Review / Przegląd
First published in Polish in 2015.

New energetic materials derived from common explosives. Review
2,4,6-Trinitrotoluen jako źródło nowoczesnych materiałów wybuchowych. Przegląd

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Abstract: *The review discusses the products of 2,4,6-trinitrotoluene reactions which have explosive properties or are potentially high-energy compounds. The following compounds are discussed: trinitrobenzene, cyanotrinitrobenzene, trinitroxylene, aminotrinitrotoluenes, trinitronitromethylbenzene, methylene bis(2,4,6-trinitrobenzene), hexanitrostilbene, nitromethyldiphenylamines, 4,4',6,6'-tetranitro-2,2'-azoxytoluene and 2,4,6-trinitrobenzylideneamine derivatives. The synthesis pathways are provided for all compounds and the detonation parameters are presented for selected compounds.*

Streszczenie: *Omówiono wybrane, mające właściwości wybuchowe lub będące potencjalnie związkami energetycznymi, produkty reakcji w których 2,4,6-trinitrotoluen jest substratem. Opisano między innymi: trinitrobenzen, cyjanotrinitrobenzen, trinitroksylen, amino-trinitrotolueny, trinitro-nitrometylo-benzen, metylenobis(2,4,6-trinitrobenzen), heksanitrostilben, nitro-metylo-difenyloaminy, 4,4',6,6'-tetranitro-2,2'-azoksytoluen oraz pochodne 2,4,6-trinitrobenzylidenoaminy. Dla każdego opisanego związku przedstawiono ścieżkę syntezy oraz dla wybranych materiałów podano parametry detonacyjne.*

Keywords: *2,4,6-trinitrotoluene (TNT), synthesis, cyanotrinitrobenzene, trinitro-nitromethyl-benzene, nitro-methyl-diphenylamine, ATNT, BTNHT, DATNT, DNTN, HNDFM, HNS, TNAT, TNB, TNBHT, TNX*
Słowa kluczowe: *2,4,6-trinitrotoluen (TNT), synteza, cyjano-2,4,6-trinitrobenzen, 1,3,5-trinitro-2-(nitrometylo) benzen, nitro-metylo-difenyloamina, ATNT, BTNHT, DATNT, DNTN, HNDFM, HNS, TNAT, TNB, TNBHT, TNX*

1. Introduction

2,4,6-Trinitrotoluene (TNT) was first developed in 1863 [1]. However, due to its low sensitivity to mechanical stimuli and relatively high critical detonation diameter, the explosive properties of the material were not immediately noticed. We can safely assume that TNT has been used in munitions since 1900 [2, 3], however, during the First World War, 2,4,6-trinitrophenol (picric acid) was the most commonly used secondary explosive. Even though 2,4,6-trinitrophenol was discovered over 100 years before TNT [4], due to its unsatisfactory properties [3], its bulk use ended with the end of the First World War. Currently, many different explosives

Table 1. Properties of selected explosives

Substance			Melting point and/or decomposition temperature [°C]	Detonation velocity [km/s] (density [g/cm³])	Sensitivity to	
Molecular formula (nitrogen content [%])	Name	Abbreviation [CAS No.]			impact [N·m]	friction [N]
$C_2H_2N_4O_3$ (43.1)	3-Nitro-1,2,4-triazol-5-on	NTO [932-64-9]	266.0 [5] 267-269 [6] 269 [7] 270 [8, 9] 270 (decomposition 270-273) [10] 274.8 [5] Decomposition: ~270 [11]	7.992 (1.84) [12] 8.4 (1.91) [11] 8.510ᵃ⁾ (1.93ᵇ⁾) [7, 12] 8.558ᵃ⁾ (1.930ᵇ⁾) [13] 8.564 (1.93) [9]	>40 [14] 51 [7]	252 [15] >353 [9, 11]
$C_2H_4N_4O_4$ 37.8	1,1-Diamino-2,2-dinitroethylene	FOX-7, DADNE [145250-81-3]	Decomposition: 215 [16, 17] Decomposition: 226 [18] Decomposition: >240 [13] Decomposition: 254 [9, 19]	8.870 (1.88-1.885) [16, 17] 9.044ᵃ⁾ (1.885ᵇ⁾) [13] 9.090 (1.885) [9]	15-40 [13] 24 [7] >30 [17]	168-288 [18] 216 [13] >350 [16, 17] >360 [9]
$C_3H_4N_4O_6$ (29.2)	1,3,3-Trinitroazetidine	TNAZ [97645-24-4]	99.0 [20] 99-101 [21] 101 [22-24] 103-104 [25] Decomposition: >240 [13]	9.006ᵃ⁾ (1.840ᵇ⁾) [13]	6 [13]	324 [13]
$C_3H_6N_6O_6$ (37.8)	1,3,5-Trinitro-1,3,5-triazacyclohexane	RDX, hexogen [121-82-4]	203 [26] 204 [7, 27-32] 205 [33] 205 (215 decomposition) [9, 10] 205-206 [34] Decomposition: 220 [17] Decomposition: 230 [13]	8.5 (1.81) [10] 8.600 (1.806) [9] 8.700 (1.80) [12] 8.75 (1.76) [30, 35] 8.780 (1.78) [7] 8.930 (1.82) [17] 8.977ᵃ⁾ (1.816ᵇ⁾) [13]	5.6 [39] 7 [17] 7.4 [13, 30] 7.5 [7, 35]	96 [15] 114 [10] 120 [17, 19, 30, 35, 39]
$C_4H_8N_8O_8$ (37.8)	1,3,5,7-Tetranitro-1,3,5,7-tetraza-cyclooctane	HMX, octogen [2691-41-0]	246 [7] 275 [27, 30] 276-286 (278 decomposition) [9] 276 [28] 278.5-280 [26, 36] 283 (decomposition ~280) [10] 285 [37] 286 [33] Decomposition: 287 [13, 38]	9.1 (1.9) [38] 9.1 (1.905-1.910) [13, 27] 9.120 (1.90) [7] 9.320ᵃ⁾ (1.910ᵇ⁾) [13]	6.4 [39] 7.4 [13] 7.5 [7, 38] 10.20 (α-) [40] 11.90 (ε-) [40]	95 [39] 120 [13, 38]
$C_6H_6N_6O_6$ (32.6)	1,3,5-Triamino-2,4,6-trinitrobenzene	TATB [3058-38-6]	321-326 [5] 330 [9] 347 (97% pure) [6] 350 (decomposition) [6, 7, 26, 27, 36, 41]	7.35 [27] 7.95 [40] 8.000 (1.94ᵇ⁾) [7] 8.108 (1.94) [9] 8.114ᵃ⁾ (1.937ᵇ⁾) [13]	50 [7, 13]	120.17 [40] 240 [15] 353 [13] >360 [9]
$C_6H_6N_{12}O_{12}$ (38.4)	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaiso-wurtzitane	CL-20, HNIW [135285-90-4]	220 (decomposition) [42] 228 (decomposition) [9] 240 (ε-) [15] 247 [42]	(α- 1.97, β- 1.99, γ- 1.92, ε- 2.04) [9] 9.580 [9] 10.000 (1) (2.02-2.04) [42]	2 [42]	78-110 [43] 80 [42]

a) calculated value; b) total maximum density (TMD)

are being tested and used with the most popular examples being given in Table 1. Table 2 shows the properties of asymmetrical trinitrotoluene isomers; Table 3 shows the properties of TNT and explosives discussed in the study. Even though modern secondary explosives are classified into a variety of chemical component groups, they all include carbon, hydrogen, nitrogen and oxygen. In recent years, new designs of explosives have shown a tendency to decrease the hydrogen content and increase the nitrogen content. A reduction in the amount of hydrogen increases the heat of explosion, whereas an increase in nitrogen content increases the standard enthalpy of formation as well as the amount of gaseous explosion products.

Despite a limited upper temperature range of application due to its low melting point (Table 3), susceptibility to photolytic decomposition [44] and susceptibility to numerous reactions in alkaline environment [45] and alternatives to it having been sought for over 115 years, TNT is one of the most commonly used secondary explosives. The main purpose of the research is the implementation of insensitive munitions (IM). The requirements for this type of munition has been discussed in [46]. It is partially due to the technological developments and hazards related to the properties listed in Table 1. TNT is much less sensitive to mechanical stimuli than other materials listed in Table 1: TNAZ, RDX, HMX and CL-20. The materials with lower sensitivity to impact and/ or friction (NTO and FOX-7), including a TNT structure (TATB) cannot compete with TNT in low-melting compositions, since they decompose during melting or melt at significantly higher temperatures and require much higher expenditure of energy. Since the melted explosive shows increased sensitivity to external stimuli compared to its solid form, a difference between the melting point (81 °C) and the decomposition temperature (min. 240 °C) of 160 °C for the TNT is its significant advantage. It provides a safety margin in the event of local overheating of the molten material.

A strong impulse for developing competitors to TNT is its significant impact on the environment and explosive hazard in its production. In Poland, the problem of effluents was resolved several decades ago *e.g.* [47] by obtaining the purest 2,4,6- isomer and is still the subject of research [48, 49]. As shown in Table 2, asymmetrical trinitrotoluene isomers, characterized by higher melting points, which also affects the TNT crystallization temperature, are treated as impurities in TNT designated for military use.

Table 2.   Melting point and/or decomposition temperature of asymmetrical trinitrotoluene isomers [°C]

Abbreviation [CAS]	Melting point and/or decomposition temperature [°C]	Source
2,3,4-TNT [602-29-9]	112	[50]
	Decomposition: starts at 282 Decomposition: 290-310	[26, 30] [50]
2,3,5-TNT [609-74-5]	97 97.2 97.5	[30] [50] [26]
	Decomposition: starts at 283 Decomposition: 333-337	[30] [50]
2,3,6-TNT [18292-97-2]	108 111	[30] [26, 50]
	Decomposition: starts at 280 Decomposition: 327-335	[30] [50]
2,4,5-TNT [610-25-3]	104	[26, 30, 50]
	Decomposition: starts at 262 Decomposition: 288-293	[30] [50]
3,4,5-TNT [603-15-6]	132 137.5	[30] [26, 50]
	Decomposition: starts at 288 Decomposition: 305-318	[30] [50]

The so called "red waters", *i.e.* TNT-contaminated effluents have also been studied abroad, *e.g.* [51-53]. New methods of disposing of asymmetrical trinitrotoluenes are also being developed. One of the latest methods is

the electrolytic reduction of nitro derivatives to amines. There is a need to develop new derivatives which show a lower sensitivity to external stimuli compared to TNT in order to reduce the explosion hazard in emergency situations, *e.g.*:

– 1917 – Great Britain [54],
– 1952 − Poland [55],
– 1996 – Japan [56],
– 1998 (as part of the composition) – USA [57].

Those hazards cannot be eliminated [58] in the TNT fabrication processes.

Initially, a pure TNT was used; currently, it is mainly a fusible component of compositions with reduced sensitivity to accidental activation, including materials with lower sensitivity compared to TNT, *e.g.* 3-nitro-1,2,4-triazol-5-on (NTO), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [59-62]. TNT is also a raw material for large-scale fabrication of non-explosive compounds. 1,3,5-trihydroxybenzene is used in the pharmaceutical and cosmetic industries [63, 64].

The unit price of mass-produced TNT (chemical plant "Nitro-Chem" S.A. in Bydgoszcz sells close to 6000 tonnes TNT annually [65]) is relatively low (*e.g.* in Poland it is *ca.* 5.5 USD/kg [66]). The retail price is low considering the concentrated acids used in the synthesis and a final stage process temperature exceeding 100 °C. The availability of this cheap and pure material means that it can be used as a feedstock for other explosives. Secondary explosives face stricter requirements for thermal resistance and low sensitivity to initiating stimuli. The synthesis of a new explosive with limited sensitivity, *e.g.* NTO or 4,4'-dinitro-3,3'-diazenofuroxan (DAAF) [67] requires the purchase or synthesis of precursors not previously used in the synthesis of explosives, generating additional costs from the start. Using TNT, easily available in special production plants, is an optimum solution which has been under discussion in Polish and international studies, for many years.

The study discusses a very small section of the extensive topic of TNT applications and modern (insensitive) TNT-based materials as components of insensitive low-melting point secondary explosive compositions. To show the extent of the wide variety of topics which need to be discussed to present a complete view of the applications of the materials under discussion, we should discuss the azotetrazole salts, studied not only regarding their performance [68] but also their microbiological activity in the soil [69]. Microbiological studies are carried out not only on the new explosives, but also on the well known hexogen, octogen, CL-20 or TNT [70, 71]. The issues omitted in this study include the evaluation of the effects of TNT alternatives on product properties, *e.g.* charge shrinkage after casting, vapour volatility [59], the ability to modify other components [72] or the ability to form low-melting eutectic systems [73, 74]. The review includes limited information on the compounds that can be obtained using 2,4,6-trinitrochlorobenzene (picryl chloride) (see section 3.6) even though those materials show some interesting properties, *e.g.* 2,2`,4,4`,6,6`-hexanitroazobenzene (HNAB) – see Table 3. A complete description of those compounds would require a separate review due to the quantity of literature data available. Studies on the synthesis of explosives in reactions between TNT and picryl chloride have been carried out in Poland for over 40 years [75].

The analysis showed that the research focus mostly on low-sensitivity TNT alternatives with different chemical compositions, however, the requirements for new components means that the optimum solution is to obtain the compounds in chemical reactions with TNT, *e.g.* those with chemical structure and selected processing properties similar to TNT, but with improved performance. The purpose of the study is to review the possible methods of obtaining new TNT-based explosives with desirable properties or at least without the evident disadvantages of TNT.

2. Reactivity of TNT

The reactivity of 2,4,6-trinitrotoluene is the focus of many theoretical and experimental studies [45, 76, 77] and will not be discussed in this study in detail, if the reaction product is not an explosive with potentially useful properties. The study will only briefly outline the synthesis pathways. The reactivity of TNT is a sum of possible reactions of the functional groups in the particle, *i.e.* methyl group, nitro groups at position 2, 4 and 6 and

hydrogen atoms at position 3 and 5. The reaction of each functional group yields components characterized by higher reactivity than pure TNT, *e.g.* see Sections 4.1 and 4.2. There is no doubt that the identified compounds show explosive properties, but the presence of a mobile hydrogen atom at the nitrogen bridge allows one to assume that the compounds will show relatively high reactivity in forming salts and catalysing metal corrosion. This effect allowed the practical elimination of hexyl in military and civil applications. The authors of [78] tested the microbiological activity of the enzymes of the *Pseudomonas putida* strain in the presence of TNT, but did not cover the explosive parameters of the compounds.

3. Properties of TNT-based explosives

A precondition of using a TNT derivative as a partial or complete alternative is that the properties of the obtained product must be an improvement over those of pure TNT. To show, how the compounds discussed in this study and other explosives are an improvement over TNT, Table 3 lists their basic properties available in the literature.

3.1. Analysis of selected properties

Literature often includes studies on the development of some new, unique explosive. This is not always the case. However, this study is a review and does not intend to verify already available information. In this respect, presenting the differences in data included in Tables 1 and 3 aims to show that the data available in literature, for any new compound, must be taken with a pinch of salt. In other words, some time after publication, it often turns out that the results presented by a research laboratory have not been verified by other laboratories or that the results differ. On the other hand, in the area of new explosives, for a relatively long time from publishing the initial results, a number of studies on the same material is usually available – the more promising the material, the longer the period.

Various results can be expected for the sensitivity to mechanical stimuli, detonation velocity, density and temperature distribution. In those cases, the results are also affected by factors which cannot be standardized on a global scale, including the presence and nature of impurities (solvent occlusion), particle size distribution and morphology of crystals or specific measuring instrument considerations. Common sales gimmicks can also be expected, as was the case with the information provided on the EURENCO website [42] that the company offers CL-20 with a detonation velocity of 10000 m/s. This is not the case with the melting point which is a strictly defined physical property of a chemical compound. Reducing the melting point has a specific physical purpose, *e.g.* it shows contamination of the sample, and may indicate that we are dealing with a completely different compound. The differences in the melting point of less than 10 °C, specified in Tables 1 and 2:

– NTO: 266-275 °C, *i.e.* 9 °C,
– HNS: 312(decomposition)-319 °C, *i.e.* 7 °C,
– TNAZ: 99-104 °C, *i.e.* 5 °C,
– RDX: 203-206 °C, *i.e.* 3 °C,

may be deemed acceptable due to the random factors specified above. The higher differences shown in Table 1:

– HMX: 246-286 °C, *i.e.* 40 °C.
– TATB: 321-350 °C, *i.e.* 29 °C,
– CL-20: 220(decomposition)-247 °C, *i.e.* 27 °C,

indicate that the evaluation of the results of the properties of new explosives should be looked at with caution, particularly if the amount of data is limited. In other words, the evaluation of the usability of a new explosive must include the analysis of several other properties. The need for a comprehensive evaluation of the properties can be illustrated by the literature data available for HMX and RDX (Table 4).

Table 3. Properties of TNT and TNT-based compounds

Molecular formula (nitrogen content [%])	Substance		Melting point and/or decomposition temperature [°C]	Detonation velocity [km/s] (density [g/cm³])	Sensitivity to	
	Name	Abbreviation [CAS No.]			impact [N·m]	friction [N]
$C_6H_3N_3O_6$ (32.6)	1,3,5-Trinitrobenzene	1,3,5-TNB; TNB [99-35-4]	122 [33] 122.5 [79] 122.5-125.5 [34] 123.1 [20]	7.3 (1.60) [80]	7.5 [9]	>360 [9]
$C_7H_5N_3O_6$ (18.8)	2,4,6-Trinitrotoluene	TNT [118-96-7]	80 [7] 80.1 [20] 80.6 [30] 80.75 [33] Decomposition: 240 [50] Decomposition: 300 [13]	6.6 (1.59) [81] 6.7±0.2 (1.60) [82] 6.870 [19] 6.881a) (1.654b) [13] 6.900 (1.60) [7] 6.9 (1.65) [72]	15 [7, 13]	353 [13]
$C_7H_2N_4O_6$ (23.5)	Cyano-2,4,6-trinitrobenzene	PiCN [37841-25-1]	134 [83] 134-135 [84]	–	–	–
$C_7H_6N_4O_6$ (23.4)	3-Amine-2,4,6-trinitrotoluene	ATNT	138 [85]	–	–	–
$C_7H_4N_4O_8$ (20.6)	1,3,5-Trinitro-2-(nitromethyl)benzene	–	114-116 [86, 87]	–	–	–
$C_7H_7N_5O_6$ (27.2)	3,5-Diamine-2,4,6-trinitrotoluene	DATNT	223 [88, 89]	–	–	–
$C_8H_7N_3O_6$ (17.4)	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX [632-92-8]	181.3 [20] 182 [80]	6.6 [80] 6.71 [40]	10.46 [40]	–
$C_8H_5N_9O_6$ (39.0)	5-(2-(2,4,6-Trinitrobenzylidene)hydrazinyl)-1H-tetrazole	TNBHT	189 [80]	7.8a) [80]	–	–
$C_{14}H_{10}N_6O_9$ (25.1)	Azo- and Azooxydinitrotoluene: 2,2',6,6'-Tetranitro-2,2'-azoxytoluene	TNAT –	– 266-268 [91]	– –	–	–
	4,4',6,6'-Tetranitro-2,2'-azoxytoluene	–	179-180 [91]	–	–	–
$C_{12}H_4N_8O_{12}$ (24.8)	2,2',4,4',6,6'-Hexanitroazobenzene	HNAB	220 [92]	7.25 (1.77) [92]	–	–
$C_{13}H_6N_6O_{12}$ (19.2)	1,1'-Methylene bis(2,4,6-trinitrobenzene)	HNDFM	232 [93]	–	–	–
$C_{13}H_4N_6O_{13}$ (18.6)	symmetrical Hexanitrobenzophenone	–	282 [94]	–	–	–
$C_{14}H_6N_6O_{12}$ (18.7)	E-2,2',4,4',6,6'-Hexanitrostilbene	HNS [20062-22-0]	311.9 (breakdown) [20] 316, 318, 319 (breakdown) [37] 316-318 [95]	7.000 (1.70) [37] 7.000-7.100 (1.74) [95] 7.08 (1.69) [96] 7.241a) (1.745b) [13]	5 [95]	240 [95]
$C_{15}H_8N_{10}O_{10}$ (28.7)	4,6-Dinitro-N-(2,4,6-trinitrobenzylidene)-1H-indazole-1-carbohydrazonamide	DNTN	184 [80]	8.2a) [80]	–	–
$C_{16}H_8N_{14}O_{12}$ (33.3)	3,6-bis(2-(2,4,6-Trinitrobenzylidene)hydrazinyl)-1,2,4,5-tetrazine	BTNHT	229 [80]	8.2a) [80]	–	–

a) calculated value; b) total maximum density (TMD)

Table 4. Melting point of octogen/hexogen composition [97]

Hexogen content in octogen [%]	Melting temperature range [°C]
0	279.5-280
20	264-270
30	222.5-260.5
40	188.5-239.5
60	187.5-198.5
70	187-193.5
80	189-196.5
90	188.5-198.5
96	196-203
99	200.8-204
100	203.3-205

The results for the HMX melting point should be correlated with its RDX content, since *e.g.* a 30% RDX content in a HMX sample may decrease the melting point by 20-58 °C compared to pure HMX. By analogy, the HMX content in a RDX sample should be correlated with the melting point of the RDX sample. A 4% HMX content decreases the RDX sample melting point by 2-9 °C (Table 4).

4. Synthesis of explosive TNT as raw material derivatives

4.1. Syntheses based on oxidation reactions

The oxidation reactions of each functional group yields components characterized by higher reactivity than pure TNT, *e.g.* 2,4,6-trinitrobenzaldehyde (oxidation) Figure 1 (Routes 1a and 1b). Multiple compounds can be used, *e.g.* to oxidize and decarboxylate trinitrobenzoic acid, *e.g.* ozone [98], KOH [99], NaOH [100], H_2SO_4 [101], and $NaClO_3$ [102].
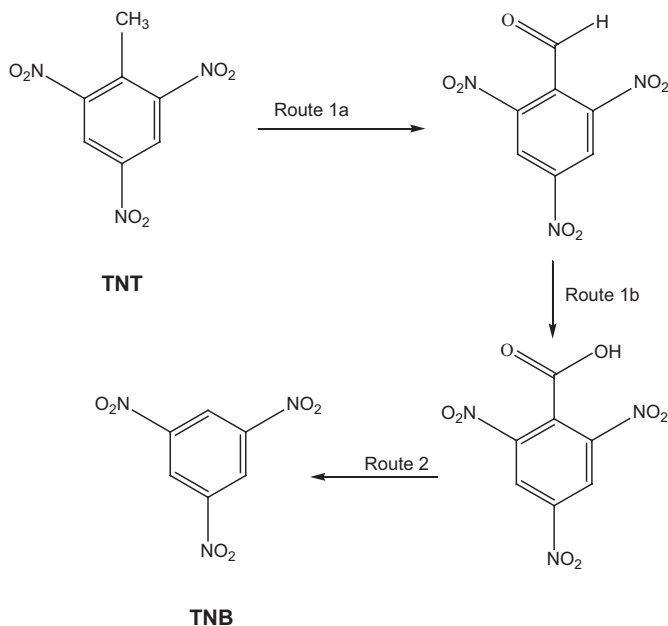
Figure 1. The diagram of the main TNT oxidation pathway (Routes 1a and 1b) and synthesis of 1,3,5-trinitrobenzene from TNT (Route 2: ΔT)

Synthesis of **1,1'-methylene bis(2,4,6-trinitrobenzene)** (Fig. 2) has been presented by Shipp's team [93, 94] – the same team that synthesized hexanitrostilbene in 1964. Using active oxidizers, hexanitrodiphenylmethane (HNDFM) can be converted into symmetrical hexanitrobenzophenone which has a higher melting point (Table 3) and better oxygen balance. HNDFM synthesis is disclosed in a Polish patent application filed in 1981 [75]. Even though the compound may have some uses, its detonation parameters are not available in the literature. In Figure 2, Route 3 is an example of the oxidation reaction and Route 4 is an example of the electrophilic substitution.
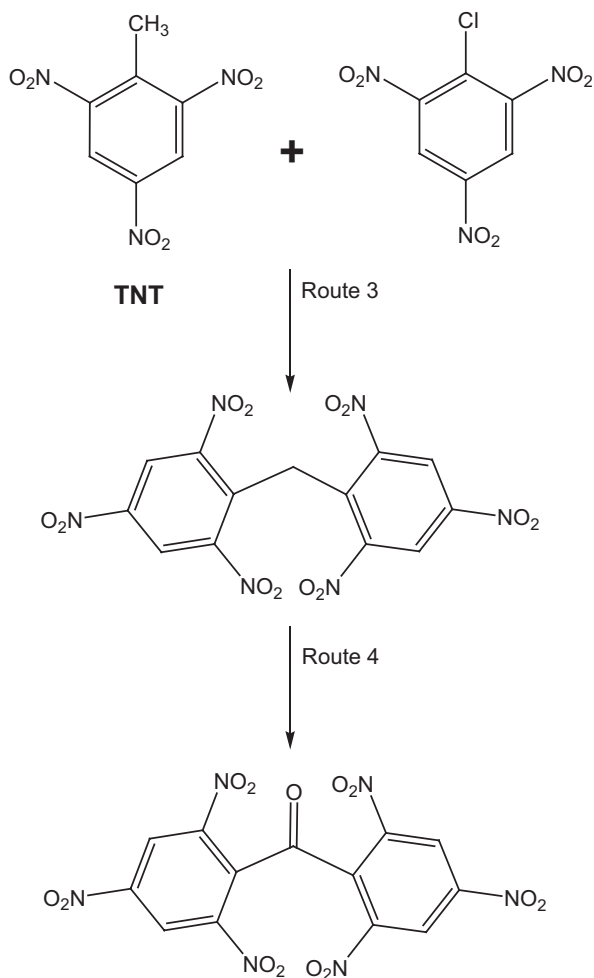
Figure 2. Synthesis of methylenebis(2,4,6-trinitrobenzene) (Route 3: KOH and R–OH) and hexanitrobenzophenone (Route 4: HNO₃ and oleum)

E-2,2',4,4',6,6'-Hexanitrostilbene (HNS) is one of the key explosives obtained directly from TNT. The compound was first synthesized in 1964 [103]; Figure 3 shows the synthesis route (Routes 5-9), where oxidation reactions are also employed. Hexanitrostilbene melts and decomposes, and shows lower sensitivity to mechanical stimuli than TNT, while maintaining similar detonation parameters (Table 3). The detonation pressure at 1.69 g/cm³ is 20.5 GPa [96]. The high melting point of HNS (Table 3) means that in certain applications it can be considered a thermoresistant explosive. Addition of 0.5-1.0% HNS to TNT or its functional form, reduces shrinkage and eliminates the number of voids in TNT castings [104].
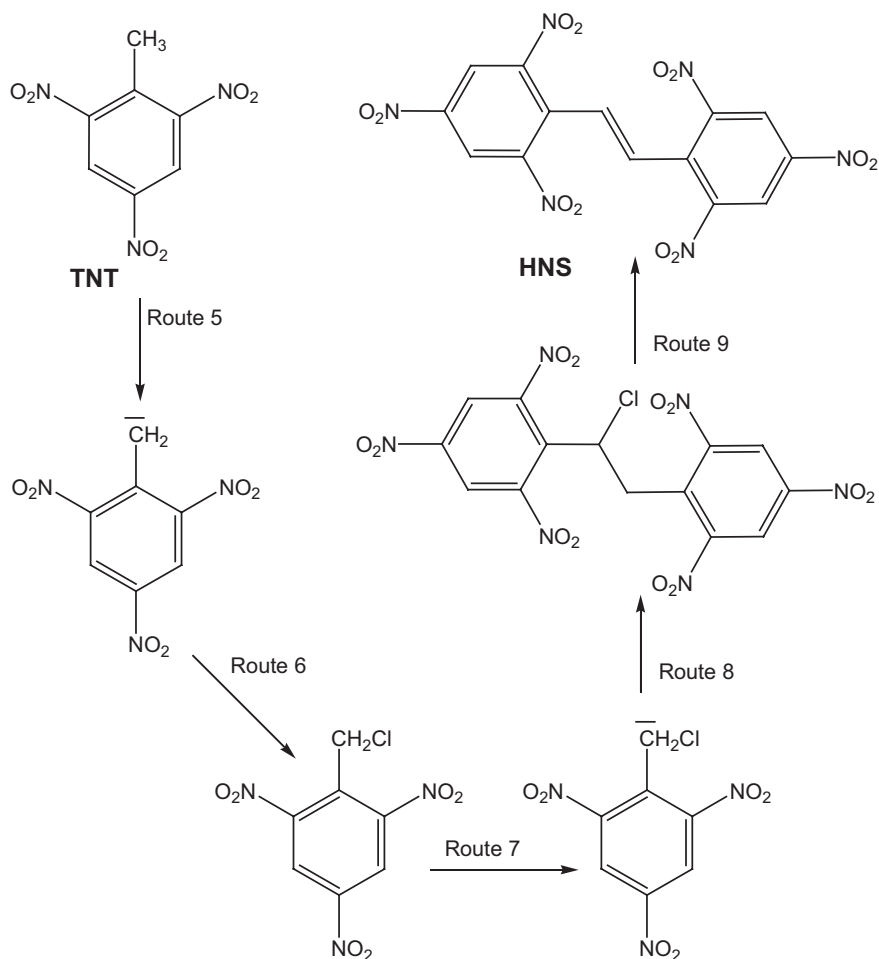
Figure 3. Hexanitrostilbene synthesis from TNT: Route 5: OH⁻, Route 6: NaOCl, Route 7: OH⁻, Route 8: Pi-CH₂Cl, Route 9: OH⁻ (– HCl)

The synthesis of azo- and **azoxydinitrotoluene (TNAT)** was first described in 1913 [105]. The synthesis of this group of compounds has been discussed in multiple studies, however, most of them involve TNT conversion in the environment, often with enzymes and microorganisms [106-108]. Figure 4 (Routes 10 and 11) show TNAT synthesis; the derivatives in which an azoxy bridge is formed by addition of nitrile groups in position 2-2 and 2-4 are also known. Table 3 shows the melting points of 2,2',6,6'-tetranitro-2,2'-azoxytoluene and 4,4',6,6'-tetranitro-2,2'-azoxytoluene. Even though the feedstock (TNT) and the reaction of azo- and azoxy compounds from nitroaromatic reactants has been known for over 100 years, not even their theoretical detonation parameters are available. Route 11 in Figure 4 is an example of the oxidation reaction, whereas Route 10 is an example of the reduction reaction.
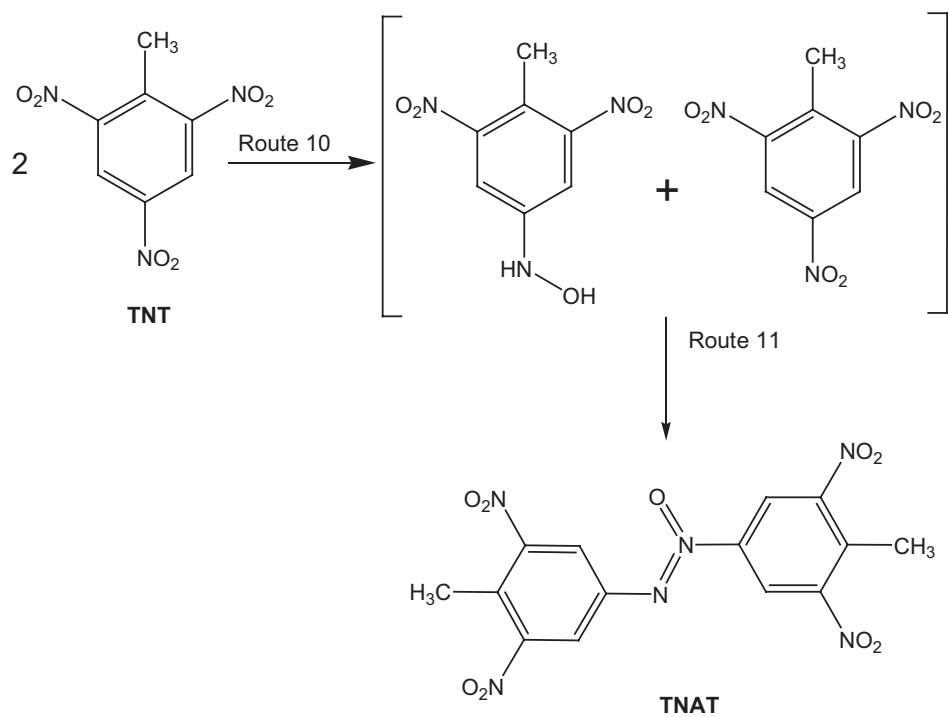
Figure 4. Synthesis of azoxydinitrotoluene

2,4,6-Trinitrobenzoic aldehyde was first obtained in 1901 [109], however, it was used in the synthesis of high-energy materials for the first time in 2014 [90]. Route 12 (Fig. 5) is an oxidation reaction. In the next steps (Routes 13-15) there was obtained a series of high-energy compounds, *e.g.* derivatives of 2,4,6-trinitrobenzylidene amine, based on condensation reactions (see Section 4.5).
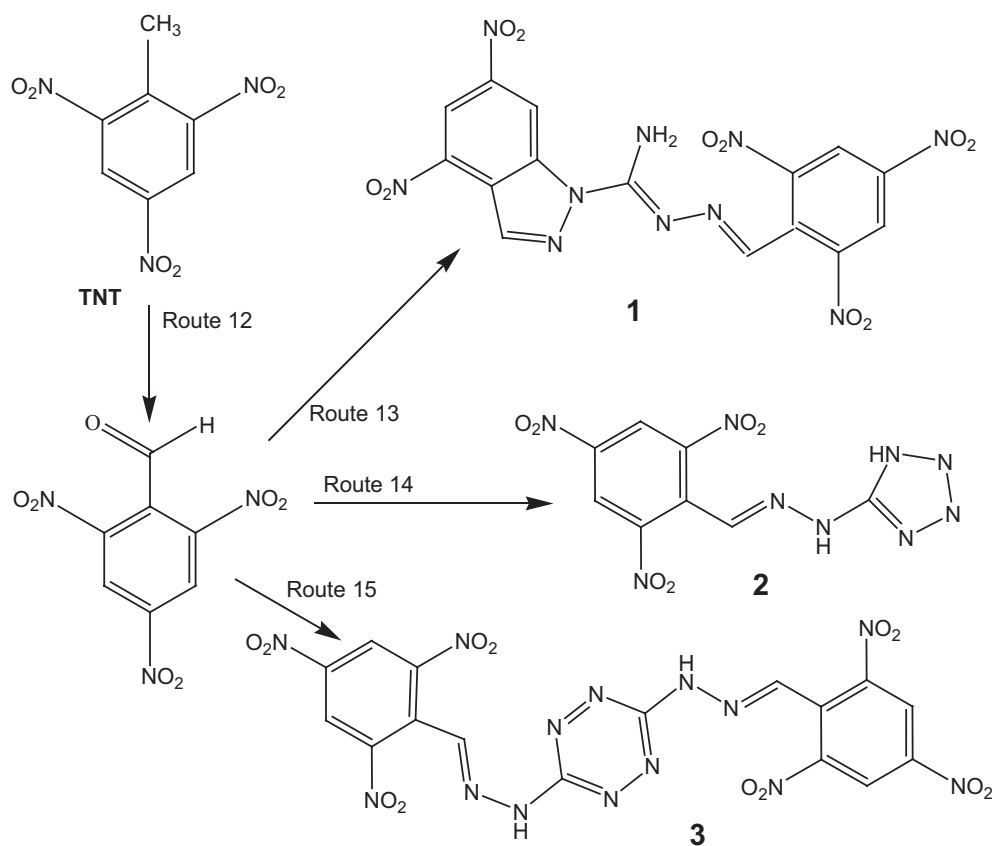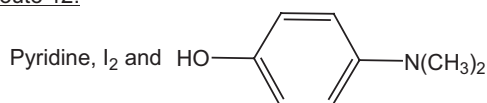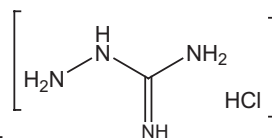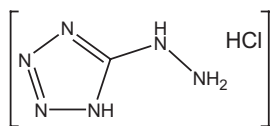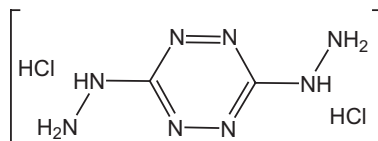
Figure 5. Synthesis of selected compounds obtained by condensation of 2,4,6-trinitrobenzaldehyde with amines (see Section 4.5)

4.2. Syntheses based on reduction reactions

The reduction reactions of each functional group yields components characterized by higher reactivity than pure TNT, *e.g.* aminodinitrotoluene (reduction) – Figure 6 (Routes 16a and 16b). Even though symmetrical hexanitrodiphenylamine (hexyl) has been known since 1874 [110], the substituted nitrodiphenylamines obtained by the reduction of TNT were first described in 2008 [78] – Figure 6 (Routes 17-19). The first explosive derived from TNT was a symmetrical **trinitrobenzene (TNB)** described in 1883 [111]. Since then, multiple methods of

obtaining TNB from TNT have been published, all based on the oxidation of the methyl group to form a carboxyl group followed by thermal decarboxylation, as shown in Figure 1 (Route 2). Another method of obtaining TNB is by gradual benzene nitration, however, due to the extreme conditions required to introduce another nitro group and the low price of TNT, this pathway is practically not used. Trinitrobenzene shows slightly better detonation parameters than TNT (Table 3). The melting point of TNB (Table 3) is too high to melt-cast TNB-based charges.
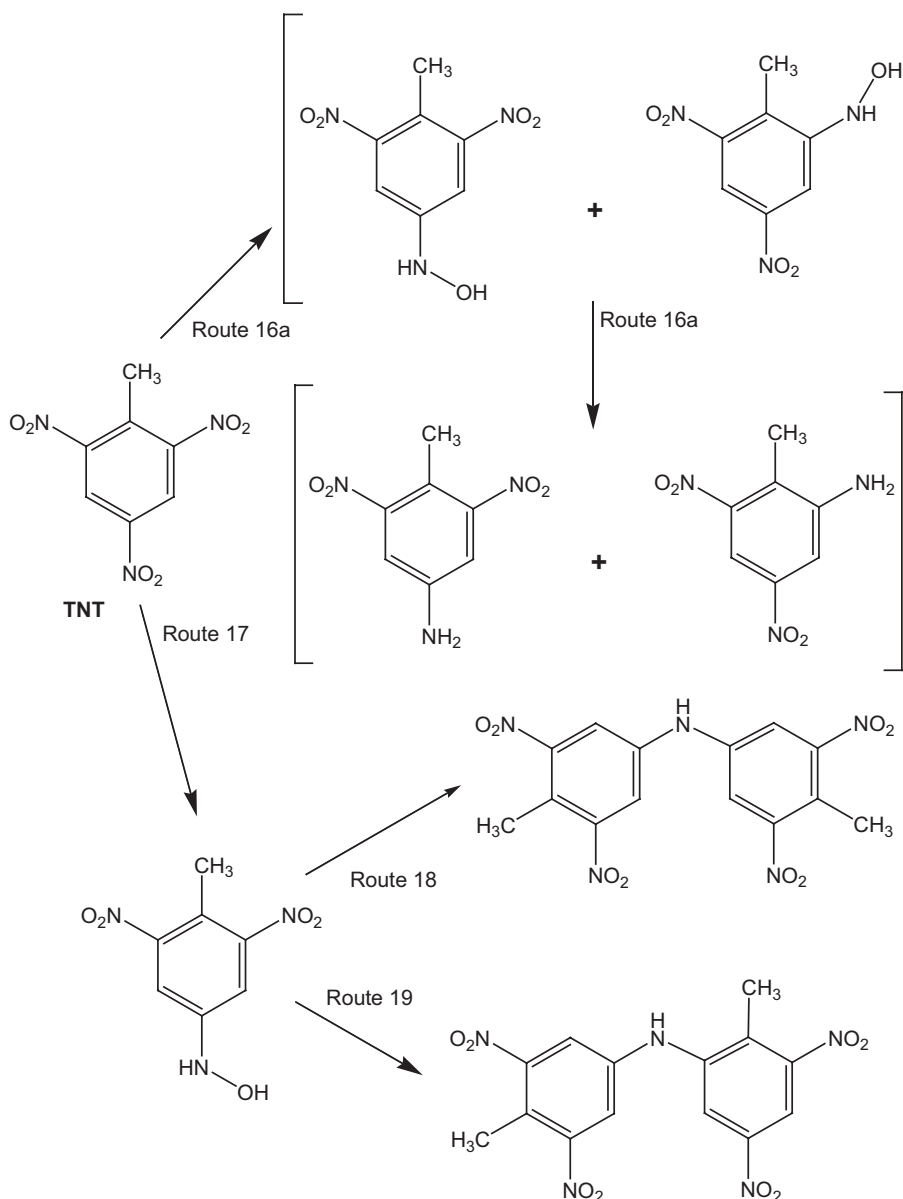

Figure 6. The diagram of the main TNT reduction pathway (Routes 16a and 16b; also Route 17: Zn and NH₄Cl) and synthesis of nitrodiphenylamine by TNT reduction (Routes 18 and 19: KBH₄)

4.3. Syntheses based on nucleophilic substitution reactions

The protons at position 3 and 5 in the ring may be substituted in vicarious nucleophilic substitution (VNS) conditions, Figure 7 [112]. Nitro group can be substituted with a sulfide group [113, 114]. Based on the Brønsted-Lowry theory, hydrogen atoms in the methyl group can also be substituted [115]. The methyl group can react with aromatic nitroso compounds forming imines [116].
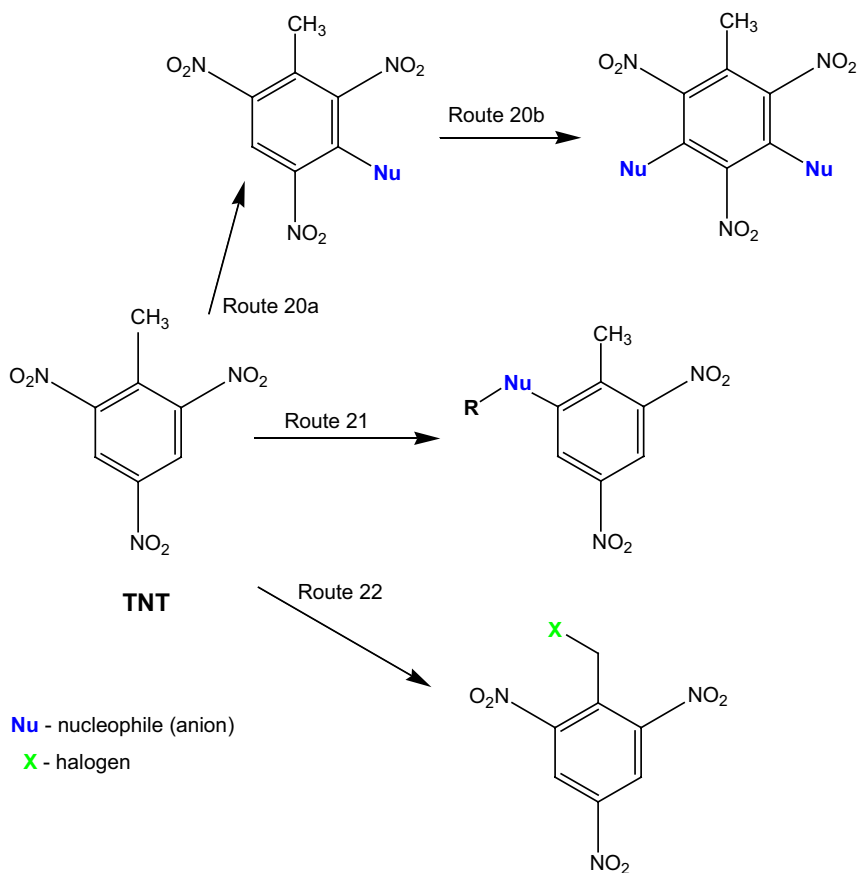

Figure 7. The diagram of the main TNT nucleophilic substitution pathways (Routes 20a and 20b: **Nu**−H; Route 21: **R**−**Nu**−H; Route 22: **Nu**−**X**)

Cyano-2,4,6-trinitrobenzene (2,4,6-trinitrobenzonitrile) can be obtained using many methods, however, one of the first being from TNT [84] – Figure 8 (Route 23). This compound has not been used as an explosive, even though its oxygen balance is better than that of TNT. One of the reasons is the hydrolytic susceptibility of the nitryl group in trinitrobenzonitrile.

The ability to directly introduce amine groups to nitroaromatic compounds occurred with the development of the reaction of vicarious nucleophilic substitution (VNS) by Mąkosza and Winiarski [117]. **Amino-nitrotoluenes** were obtained previously [85, 118, 119] without using TNT directly. Using hydroxylamine hydrochloride, a single amine group can be introduced to TNT forming 3-amino-2,4,6-trinitrotoluene (ATNT) [85]. Using trimethyl hydrazinium iodide or 4-amino-1,2,4-triazole, ATNT or directly TNT, can be used to obtain 3,5-diamino-2,4,6-trinitrotoluene (DATNT) (Fig. 8, Routes 24a and 24b) [88, 89]. ATNT and DATNT are characterized by lower sensitivity to impact than TNT [120, 121], the melting points of both substances being specified in Table 3.
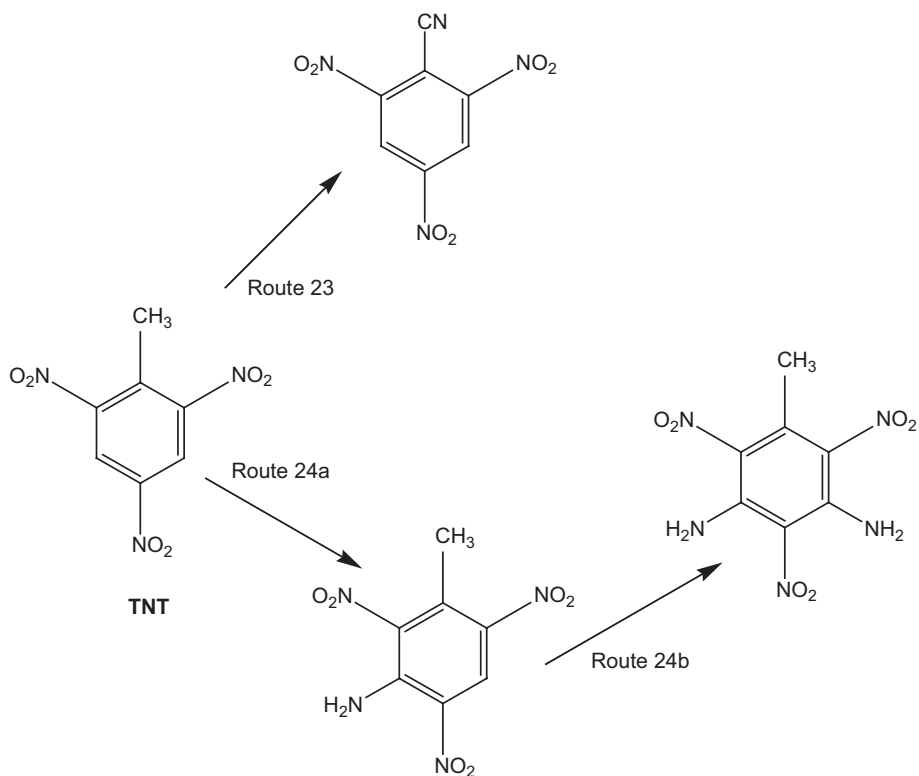
Figure 8. Synthesis of 2,4,6-trinitrobenzonitrile (Route 23: NOCl, pyridine, −5 °C) and TNT amination diagram in vicarious nucleophilic substitution (VNS) conditions (Routes 24a: NH2OH, HCl, R−ONa, DMSO and 24b: TMHI or 4AT, R−ONa, DMSO)

4.4. Syntheses based on electrophilic substitution reactions

1,3-dimethyl-2,4,6-trinitrobenzene (trinitroxylene, TNX) was first synthesized in 1868 [122], however, its explosive properties were not noticed. TNX could be obtained by the methylation of TNT [123] – Figure 9 (Route 25). With the development of the oil industry, this compound was being obtained by the direct nitration of xylene – Figure 9 (Route 26). The presence of two methyl groups in the ring allows the xylene nitration process to proceed under milder conditions compared to toluene. Trinitroxylene is characterized by lower toxicity to living organisms than TNT [80]. For a long time, it was used as an alternative to TNT in large volume charges. It features lower detonation parameters and a higher melting point than TNT (Table 3).

1,3,5-Trinitro-2-(nitrometylo)benzene was first described in 1964 [124] as a contaminant in TNT, and the first study of this compound was published in 1971 [125]. No results of detonation parameter tests for this compound have been published. However, it can be used in the form of a pure salt as a component of a composition, *e.g.* in ignition heads. The compound has a relatively low melting point (Table 3), but the presence of an acceptor substituent at the methyl carbon group results in an increased reactivity of the methylene hydrogen atoms compared to TNT. Trinitro-nitrometylo-benzene may be obtained from a reaction between trinitrobenzene and nitromethane or TNT's reaction with trinitrofluromethane [126] (Fig. 9, Routes 27 and 28).
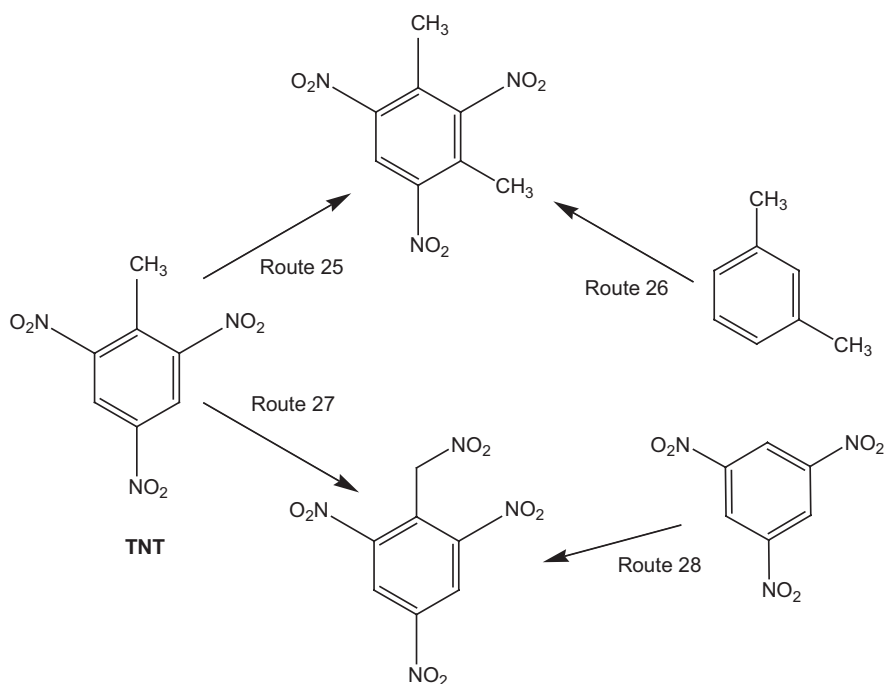
Figure 9. Synthesis of trinitroxylene from TNT (Route 25: Pb(OCOCH$_3$)$_4$, CH$_3$COOH) or *m*-xylene (Route 26: HNO$_3$ and H$_2$SO$_4$) and synthesis of 1,3,5-trinitro-2-(nitromethylo)benzene (Routes 27: FC(NO$_2$)$_3$ and KOH/H$_2$O, and 28: CH$_3$NO$_2$, *t*-Bu–O–LI, DMI)

Another example of electrophilic substitution is Route 3 in Figure 2,

4.5. Syntheses based on condensation reactions

Routes 13-15, presented in (see Section 4.1, in Fig. 5) are based on condensation reactions. They allow to obtained a series of high-energy compounds (*e.g.* **derivatives of 2,4,6-trinitrobenzylidene amine)** with high nitrogen content, including:

– 4,6-dinitro-N-(2,4,6-trinitrobenzylidene)-1*H*-indazole-1-carbohydrazonamide (DNTN),
– 5-(2-(2,4,6-trinitrobenzylidene)hydrazinyl)-1*H*-tetrazole (TNBHT), and
– 3,6-bis(2-(2,4,6-trinitrobenzylidene)hydrazinyl)-1,2,4,5-tetrazine (BTNHT),

The obtained compounds (Fig. 5, *1*, *2* and *3*, correspondingly) are physically and chemically stable solids with a melting point of 200 °C and a detonation velocity of 8 km/s (Table 3). The sensitivity of the compounds to friction varies between 288-360 N, which means that the compound may be safely handled during standard analytical operations.

5. Conclusions

The review of available literature identified 10 groups or chemical compounds which can be obtained using commercially available 2,4,6-trinitrotoluene as the substrate. Among the 10 groups of chemical compounds, the following classes can be identified by application:

–   Class 1. Currently used explosives, *e.g.* HNS.
–   Class 2. Compounds known for decades with limited usability, *e.g.* due to specific reactivity or lack of demand, *e.g.* 3,5-trinitro-2-(nitromethyl)benzene, 3,5-diamine-2,4,6-trinitrotoluene.

- Class 3. Compounds which should show explosive properties, but for which no literature data is available, *e.g.* 4,4',6,6'-tetranitro-2,2'-azoxytoluene.

An analysis of the properties of the reviewed compounds shows that some of the compound classes will develop dynamically. For example, the reaction of trinitrobenzoic aldehyde with amines may yield hundreds of compounds with high nitrogen content. The reactivity of methylene protons in 1,3,5-trinitro-2-(nitromethyl) benzene enables the attachment of many high-energy substituents to its methyl group. The low price of TNT makes it a widely researched feedstock for many high-energy compounds and a topic of numerous publications. The extensive development of organic chemistry seen over the last several decades, shows that in the nearest future, new compounds will be obtained directly or indirectly from TNT. The compounds with high nitrogen content are currently of particular interest and will be the topic of further research on obtaining heterocyclic compounds based on the TNT structure.

Acknowledgements

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