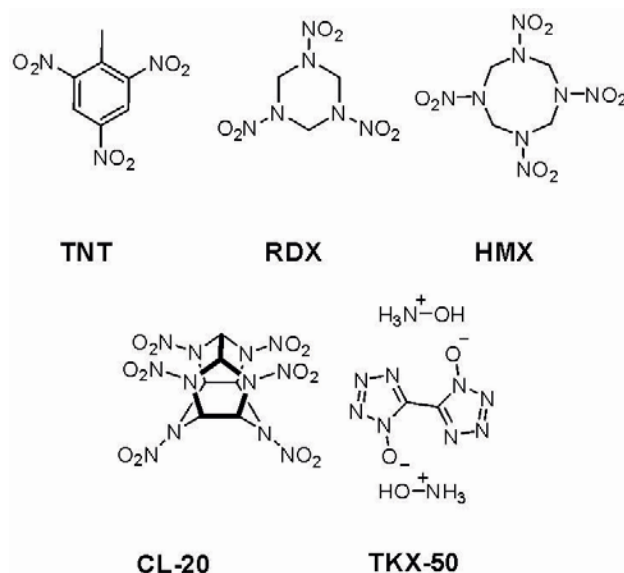
### 1. INTRODUCTION

Energetic materials are most commonly used in either high explosives or propellant formulations. Certain parameters are important in determining the effectiveness of new molecules in these formulations, including high densities ( $\rho$ ), good oxygen balance ( $\Omega$ ) and high detonation/combustion temperatures and high specific impulses ( $I_{sp}$ ) for rocket propellant formulations and lower combustion temperatures combined with a high force and pressure and a high  $N_2/CO$  ratio of the reaction gases for gun propellants. Figure 1 shows five of the most popular energetic compounds.[1-3]

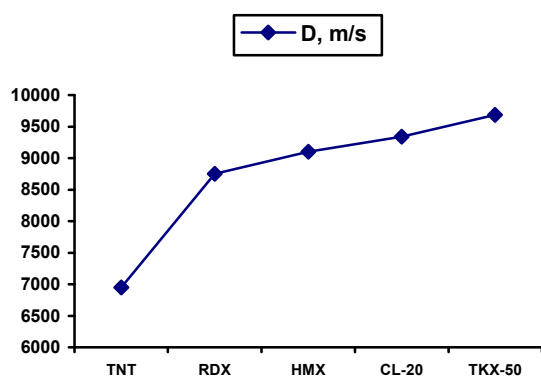
Using the heat of explosion (Q), the detonation velocity (D) and the detonation pressure (P) as a measure for the performance of a high explosive, one can clearly see from Figure 2 that since the time TNT was taken into service the performance of chemical explosives has improved substantially.[1,2,4]

In spite of the many years of research, there are limited possibilities to realize a substantial increase in performance from conventional C-H-N-O explosives. Recent advances in energetics energy output have come in improved processing or inclusion of energetic binders to increase overall formulation energy, but limited success has been realized in the development of novel energetics. One reason for this is that conventional nitramine and nitroaromatic explosives such as TNT, RDX, HMX and

other similar molecules share the same three limitations (Table 1):



**Figure 1.** Chemical Structure of TNT (2,4,6-Trinitrotoluene), RDX (1,3,5-Trinitro-1,3,5-triazinane), HMX (1,3,5,7-Tetranitro-1,3,5,7-tetrazocane), CL-20 (Hexanitrohexaazaisowurtzitane) and TKX-50 (Dihydroxylammonium-5,5'-bitetrazole-1,1'-dioxide).



**Figure 2.** Detonation velocities (D) of chemical explosives.

- (i) they are not nitrogen-rich ( $N \leq 50\%$ );
- (ii) the oxygen-balance is not close to zero;
- (iii) formulations (mixtures of various HEs) are required to achieve a good oxygen balance.

**Table 1.** Nitrogen content (N) and oxygen balance regarding  $\text{CO}_2$  ( $\Omega$ ) of conventional HEs.

	N [%]	$\Omega_{\text{CO}_2}$ [%]
TNT	18.5	-73.9
PETN	17.7	-10.1
RDX, HMX	37.8	-21.6

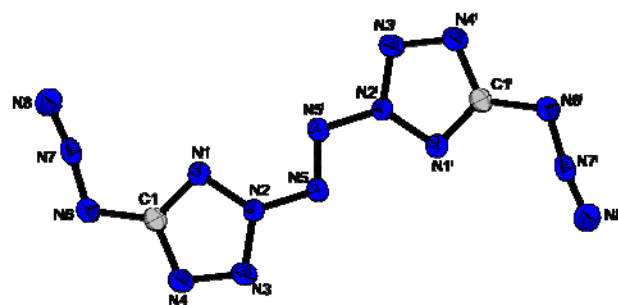
Nitrogen rich molecules are desired as energetics because of the high energy content in N-N bonds. Oxygen balance is defined as the percentage of used oxygen that remains or is needed after an oxidation reaction and can therefore be positive or negative. Materials with an oxygen balance close to zero are typically, but not always, more effective energetics since all of the oxygen is used up in reaction. An oxygen balance can be modified through formulation additions to bring the overall formulation oxygen balance close to zero.[1-3]

### Interest of the synthesis of energetic materials

The synthesis of new energetic materials can be pursued with different interests. The interest of industry is mainly to find substitutes for the currently used "state of the art" molecules that surpass them in their properties or at least do not have their disadvantages, such as toxicity to humans and the environment. For the synthesis of new energetic compounds, different strategies can be used to achieve certain properties, e.g. increasing stability or energy content by adding certain functional groups to the molecular framework. As mentioned before, the strategy of a high nitrogen content in the compounds is desirable as it leads to good properties.

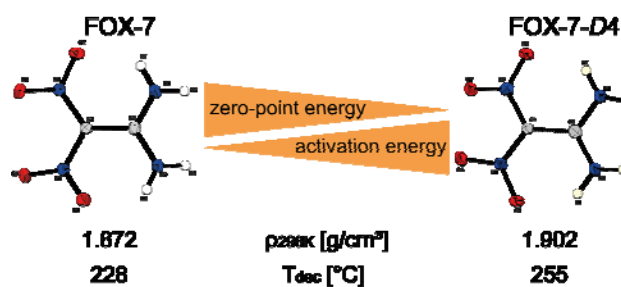
On the other hand, there is the pure academic interest, which consists for example in the synthesis of exotic compounds with an extremely high nitrogen content. A recent example is the synthesis of the extremely sensitive compound 2,2'-azobis-(5-azidotetrazole) ( $\text{C}_2\text{N}_{16}$ ) as a

representative of binary CN-compounds with a nitrogen content of 90.3%. The chemical structure of  $\text{C}_2\text{N}_{16}$  is shown in Figure 3.[5]



**Figure 3.** Crystal Structure of 2,2'-azobis-(5-azidotetrazole) ( $\text{C}_2\text{N}_{16}$ ).

Alternatively, another example of the synthesis of new compounds with academic interest is the introduction of unusual elements or even isotopes into molecules. A recent example here is the synthesis of deuterated FOX-7 (1,1-diamino-2,2-dinitroethylene) and the comparison of its structural behavior and energetic properties with the hydrogenated homologues, you can see the chemical structures and some properties in Figure 4.[6]



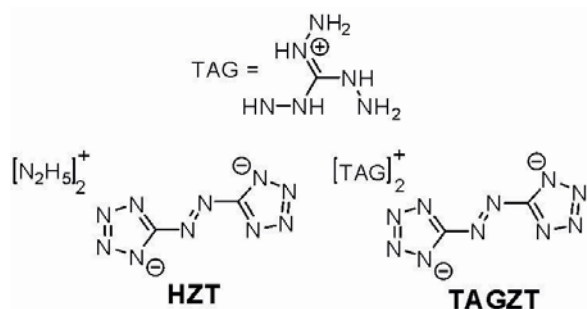
**Figure 4.** Chemical Structure of FOX-7 and FOX-7-D4 with some properties.

But not only the synthesis of such extraordinary compounds is of academic interest, it is also the complete characterization and analysis of already known compounds which is important. In order to better understand their structure-properties-relationship and possibly find new applications for them.

### Replacements and future energetics

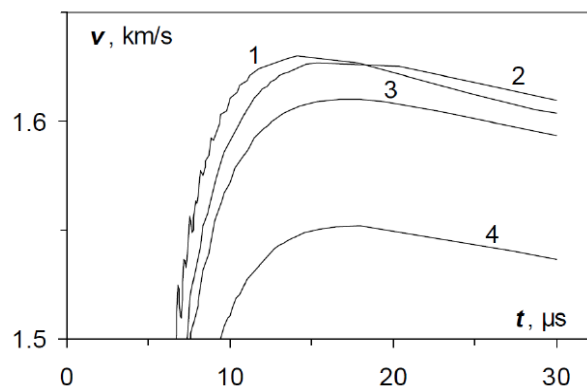
Researchers have already realized the energy content limit for CHNO based molecules. Research needs to expand beyond this way of thinking and increase efforts to explore different molecular structures and molecular make-up in order to realize the substantial increase in performance that will be required for future combat systems. Early research has shown that materials with a high nitrogen content offer many advantages to those with carbon backbones, including the potential for vastly increased energy content. Research into molecules with high nitrogen content (>50%) has shown potential for a substantial increase in available energy. The first generation of high-nitrogen compounds, such as hydrazinium azotetrazolate (HZT) and triamino-guanidinium azotetrazolate (TAGZT) (Figure 5), did indeed meet the criteria for being nitrogen rich and

proved to be very desirable ingredients in erosion-reduced gun propellants, however, due to the unfavorable oxygen balance such compounds are not suitable as energetic fillers in high explosive compositions.[1]



**Figure 5.** Chemical Structure for HZT (hydrazinium azotetrazolate) and TAGZT (triamino-guanidinium azotetrazolate).

The second generation of high-nitrogen compounds which have improved oxygen balances such as TKX-50 (Figure 1), combines desirable high nitrogen content with a good oxygen balance.[4] These compounds are therefore more suitable for use in high-explosive formulations. Moreover, materials with an oxygen balance close to zero are also suitable as powerful ingredients in solid rocket propellants. An increase of the  $I_{sp}$  of only 20 seconds would be expected to increase the payload or range by ca. 100%. Related to this, Figure 6 shows the computed performance parameters for conventional and high-N gun propellants.[1]



**Figure 6.** Acceleration of  $T_a$  cylindrical layers by TKX-50 (1), HMX (2) & RDX (4).

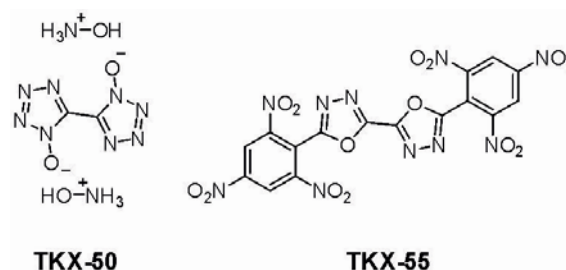
The computed and predicted performance values not only exceed the first generation of high-nitrogen compounds (e.g. HZT) but, in case of TKX-50, also the performance values of RDX and HMX (Fig. 2).[1]

LMU Munich is constantly researching possible better substitutes and environmentally friendly replacements. In the following you can find further areas of energetic materials research at LMU:

- High Explosives (HEDM, RDX replacements)
- Lead-free Primary Explosives
- High Oxidizers (HEDO)
- Nitrogen-rich Gun Propellants
- Visible Pyrotechnical Compositions & Smokes

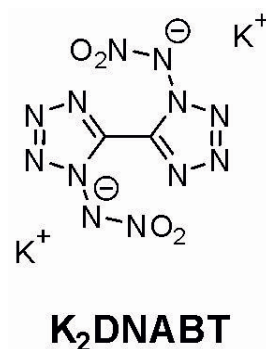
- Flow chemistry for energetics
- NIR Illuminants
- Agent Defeat Weapons (ADW)
- Energetic Polymers & Reactive Struct. Materials

A promising RDX replacement is of course TKX-50, as already mentioned, but TKX-55 also has very good thermostable properties. Figure 7 shows the structures of both compounds.[4,7]



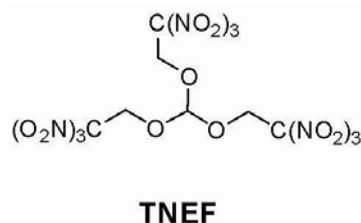
**Figure 7.** Chemical Structure of TKX-50 (Dihydroxylammonium-5,5'-bitetrazole-1,1'-dioxide) and TKX-55 (5,5'-bis(2,4,6-trinitro-phenyl)-2,2'-bi(1,3,4-oxadiazole)).

A possible lead-free primary is  $K_2$ DABT, shown in Figure 8.[8]



**Figure 8.** Chemical Structure of  $K_2$ DNABT (Dipotassium dinitraminobistetrazolate).

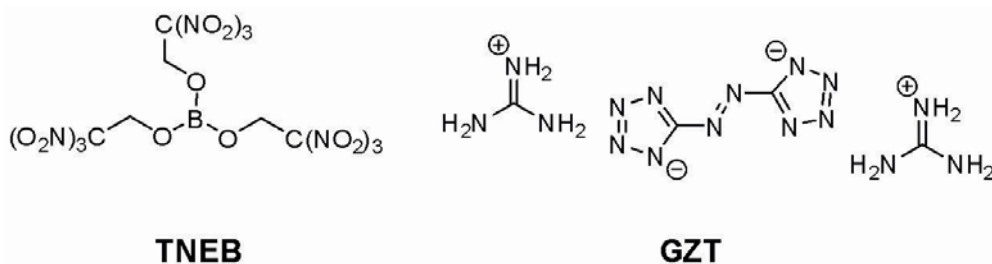
A possible ammonium perchlorate replacement as a non-toxic oxidizer is TNEF (Figure 9).[9]



**Figure 9.** Chemical Structure of TNEF (2,2-trinitroethyl orthoformate).

Furthermore, promising visible pyrotechnical compositions & Smokes mixtures were developed based on TNEB and GZT, shown in Figure 10.[10,11]

Moreover our group at LMU has been working on TBX formulations with improved oxidizers and energetic fillers.[1]



**Figure 10.** Chemical Structure of TNEB (tris(2,2,2-trinitroethyl)borate) and GZT (Guanidinium 5,5'-azotetrazolate).

**Table 2.** Comparison of the heat heats of reaction ( $Q_{ex}$ ) of a conventional high-explosive HMX-based formulation and two thermobaric compositions.

	anaero <sup>b</sup>	aerob <sup>a,b</sup>	anaero <sup>b</sup>	aerob <sup>a,b</sup>	anaero <sup>b</sup>	aerob <sup>a,b</sup>
HMX	85	85	45	45	45	45
AP			10	10		
TNEF					10	10
Al			15	15	15	15
Mg			15	15	15	15
EXPLO5 V6.06.01						
$\Omega(\text{CO}_2) / \%$	-66.2	0	-77.4	0	-79.8	0
$\rho / \text{g cm}^{-3}$	1.63	1.63	1.68	1.68	1.67	1.67
$Q_{ex} / \text{kJ kg}^{-1}$	4878	13769	8301	18113	8539	18916
T / K	3158 <sup>d</sup>	6118 <sup>c</sup>	4583 <sup>d</sup>	7408 <sup>c</sup>	4705 <sup>d</sup>	7486 <sup>c</sup>
$p_{C-J} / \text{GPa}$	22.4		15.8		15.4	
D / $\text{m s}^{-1}$	7645		6443		6372	

a) Aerobic calculation done using isochoric combustion run, loading density 0.001 g/cm<sup>3</sup>; b) Al<sub>2</sub>O<sub>3</sub> and MgO taken to be solid; c) Adiabatic combustion (with oxygen) temperature; d) Detonation temperature.

Ideal molecular high explosives (HE) such as TNT, RDX, PETN and HMX generate during detonation fast decaying blast waves of high peak pressure with very short duration and are designed to throw shrapnel, shatter structures or penetrate armors. However, they are lethal only within their immediate vicinity and show visible shortcomings for defeating hardened targets such as tunnels and caves. To overcome these shortcomings, great efforts have been focused on the development of new weapons able to generate higher impulse, higher blast and able to use its energy not to destroy corners or walls, but to travel around it efficiently and defeat hardened targets

Today, cast composite thermobaric explosives most often consist of a high explosive (RDX, HMX), polymeric binder (e.g. HTPB), fuel component (metal powder for enhancement of the blast effect, e.g. Al, Mg) and an oxidizer (AP or AN).

Table 2 shows a comparison of the detonation temperatures and combustion temperatures with afterburn of a conventional explosive formulation (HMX-HTPB) and a thermobaric composition.

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