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**Title:** 2,4,6-Trinitrotoluene - A Useful Starting Compound in the Synthesis of Modern Energetic Compounds

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# 2,4,6-Trinitrotoluene – A Useful Starting Compound In the Synthesis of Modern Energetic Compounds

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**Abstract:** This review presents a history, properties, and environmental fate of 2,4,6-trinitrotoluene (TNT). Industrial methods of TNT production are discussed, as are several energetic derivatives of TNT. The performances and applications of these TNT derivatives are also described.

## 1. Introduction

2,4,6-trinitrotoluene (TNT) was first produced by Wilbrandt in 1863<sup>[1]</sup>, though its explosive properties were not immediately recognized due to its low sensitivity to mechanical stimuli and a relatively high critical diameter. It can be assumed that TNT was first used for military purposes around the year 1900<sup>[2]</sup>, while 2,4,6-trinitrophenol (picric acid) was still used on a massive scale as a secondary explosive during WWI. Although picric acid was discovered approximately 100 years before TNT<sup>[3]</sup>, its widespread use largely ended with the close of WWI. TNT is still one of the most common secondary explosives that has been in nearly continuous use for 155 years. TNT was initially used in its pure form, though it is now more popularly used with RDX to form Composition B, and as a component of melt-cast explosive compositions with a reduced sensitivity to unintentional initiation. The other ingredients of these latter kinds of compositions are also low sensitivity explosives such as 3-nitro-1,2,4-triazolone (NTO) or 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)<sup>[4]</sup>. Due to the mass production of TNT in many countries, its price is relatively low (\$5.50 per kg<sup>[5]</sup>). The low-cost and high purity of commercial TNT explains why this compound can be considered to be an attractive substrate for the synthesis of other explosives.

Currently, the use of secondary explosives for military purposes must meet increasingly stringent requirements concerning high heat resistance and low sensitivity to

mechanical stimuli. The synthesis of a new energetic compound with reduced sensitivity (e.g. NTO) requires the purchase or synthesis of precursors that are not energetic, and that have not been used in the synthesis of explosives. The application of readily available TNT to the synthesis of other energetic compounds—especially in explosives manufacturing plants—is a very attractive solution mentioned in scientific literature.

The aim of this paper is to examine the possibility of using TNT to produce new attractive explosive mixtures with desired properties that do not share TNT's major downsides as a standalone ingredient. The most frequently mentioned disadvantages of TNT include its relatively high vapor pressure<sup>[6]</sup>, its susceptibility to photolytic degradation<sup>[7]</sup> and its susceptibility to reactions in an alkaline environment<sup>[8]</sup>.

## 1.1. Synthesis of TNT

Since the first synthesis of TNT by nitration of toluene by Wilbrandt in 1863<sup>[1]</sup>, many methods of its synthesis from a variety of substrates were described. Tiemann synthesized TNT by nitration of 2-nitrotoluene.<sup>[9]</sup> Jackson and Phinney obtained TNT by thermal decarboxylation of 2,4,6-trinitrophenyl acetic acid.<sup>[10]</sup> Alfthan produced trinitrotoluene during nitration of 1-isopropyl-4-methylbenzene with mixed acid.<sup>[11]</sup> TNT was also obtained through the nitration of dinitroanisole (DNAN) in 1935 by James.<sup>[12]</sup> 4-nitrotoluene was applied for synthesis of the title compound by Titow.<sup>[13]</sup> TNT was also obtained by methylation of 1,3,5-trinitrobenzene.<sup>[14]</sup> Technologists have worked on waste minimisation during the TNT synthesis, and some papers report the concern of “red water” problem. Elimination of red water formation from TNT manufacture, and improvements of the regioselectivity in the nitration of toluene, have been published<sup>[15]</sup> but efforts are still ongoing to address these shortcomings.

## 1.2. Technology of TNT

Production of TNT on an industrial scale is carried out in periodic mode by stepwise introduction of nitro groups to toluene. In almost all known industrial methods, the process is realized in three steps<sup>[16-19]</sup>, though methods have also involved two step processes.<sup>[20]</sup> In each subsequent nitration step, the concentration of nitric and sulphuric acid increase, while the concentration of water decreases. Introduction of each nitro group onto the toluene ring requires higher temperatures in excess of 100 °C. The available details of TNT production on the industrial scale are presented in Table 1.

Continuous methods of TNT synthesis have been developed in Great Britain<sup>[21]</sup>, Germany<sup>[22]</sup>, Sweden<sup>[23]</sup> and Sweden-Norway.<sup>[24, 25]</sup> These methods consisted of the nitrator-separator system. Depending on plant conception, the installation can comprise up to eighteen units. Continuous methods applied for explosive synthesis are safer because reactor capacities are smaller. At any moment during production, there is the risk of hazardous material accumulation. The specific details of contemporary continuous TNT plants are unpublished at this time. Nonetheless, for the aforementioned methods described to prepare TNT, the crude product is purified to remove nitric and sulphuric acid, TNT non-symmetric isomers, and other side products such as tetranitromethane, and trinitrobenzene. Removal of the by-products are realized by mixing the solid or molten crude TNT product with water, followed by filtration. The

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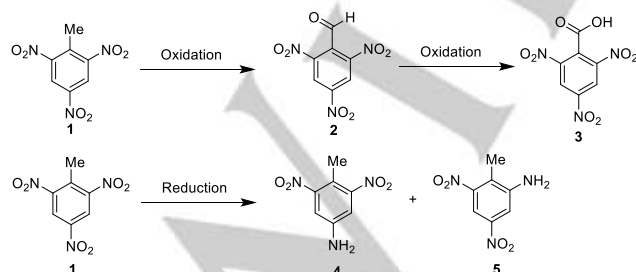
filtered solid then undergoes sulphitation to yield flakes of TNT, which are dried to obtain the pure product.<sup>[19, 22]</sup>

**Table 1.** Conditions of TNT synthesis in industrial scale.

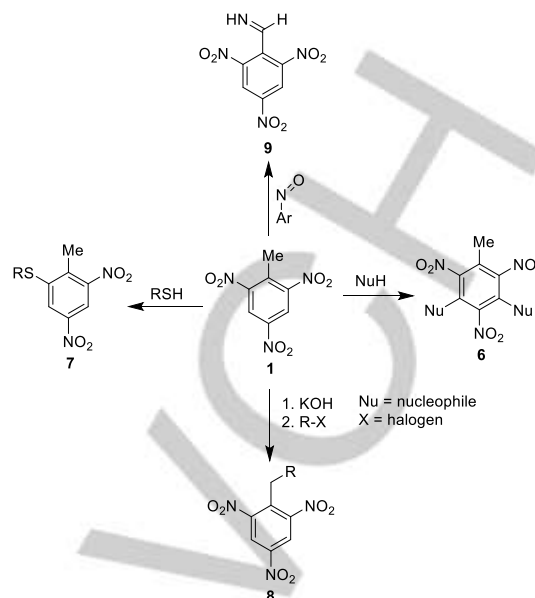
Method	Step	Concentration, %			Temperature, °C
		HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	
French, 1925 <sup>[16]</sup>	I	28	56	16	60
	II	32	61	7	90
	III	49	49	2	105
British, 1914-1918 <sup>[17]</sup>	I	na	na	na	50
	II	na	na	na	na
	III	79.5	17.8	2.7	66-100
USSR, 1940 <sup>[18]</sup>	I	27-28	54-55	17-19	40-50
	II	23	67	10	80-105
	III	17.5-18.5	81.5-82.5	-	115
German, 1945 <sup>[19]</sup>	I	28	56	16	34-40
	II	na	na	na	60-65
	III	24	70	6 SO <sub>3</sub>	96
Italian, 1934 <sup>[20]</sup>	I	28	60	12	75
	II	24	70	6	96

### 1.3. General reactivity of TNT

Since the reactivity of TNT has been the subject of numerous theoretical and experimental research efforts,<sup>[26, 27]</sup> the reactivity of TNT will not be discussed further if the product of the reaction is not an explosive or does not have potentially useful properties. This review intentionally omits all compounds that are commonly known universal substrates in synthesis (e.g. picryl chloride). The chemical reaction on each functional group of TNT leads to the formation of compounds with a higher reaction potential than pure TNT. For example, oxidation of the methyl functional group of TNT (**1**) can lead to 2,4,6-trinitrobenzaldehyde (**2**) or 2,4,6-trinitrobenzoic acid (**3**), whereas reduction of TNT is possible, thus converting the nitro groups to the amino derivatives **4** and **5** (Scheme 1). Protons at the 3- and 5-position of TNT may undergo vicarious nucleophilic substitution (VNS) to give **6**, as shown in Scheme 2.<sup>[28]</sup> The nitro group may be substituted, for instance, with the sulphide group to give **7**.<sup>[29, 30]</sup> Use of Bronsted bases allows for the  $\alpha$ -deprotonation of the methyl group, which can then undergo nucleophilic substitution reactions to give **8**.<sup>[31]</sup> The methyl group can also react with aromatic nitroso-compounds to yield imine-based materials, such as **9**.<sup>[32]</sup>



**Scheme 1.** General oxidation and reduction paths of TNT.

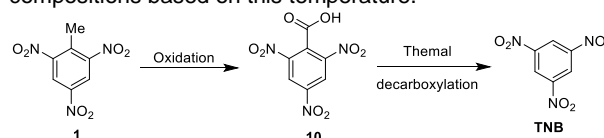


**Scheme 2.** Representative examples of nucleophilic substitutions of TNT

## 2. Synthesis of explosives from 2,4,6-trinitrotoluene

### 2.1. 1,3,5-trinitrobenzene

The oldest explosive synthesized from TNT was symmetrical trinitrobenzene (TNB), first described in 1883 by Claus and Becker.<sup>[33]</sup> Since then, many methods of TNB synthesis have been identified, although these methods are based on the oxidation of the methyl group to the carboxyl group to afford **10**, followed by thermal decarboxylation (Scheme 3).<sup>[34-37]</sup> Another method for the preparation of TNB is a stepwise nitration of benzene, although this method is not used in practice due to the harsh conditions required in successive nitration reactions. The detonation parameters of TNB are slightly higher than those of TNT. At a density of 1.60 g/cm<sup>3</sup> the detonation velocity of TNB is 7.3 km/s.<sup>[19]</sup> Unfortunately, the melting point of TNB is 122 °C and is thus too high to prepare standalone melt cast explosive compositions based on this temperature.

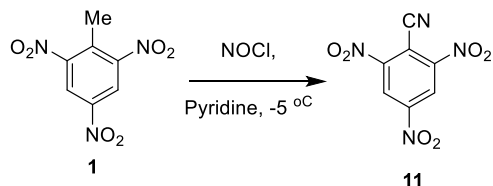


**Scheme 3.** Synthesis of 1,3,5-trinitrobenzene from TNT.

### 2.2. Cyano-2,4,6-trinitrobenzene

While cyano-2,4,6-trinitrobenzene (trinitrobenzotrile, **11**) can be prepared using many methods, one of the earliest methods involved the use of TNT<sup>[38]</sup>, as summarized in Scheme 4. The compound melts at 134 °C<sup>[39]</sup>, although it has not been regarded

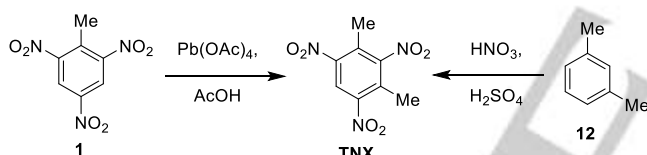
as an explosive, despite it being characterized by a more favorable oxygen balance than TNT. This is presumably due to the nitrile functionality of trinitrobenzotrile being susceptible to hydrolysis.



Scheme 4. Synthesis of trinitrobenzotrile.

### 2.3. 1,3-dimethyl-2,4,6-trinitrobenzene

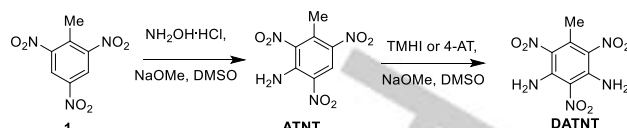
Symmetrical trinitroxylenes (TNX) were first obtained in 1868<sup>[40]</sup>, though at the time, its explosive properties were not recognized. Fieser et al. demonstrated that TNX can be prepared through the direct methylation of TNT (Scheme 5).<sup>[41]</sup> As the petroleum industry developed, the compound became available, and its synthesis was carried out through direct nitration of *m*-xylene (12). The presence of two methyl groups on the benzene ring allows the nitration of xylene to be achieved under milder conditions compared to toluene. Although TNX was once used as a replacement for TNT in shells and bombs with a larger mass, it unfortunately has a higher toxicity to living organisms than TNT.<sup>[19]</sup> Though TNX has a slightly lower performance than TNT (VOD 6.6 km/s) it has a significantly higher melting point (182 °C).<sup>[19]</sup>



Scheme 5. Synthesis of TNX from TNT or *m*-xylene.

### 2.4. Amino-2,4,6-trinitrotoluenes

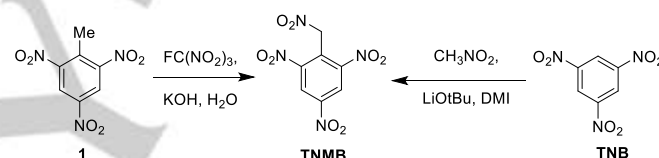
The possibility to introduce amino groups directly into aromatic rings appeared following the development of the vicarious nucleophilic substitution (VNS) reaction by Małosza and Winiarski.<sup>[42]</sup> Although amino-nitro compounds had already been synthesized before<sup>[43-45]</sup>, the direct use of TNT was not possible. As summarized in Scheme 6, through the use of hydroxylamine hydrochloride, it was possible to introduce one amino group to a TNT molecule in order to obtain 3-amino-2,4,6-trinitrotoluene (ATNT), which melts at 138 °C.<sup>[45]</sup> By using trimethyl hydrazinium iodide (TMHI) or 4-amino-1,2,4-triazole (4-AT or ATA), a second amino group can be installed, thus obtaining 3,5-diamino-2,4,6-trinitrotoluene (DATNT), which melts at 223 °C.<sup>[46, 47]</sup> Presumably due to intramolecular hydrogen bonding, ATNT and DATNT have a lower sensitivity to mechanical stimuli than TNT.<sup>[48, 49]</sup>



Scheme 6. Amination of TNT by using vicarious nucleophilic substitution (VNS).

### 2.5. 1,3,5-trinitro-2-(nitromethyl)benzene

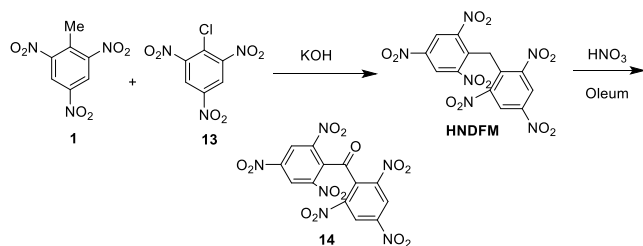
1,3,5-Trinitro-2-(nitromethyl)benzene (TNMB) was first described in 1964<sup>[50]</sup> as an impurity in TNT, although the first comprehensive research paper examining this compound was published in 1971.<sup>[51]</sup> The melting point of this compound is in the range 114–116 °C,<sup>[52-53]</sup> but the presence of an electron withdrawing substituent on the  $\alpha$ -carbon causes an increase in the reactivity of the methylene hydrogens in comparison to the TNT methyl group. TNMB may be obtained as a result of the reaction between 1,3,5-trinitrobenzene and nitromethane or by proton abstraction of TNT, followed by nitrate trapping the resulting anion with fluoro trinitromethane (Scheme 7).<sup>[54]</sup> The compound could be used in pure form as an ingredient in a variety of energetic compositions, such as in the electric match head. To date, there are no published detonation parameters for this compound.



Scheme 7. Synthesis of sym-trinitrobenzene.

### 2.6. 1,1'-Methylene bis-(2,4,6-trinitrobenzene)

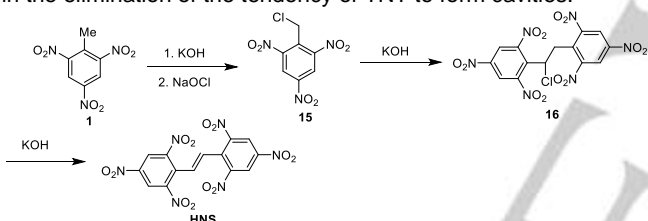
The synthesis path to 1,1'-methylene bis-(2,4,6-trinitrobenzene) (hexanitrodiphenylmethane, HNDFM) was patented and subsequently published by Shipp et al.<sup>[55-56]</sup>, as depicted in Scheme 8. Abstraction of the  $\alpha$ -hydrogen of TNT, followed by nucleophilic aromatic substitution with picryl chloride (13) affords HNDFM. The melting point of HNDFM is 232 °C,<sup>[55]</sup> but after treating it with active oxidizers, the compound can be transformed into hexanitrobenzophenone (14) with a melting point of 282 °C.<sup>[56]</sup> In spite of the potential, stability, and favorable oxygen balance of this compound, the available literature does not even specify its estimated detonation parameters.



Scheme 8. Synthesis of HNDFM and hexanitrobenzophenone

## 2.7. E-2,2',4,4',6,6'-hexanitrostilbene

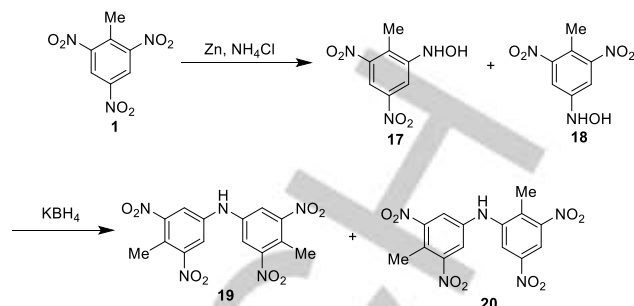
One of the most important explosives derived directly from TNT is (*E*)-2,2',4,4',6,6'-hexanitrostilbene (HNS). This compound was first prepared in 1964<sup>[57]</sup> and its synthesis is presented in Scheme 9. Hydrogen abstraction of TNT, followed by chlorinated affords **15**, which then undergoes self-nucleophilic addition upon exposure to base to yield **16**. Further treatment with base affords HNS. HNS melts with decomposition at 316 °C and has similar detonation parameters to TNT, albeit with a higher sensitivity to mechanical stimuli (see Table 1). The detonation velocity and pressure at a density of 1.69 g/cm<sup>3</sup> are 7.08 km/s and 20.5 GPa, respectively.<sup>[58]</sup> Due to its relatively high melting point, HNS can be considered as a thermally stable explosive in certain modes of application (heat-resistant detonators, shape charges in the oil industry). It has been demonstrated that when a small amount of HNS (0.5-1.0 %) is added to melted TNT, this results in the elimination of the tendency of TNT to form cavities.<sup>[59]</sup>



Scheme 9. Synthesis of HNS from TNT.

## 2.8. Nitro-methyl-diphenylamines

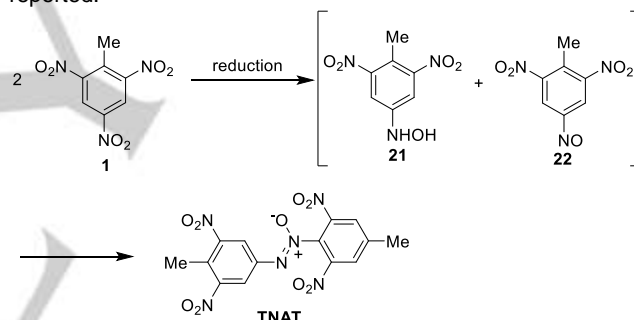
Symmetrical hexanitrodiphenylamine (hexyl) has been known since 1874,<sup>[60]</sup> although the synthesis of nitrodiphenylamines through reduction of TNT was only described for the first time in 2008 (Scheme 10).<sup>[61]</sup> Since the authors of this study investigated the microbial activity in the presence of TNT, the determination of energetic parameters was not in their field of interest. While the identified compounds are undoubtedly explosives, the presence of an N-H proton suggests that this compound is very reactive and can form salts with weak or strong bases. Compounds with a similar structure to hexyl are known as corrosion catalysts, possessing properties that practically preclude the use of such explosives for military or civilian purposes. Title compounds can be used as a markers of TNT presence in the soil or in groundwater.



Scheme 10. Synthesis of nitro diphenylamines by reduction of TNT.

## 2.9. Tetranitro-2,2'-azoxytoluene

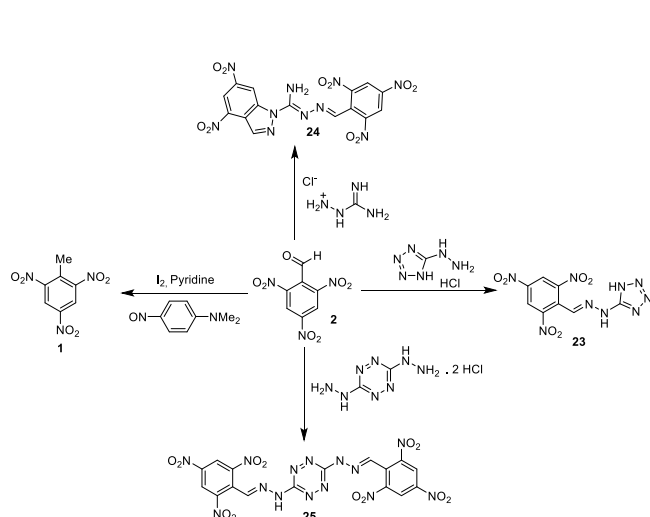
The synthesis of tetranitroazoxy toluene (TNAT) was described for the first time Brandt and Eisenmenger in 1913.<sup>[62]</sup> While there are many papers about the synthesis of compounds from this group, most of them concern the transformation of TNT in the natural environment and in the presence of enzymes or microorganisms.<sup>[63-65]</sup> The synthesis of TNAT from TNT is shown in Scheme 11. The melting point of TNAT is 266-268 °C.<sup>[66]</sup> Although TNAT has been known for over 100 years, the detonation parameters for this compound have not been reported.



Scheme 11. Synthesis of TNAT.

## 2.10. Derivatives of 2,4,6-trinitrobenzylidene amine

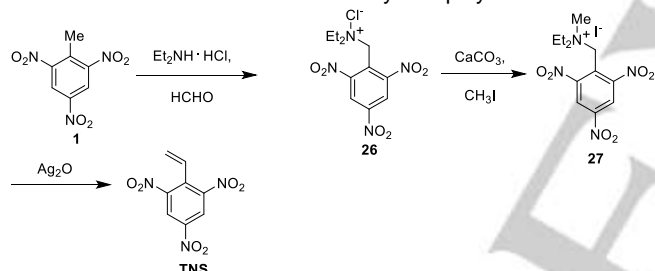
2,4,6-trinitrobenzaldehyde was prepared for the first time in 1901 by Sachs and Everding<sup>[67]</sup>, but it was found to be too reactive to be used in practice as an explosive. It was only in 2014 that it was first used for the synthesis of energetic compounds.<sup>[68]</sup> Wu et al. synthesized many energetic compounds with a high-nitrogen content in a reaction of the aforementioned aldehyde with amines. Most important ones include: 5-(2-(2,4,6-Trinitrobenzylidene)hydrazinyl)-1H-tetrazole (**23**) (m.p. = 184 °C); 4,6-dinitro-N-(2,4,6-trinitrobenzylidene)-1H-indazole-1-carbohydrazonamide (**24**) (m.p. = 189 °C); and 3,6-bis-(2-(2,4,6-trinitrobenzylidene)hydrazinyl)-1,2,4,5-tetrazine (**25**) (m.p. = 229 °C) (Scheme 12). The detonation velocities calculated by the authors are 8.2; 7.8 and 8.2 km/s, respectively. The friction sensitivity for the aforementioned compounds varies within a range of 288-360N, so typical analytical operations with those compounds are safe.



**Scheme 12.** Synthesis of chosen compounds obtained in reaction 2,4,6-trinitrobenzaldehyde with amino functionalities.

### 2.11. 2,4,6-trinitrostyrene

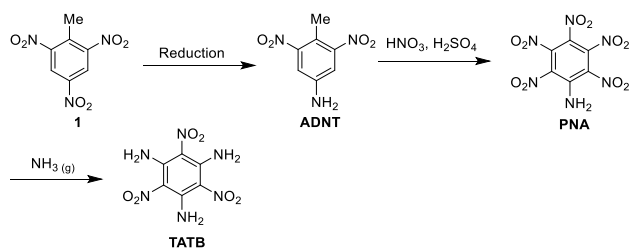
2,4,6-trinitrostyrene (TNS)<sup>[69]</sup> may be an attractive substrate for synthesis of energetic polymers and copolymers.<sup>[70]</sup> TNS can be prepared directly from TNT in three steps (Scheme 13), and is formed via a Hoffmann elimination. Pure TNS (m.p. 64–65 °C) is relatively reactive, but attempts to polymerize it were unsuccessful because TNS inhibits styrene polymerizations.



**Scheme 13.** Synthesis of TNS.

### 2.12. 1,3,5-triamino-2,4,6-trinitrobenzene

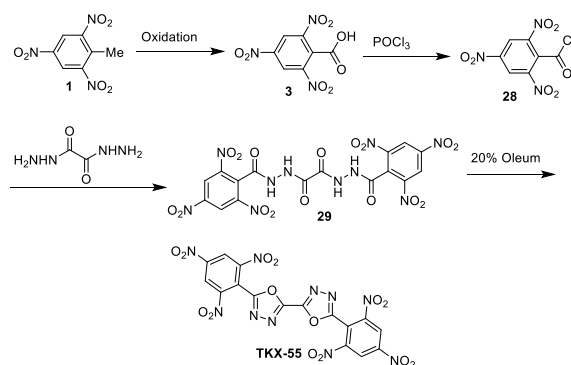
1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is a commonly accepted standard for explosives with reduced sensitivity for mechanical stimuli. There are many methods for synthesis of TATB, but a common method starts from TNT (Scheme 14). In the first step, the nitro group in the *para* position is reduced to the amino moiety (ADNT). Afterwards, nitration/oxidation of ADNT gives pentanitroaniline (PNA). Finally, selected nitro groups in PNA are substituted by amino groups by using gaseous ammonia.<sup>[71]</sup> TATB obtained by this method with quantitative yield reveals melting/decomposition temperatures of 375 °C. While pentanitroaniline is an explosive, it is too sensitive and reactive for practical use.



**Scheme 14.** Synthesis of TATB obtained from TNT.

### 2.13. 5,5'-Bis-(2,4,6-trinitrophenyl)-2,2'-bi-(1,3,4-oxadiazole)

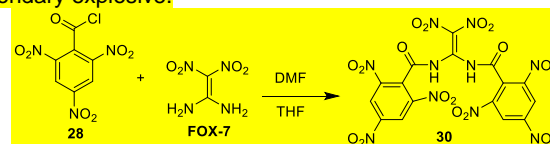
In 2016, as summarized in Scheme 15 Klapoetke and Witkowski published the new thermally stable compound synthesized from TNT which is formally dipicryl derivative of bi-(1,3,4-oxadiazole).<sup>[72]</sup> The authors call the new compound with acronym TKX-55. It is synthesized in a 4-step process from TNT. The compound is classified by the authors as thermally stable (decomposition 335 °C) high-explosive. Calculated detonation velocity and pressure (for density 1.837 g/cm<sup>3</sup>) are 8030 m/s and 27.3 GPa respectively. The impact and friction sensitivity of TKX-55 is >360 N and 5 J, respectively. Since this is a relatively new molecule, its full potential applications as a thermally stable material are not yet known.



**Scheme 15.** Synthesis TKX-55 from TNT.

### 2.14. 1,1-Dinitro-2,2-di-(2,4,6-trinitrobenzoyl amino)ethylene

Another compound synthesized by using **28** is 1,1-Dinitro-2,2-di-(2,4,6-trinitrobenzoyl amino)ethylene (TNB-DADNE, **30**), which is derived from FOX-7 (Scheme 16). The compound decomposes exothermically without melting at 167 °C. Calculated detonation velocity and pressure are 7.434 km/s and 23.67 GPa respectively.<sup>[73]</sup> The compound can be classified as secondary explosive.

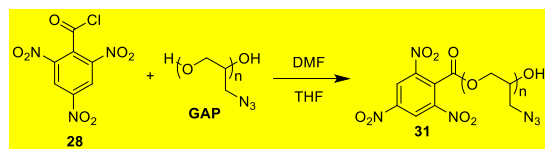


**Scheme 16.** Synthesis of TNB-DADNE.

### 2.15. Acyl terminated glycidyl azide polymer (TNB-GAP)

Trinitrobenzoyl chloride was used for functionalization of glycidyl azide polymer (GAP) and trinitrobenzoyl terminated GAP was

synthesized (TNB-GAP, **31**) (Scheme 17). The product has been proposed as a new energetic plasticizer for energetic and non-energetic polymers used in propellants. Glass transition temperature for the new polymer is  $-46\text{ }^{\circ}\text{C}$ , and the materials decomposes exothermically at  $251\text{ }^{\circ}\text{C}$ .<sup>[74]</sup>



**Scheme 17.** Synthesis of TNB-GAP.

### 3. Environmental fate of TNT and related compounds

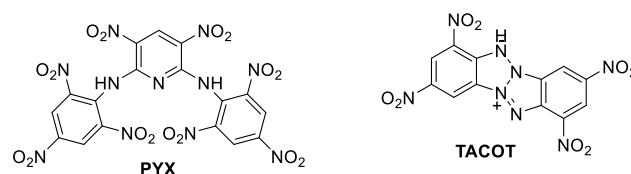
The use explosives for military and civilian purposes caused in intended and unintended contamination of environment. TNT is one of the most important high explosives from a military point of view. As such, this material was carefully investigated as a potential toxicant in ground and water environment. There are many papers and a books concerning the ecotoxicological aspects of explosives.<sup>[75]</sup> Toxicity of compounds for living organisms strongly depends on the water solubility and octanol/water partition coefficient. Lethal dose (LD) and lethal concentration (LC) of some metabolites of TNT are lower than for pure TNT. For example, the  $\text{LC}_{50}$  after 48 h of TNT for *Daphnia Magna* is equal  $1.27\text{ mg}\cdot\text{dm}^{-3}$ . However, the  $\text{LC}_{50}$  values of trinitrobenzotrile and dinitroanthranil (TNT metabolites) are 1.0 and  $0.34\text{ mg}\cdot\text{dm}^{-3}$  respectively. Acute oral toxicity ( $\text{LD}_{50}$ ) of TNT for rats is relatively high, equal to  $1010\text{ mg}\cdot\text{kg}^{-1}$  in males and  $820\text{ mg}\cdot\text{kg}^{-1}$  in females. TNT and aminonitrotoluenes are identified as genotoxic.<sup>[75]</sup>

### 4. Conclusion

Based on the literature review from 1771 to 2017, thirteen groups of compounds (or single compounds) are listed, which can be prepared using commercially available TNT. Among the listed groups, the following classes can be identified based on their applicability. Class 1: explosives already used (e.g. HNS). Class 2: compounds known for decades, but their use is limited due to their specific reactivity (e.g. 3,5-trinitro-2-(nitromethyl)benzene (C-H acidity) or 3,5-diamino-2,4,6-trinitrotoluene (there are other cheaper compounds with similar properties). Class 3: An analysis of the structure and properties suggests that these compounds should be explosive but there is no information about this in the available literature (e.g. tetranitro-2,2'-azoxytoluene).

Based on the analysis of the properties of the listed compounds (Table 2), it can be concluded that some of the classes or compounds will be developed dynamically. The well known compounds like TATB, PYX, TKX-55 and TACOT (Figure 1) were presented as reference compounds. For example in a reaction of trinitrobenzaldehyde with the appropriate amines, hundreds of high-nitrogen compounds can be prepared. The

reactivity of protons in the methyl group in 1,3,5-trinitro-2-(nitromethyl) benzene makes it possible to attach many energetic substituents to compounds. Due to the low price of commercial TNT, the compound is still keenly studied as a substrate for synthesis of energetic compounds as evidenced by numerous publications in the peer-reviewed literature.



**Figure 1.** Chemical structures of PYX and TACOT.

DATNT has good thermal stability ( $223\text{ }^{\circ}\text{C}$ ) and sensitivity for impact, thus exceeding TATB. The compound can be synthesized directly from TNT by a VNS reaction. Wide use of DATNT is limited by the low yield of the synthesis and the expensive purification procedure. The two new compounds, which combine the picryl methyl functionality with high-nitrogen functionality are very attractive. The high detonation parameters are accompanied by impact sensitivity exceeding TKX-55 and TACOT.<sup>[77]</sup> TNX is known over 100 years and is relatively cheap in synthesis and has better thermal stability but its detonation parameters are slightly worse.

**Table 2.** Physical and energetic properties of explosives synthesized from TNT.

Compound	Melting point, $^{\circ}\text{C}$	$\rho$ [g $\cdot\text{cm}^{-3}$ ]	$\Delta_f H^{\circ}$ [kJ $\cdot\text{mol}^{-1}$ ]	$V_{\text{det}}$ [ms $^{-1}$ ]	$P_{\text{cj}}$ [GPa]	ESD [J]	FS [N]	IS [J]
TNT, <b>1</b> <sup>[76]</sup>	80.6	1.65	-63.2	6900	21	0.25	>353	15
TNB <sup>[24]</sup>	122.5	1.76	-37.2	7300	22.3	na	>353	7.5
<b>11</b> <sup>[39]</sup>	134-135	na	na	na	na	na	na	na
ATNT <sup>[45]</sup>	138	na	na	na	na	na	na	na
DATNT <sup>[46, 47]</sup>	223	1.8	na	7800	25	na	>353	117
HNS <sup>[6, 76]</sup>	318	1.74	78.3	7100	24	7	240	5
TNX <sup>[6]</sup>	182	1.52	-102.7	6600	na	na	>353	10.5
TNAT <sup>[66]</sup>	266-268 $^{\circ}\text{C}$	na	na	na	na	na	na	na
<b>23</b> <sup>[68]</sup>	184	1.77	652.06	8200	28.4	0.77	>360	35
<b>24</b> <sup>[68]</sup>	189	1.68	525.42	7800	24.8	0.71	320	32
<b>25</b> <sup>[68]</sup>	229	1.79	989.52	8200	28.4	0.82	120	6
TNB-DADNE <sup>[73]</sup>	167	na	na	7434	23.67	na	na	na
TATB <sup>[6]</sup>	375	1.93	139.6	8000	27.8	12	>353	60
PYX <sup>[6]</sup>	360	1.76	43.7	7700	24.5	0.5	>353	10
TKX-55 <sup>[72]</sup>	335	1.76	197.6	8030	27.3	1	>360	5
TACOT <sup>[76]</sup>	378	1.85	536	7250	24.5	7	>353	28

[a]  $\rho$  = density; [b]  $\Delta_f H^{\circ}$  = standard enthalpy of formation; [c]  $V_{\text{det}}$  = detonation velocity; [d]  $P_{\text{cj}}$  = detonation pressure; [e] ESD = electrostatic discharge sensitivity; [f] FS = friction sensitivity; [g] IS = impact sensitivity

The rapid and intensive development of organic synthesis observed over the decades means that in the near future many new compounds will certainly be synthesized from TNT or from its derivatives. The current overwhelming interest in high-nitrogen compounds is, and will be the reason behind other studies on the synthesis of heterocyclic compounds based on the TNT molecule skeleton.

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**Keywords:** TNT • trinitrotoluene • energetic materials • synthesis • explosive

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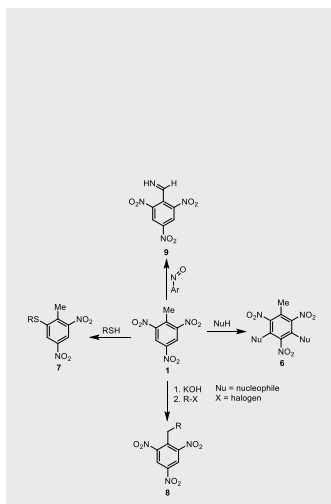


## Entry for the Table of Contents (Please choose one layout)

Layout 1:

## REVIEW

This review presents a history, properties, reactivity and environmental fate of 2,4,6-trinitrotoluene (TNT)

*M. Szala\*, Jesse J. Sabatini*

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2,4,6-Trinitrotoluene – A Useful Starting  
Compound In the Synthesis of Modern  
Energetic Compounds

Accepted Manuscript

Dr. Mateusz SZALA graduated from the Faculty of Chemistry at the Warsaw University of Technology (2004). He received his doctoral degree at the Faculty of New Technologies and Chemistry, Military University of Technology (2008) where he currently works as an assistant professor. He is co-author of 3 monographs, 2 patents, 44 papers in international scientific journals and 52 communications at domestic and international conferences. His research interests include: synthesis of high-nitrogen compounds and the combustion synthesis of carbon and ceramic materials.



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