Propellants,
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RESEARCH ARTICLE

A rocky road toward a suitable TNT replacement – A closer look at three promising azoles

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Abstract

The goal of this research project was to establish a literature known explosive, which can be used as a future melt-cast explosive. The substance should not only be theoretically suitable as a substitute but also meet all industrially relevant requirements. Therefore, intensive literature research was executed to filter appropriate candidates. The three most promising substances were re-synthesized to verify their key properties. If all criteria meet the requirements, synthesis optimization and preindustrial upscaling should be carried out.

KEYWORDS
green chemistry, melt-cast explosives, performance enhancement, synthesis, toxicity

1 | INTRODUCTION

TNT (2,4,6-trinitrotoluene) is one of the most common energetic materials ever synthesized and is often used colloquially as a term for explosives [1]. The compound has been produced on a large scale for more than 120 years and is still used today in many kinds of explosives. Predominantly, TNT is used as a so-called melt-castable explosive. The use of a melt-castable component in explosive charges prevents cracks in the packing and results in an ideal filling of the cavity [2]. To be considered as such, certain thermal properties have to be fulfilled. The thermal properties of TNT are highly favorable. The melting range is around 80 °C. This is particularly attractive for industrial use as a melt-cast explosive, as the melting process can be carried out with the use of a steam bath. In addition, the decomposition temperature is more than 200 °C above ($T_{dec} = 291$ °C) and thus in a perfect safety range for explosives.

In addition to its positive thermal properties, other characteristics of TNT have made it popular for use to this day. The simple synthesis based on readily available starting materials (toluene and a mixture of sulfuric acid and nitric acid) is beneficial, especially from an industrial point of view [3].

Moreover, the sensitivity values towards external stimuli such as impact (IS), friction (FS), and electrostatic discharge (ESD) remain within acceptable ranges and thus favor problem-free handling even of larger quantities [4–6].

Nevertheless, there are two key points why TNT urgently needs to be substituted. The environmental impact of pure trinitrotoluene and its degradation and partially less nitrated intermediate and by-products is high

and has led to increased groundwater and soil contamination near production sites [7–8]. With the increased green and environmentally friendly demands evolved in recent years, these materials need to be replaced as a matter of urgency. In addition, the demand for military explosives, which is what TNT is mainly used for, is primarily driven by ever more powerful explosives [9–11].

In order to maintain the standards, set by TNT and to complement them with better performance and environmental sustainability, we have undertaken an extensive literature review to identify suitable targets. We set a number of strict criteria for exclusion, which made it possible to exclude numerous propagated melt-castable substitutes known from the literature only because of some physico-chemical properties. The prerequisites are listed in Figure 1.

Additionally, other, mainly environmental and industrially relevant specifications must be considered. The key issue is to find a synthesis that is as simple, atom-economical, short (reaction steps), and cheap as possible. In addition, no chemicals should be used that are already banned by REACH or on the list of candidates of high concern [12]. Finally, special attention should be paid to the toxicity/mutagenicity of intermediate and end products, as this is one of the main points for substitution search.
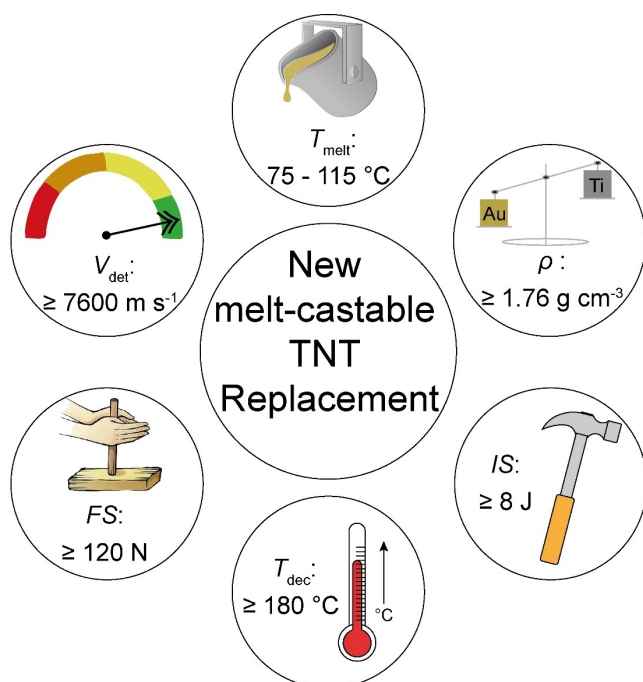
2 | RESULTS AND DISCUSSION

2.1 | Selection of target molecules

Based on the selected parameters, our screening was mainly focused on N-heterocyclic azole systems, as these provide promising results for many of the benchmarks listed. We have assembled a candidate list and synthesized the respective compounds to ensure that all relevant physico-chemical properties correspond to the published values. Thereafter, supplementary measurements such as compatibility tests with other common explosives and toxicity/mutagenicity determinations should be carried out in order to proceed to possible synthesis optimization as well as a larger upscale.

Based on the respective properties of the materials, we proceeded according to internally developed prioritization. Based on the detonation characteristics combined with the auspicious published thermal behavior, BNFF was determined as our number 1 target molecule. In case of discrepancies with BNFF, we have selected MTNI and BODN as further promising compounds (Figure 2, Table 1).

2.2 | Synthesis of target molecules and review of their key features

The synthesis of BNFF was performed according to the literature-known procedure by Kuklja *et al* [13]. They started from malononitrile and came up with an overall yield of 39 %. We could obtain similar yields. At an initial stage, we tried to optimize the third reaction step, which requires silver carbonate, by using other monovalent carbonate bases (NH_4, K, Cs) for cost reduction purposes, but without any result.

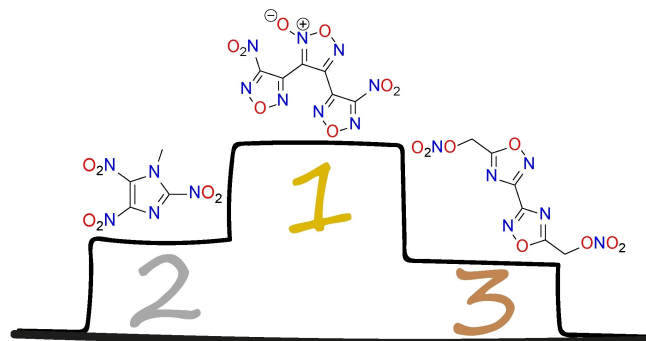**FIGURE 1** Required physico-chemical properties for a new melt-castable TNT replacement.

FIGURE 2 Promising literature known target molecules as potential TNT substituents with prioritization order taken from a literature research in 2020: (1st: bis(nitrofurazano)furoxan (BNFF), 2nd: 1-methyl-2,4,5-trinitroimidazole (MTNI), 3rd: 5,5'-bis-(1,2,4-oxadiazole)-3,3'-bismethylene dinitrate (BODN)).

TABLE 1 Energetically relevant physico-chemical parameters of BNFF, MTNI, BODN and TNT according to the published literature.

	BNFF [13]	MTNI [14]	BODN [15]	TNT [2, 16]
IS [J][a]	10	17	8.7	15
FS [N][b]	120	360	282	> 360
ρ [g cm^{-3}][c]	1.875	1.82	1.832	1.65
T_{melt} [°C][d]	109	95	84.5	80
T_{dec} [°C][d]	279	310	183.4	295
V_{det} [m s^{-1}][e]	8970	8541	8180	6823
synth. steps	4[f]	4[g]	4[h]	1[i]

[a] Impact sensitivity (BAM drophammer (1 of 6));

[b] Friction sensitivity (BAM friction tester (1 of 6));

[c] From X-Ray diffraction analysis recalculated to 298 K:

[d] Melt and decomposition temperatures (DTA; $\beta = 5$ °C min^{-1});

[e] Detonation velocity calculated using EXPLO5 V6.05.02,

[f] Starting from malononitrile;

[g] Starting from 4-nitroimidazole;

[h] Starting from aqueous glyoxal solution;

[i] Starting from toluene.

After the successful synthesis, the sensitivity values could be verified. During the verification of the thematic behavior, we found inconsistencies with the literature values. First, based on the DTA measurement, we assumed that a melting point at 106 °C was present, as described in the literature.

In the subsequent TGA measurement, it turned out that the endothermic signal clearly refers to a melting point. However, it can be clearly seen that the melt of BNFF has a high volatility and evaporates almost completely up to 199 °C when heated further (Figure 3). This characteristic could not be distinguished from melting by DTA because of the different structures of the containers of DTA and TGA measurements. Due to the instability at temperatures above 111 °C, BNFF was
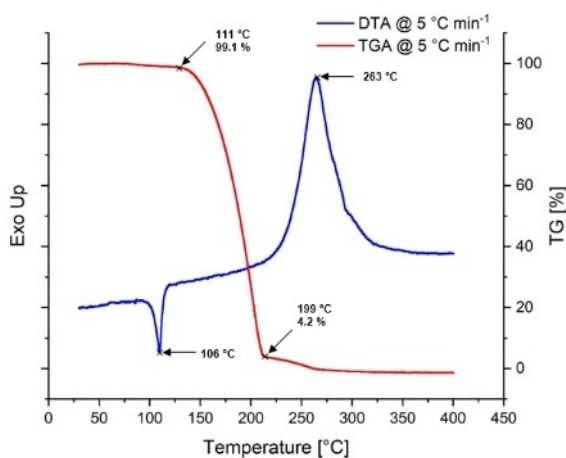
eliminated as a possible melt-castable substitute and we tried to produce the second candidate on our prioritization list (MTNI).

1-Methyl-2,4,5-trinitroimidazole (MTNI) was synthesized by the route of Anniyappan et al [14]. via N-nitration of 4-nitroimidazole, nitro group rearrangement, methylation and final C-nitration The N-nitration yielded 1,4-dinitroimidazole quantitatively. During the handling of the compound and while preparing the rearrangement reaction, three co-workers were afflicted by rashes on the hands and arms and additional irritation across the face. Therefore, the compound was subjected to a toxicological test (aqua toxicity toward *Aliivibrio fischeri*) and was considered as very toxic [17]. Accordingly, work on MTNI was discontinued and attention turned to the third prioritization compound, BODN.

5,5'-Bis-(1,2,4-oxadiazole)-3,3'-bismethylene dinitrate (BODN) can be synthesized through a four-step procedure (Figure 4) starting from an aqueous glyoxal solution. After the quantitative reaction with hydroxylamine toward diaminoglyoxime [18], the double ring closing condensation was performed using acetoxyacetyl chloride. After deprotection of the hydroxy group and nitration to the nitrate ester, BODN was obtained with the same yield (44% overall) and batch size (25 g of BODN) as published by Sabatini et al. [15]. Both the results of the thermal investigations ($T_{melt} = 82$ °C and $T_{dec} = 185$ °C vs $T_{melt}^{lit} = 84.5$ °C and $T_{dec}^{lit} = 183.4$ °C) and the sensitivity values were confirmed by our own measurements. In the case of impact sensitivity, we measured a slightly higher sensitivity ($IS = 8$ J vs $IS^{lit} = 8.7$ J), but we were able to measure our product as lightly less sensitive to friction ($FS = 324$ N vs $FS^{lit} = 282$ N) than the authors of the original publication [15].

FIGURE 3 Combined DTA (blue) and TGA (red) measurements of bis(nitrofurazano)furoxan (BNFF) with heating rates of 5 °C min^{-1}.
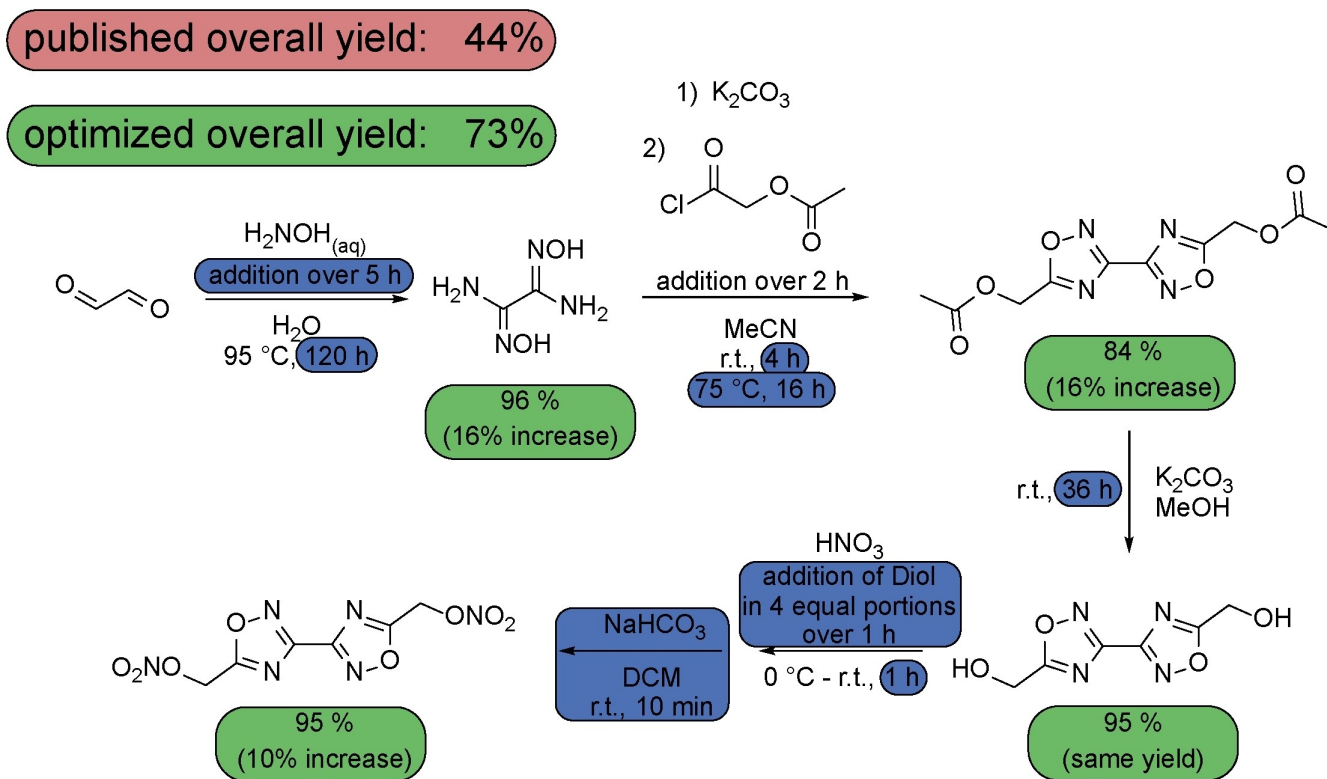
FIGURE 4 Optimized reaction scheme toward BODN. The green boxes show the optimized yields and the improvement. The blue boxes show the added or modified reaction steps.

2.3 | Synthetic optimization of BODN

After checking the most important properties, work was started on optimizing the synthesis of BODN. The route of Sabatini *et al.* seemed suitable since the yields are already in fine ranges and the used chemicals are readily available and mainly affordable. Therefore, a completely new synthesis route was ruled out. However, we tried to increase the overall yield mainly by changing the reaction time, reaction temperature, and addition rate and were able to increase it to 73%. All final optimization steps were performed in the same batch size as in the original procedures to ensure comparability. All detailed experimental procedures can be seen in the SI.

The formation of diaminoglyoxime (DAG) toward the condensation of aqueous glyoxal solution with hydroxylamine could be optimized to a nearly quantitative yield of 96% by controlling and reducing the dripping rate to 5 h and increasing the reaction time to 120 h. However, the reaction time is too long for an industrial process, which is why a compromise has to be made here with the newly developed synthesis known from the literature.

In the subsequent condensation to the 3,3′-bis(1,2,4-oxadiazole) backbone, we were also able to increase the yield by 16% to a total of 84%. For this purpose, strict

adherence to the addition rate was ensured. The reaction solution was then stirred at ambient temperature for four hours, followed by a reaction at 75 °C for 16 h to complete the condensation.

For the basic deprotection of the acetyl-protecting group to the hydroxymethyl function, the excellent yield of the original publication was confirmed. However, by the continuous sampling of the reaction solution by NMR spectroscopy, we were able to determine that the reaction had already been completed after 36 hours.

The nitration step was improved by some modification of the reaction time and speed of addition. After the complete addition of the diol within one hour in four equal portions, the ice bath was removed and the reaction solution was stirred for another hour, reaching room temperature. After that time, the nitration was already completed, which was checked by NMR measurements of the water-quenched solid.

Despite washing the resulting solid with extensive amounts of water, we observed the formation of nitrous gases and a decomposition of our product after a few weeks of storage. Therefore, we included a workup step, since we concluded that the destructive NO_x formation results from the remaining acid in the product. Thus, we dissolved the crude BODN in DCM and washed the organic phase with 2% $NaHCO_3$ solution. The cleanup step

yields BODN quantitively. The overall yield could be improved to 73% over 44% using the published procedures.

Since we are still dealing with the synthesis of a few grams here and all reactions were carried out in a batch, further optimizations or changes in the reaction conditions may well occur as soon as the batch size is increased further. In our case, the desired quantity of 100 g, as the first milestone could be produced in three batches.

2.4 | Compatibility with other common explosives

With the optimized reaction protocol in hand, we started further tests concerning the compatibility of BODN with other commonly used explosives. Since most explosive charges consist of mixtures of several explosives, it is particularly important that these are compatible, i.e. that their physicochemical properties do not influence each other or react with each other in the ground state in the substance mixture.

Therefore, we tested the thermal decomposition of BODN with selected high explosives and wax by DSC measurements. The formulations were prepared by mixing both components (grain size $100-500\,\mu m$) in their solid state with a stirring bar for a few minutes to ensure homogeneity. We defined two compounds as being compatible with each other if the thermal events of the mixture did not differ by more than 10 °C from those of the pure substances.

Table 2 shows the results of the measurements. The graphic illustrations of the thermal investigations can be seen in the SI.

The thermal measurements showed that BODN is compatible with RDX, HMX, CL-20, and wax with no drastic change in the temperature of thermal events. The

mixture with TNT shows an endothermic event (melting) in the DSC curve at 58 °C, therefore a ΔT_{endo} of 24 °C is observed. As a change in thermal events over 10 °C implies incompatibility, BODN is compatible with RDX, HMX, CL-20 and Wax but not with TNT. The composition BODN/RDX (60:40) shows an endothermic event (melting) at 81–83 °C with a thermal decomposition beginning at 176 °C with a maximum at 198 °C.

The DTA curve of the BODN/TKX-50 formulation shows an endothermic signal at around 77 °C, indicating a melting point as expected for BODN. Unfortunately, a sharp exothermic event appears a 125 °C, which suggests that a reaction has occurred between the two compounds in the melt of BODN and TKX-50, and that the resulting product decomposes at 125 °C. In the subsequent temperature range, no further signals are visible, indicating complete decomposition. It can therefore be concluded that BODN is not compatible with TKX-50. Unfortunately, it is not possible to identify exactly which of the components of TKX-50 (hydroxylammonium cation or $BTDO^{2-}$ anion) is responsible for the decomposition reaction of BODN. To get a more detailed insight a mixture of BODN with Li_2BTDO tetrahydrate as well as with $(NH_4)_2BTDO$ (ABTOX) was prepared and thermally investigated.

The DTA measurement of BODN/$Li_2BTDO\cdot 4\,H_2O$ shows an endothermic event at 81 °C corresponding to the melting point of BODN. Further endothermic events occurring at 109 °C and 163 °C correspond to a loss of water in a two-step mechanism, which is known for $Li_2BTDO\cdot 4\,H_2O$ [19]. The exothermic signal at 186 °C derives from an exothermic decomposition, which suggests a compatibility of Li_2BTDO and BODN.

The DTA plot of BODN/ABTOX (1:1) shows an endothermic signal at 83 °C which refers to the melting point of BODN. The exothermic signal is detected at 135 °C which indicated a sharp decomposition of the mixture. ABTOX is also incompatible with BODN as the

TABLE 2 Results of the DSC/DTA measurements of formulation of BODN with other prominent high explosives and wax.

Formulation[a]	T_{endo} [°C][b]	T_{exo} [°C][b]	Result
BODN (100%)	82	185	–
BODN/RDX	81	175	compatible
BODN/HMX	83	175	compatible
BODN/TNT	58	183	not compatible
BODN/Wax	39	179	compatible
BODN/CL-20	82	180	compatible
BODN/RDX (40:60)	81	177	compatible
BODN/TKX-50	77	125	not compatible

[a] Formulations were prepared with a mass ratio of 1:1, if not indicated otherwise;
[b] Onset points of the first endothermic/exothermic signal.

mixture owns a premature decomposition point compared to the pure compounds (T_{dec} (ABTOX) = 290°C) [20]. Therefore, we resume that the incompatibility of BODN/TKX-50 origins by the ammonium and hydroxyl ammonium cation, particularly by their acidic character. The proton-promoted decomposition could also be observed in the preparation of BODN as described in the synthetic optimization part.

2.5 | Toxicology and mutagenicity

One main drawback of TNT is its toxicity. Therefore, the ultimate goal in general is to establish a nontoxic and non-mutagenic replacement. Hence, BODN was investigated according to its toxicity (bacterial cytotoxicity toward *E.coli*) and mutagenicity (Ames-Test toward *Salmonella typhimurium*), since the validation of its physico-chemical properties were promising. We were not able to measure the aqua toxicity toward *Aliivibrio fischeri* since BODN is sparingly soluble in water [17].

BODN did not exhibit bacterial cytotoxicity under the experimental conditions up to the highest concentration (1000 µg/ml) tested for *E.coli*. The bacterial reverse mutation assay (Ames-Test) was performed with five strains of *Salmonella typhimurium* (TA98, TA100, TA102, TA1535 and TA1537) [21]. The test was performed in one experiment in the presence and absence of metabolic activation, with +S9 standing for the presence of a metabolic activation, and −S9 standing for the absence of metabolic activation. The strains TA100 and TA1535 showed a relevant and dose-dependent increase in revertant with and without metabolic activation. According to the criteria of the guideline OECD 471 [21], the result of this study is positive, as there is a concentration related increase in revertant, a biological relevant increase in at least one concentration compared to the concurrent solvent control and at least one con-centration with an increase above the distribution of historical solvent control data. Based on the results of this study it is concluded that BODN is mutagenic in the *Salmonella typhimurium* strains TA100 and TA1535 in the presence and absence of metabolic activation.

Since mutagenicity is a no-go criterion for a possible TNT replacement, BODN had to be excluded.

3 | CONCLUSION

After an intensive and abundant literature research for a suitable melt-cast explosive replacement meeting several key criteria (T_{melt} = 75–115°C, $T_{dec} \geq 180$°C, $V_{det} \geq 7600$ m s^{-1}, $\rho \geq 1.76$ g cm^{-3}, FS ≥ 120 N, IS ≥ 8 J, nontoxic

and non-mutagenic) three candidates were selected as most promising (BNFF, MTNI and BODN). BNFF could be synthesized as described in literature but showed no melting point in the thermal investigation but a sublimation point, instead. Therefore, we switched to MTNI, which caused drastic skin irritations and severe rashes at the synthetic chemists during the preparation and handling of 1,4-dinitroimidazole. That's why BODN was investigated instead. The synthesis is reproduceable as are the physico-chemical properties. We were able to optimize the synthesis to an overall yield of 73% (44% starting yield) and test the substance mainly positive toward its compatibility with other prominent explosives to guarantee a possible formulation stability. Unfortunately, the mutagenicity determined by a positive Ames-Test excludes BODN for further testing.

Hence, the hunt for new possible melt-cast replacements continues. Unluckily, many compounds are synthesized and published with only the minimal standard of analytic data. However, to explore the feasibility for industrial use as a substitute, much more effort and experimental insights are required than just stating "potential TNT substitute" as conclusion at the end of a publication.

DATA AVAILABILITY STATEMENT
Data may be requested via the authors.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.