Review

A review of advanced high performance, insensitive and thermally stable energetic materials emerging for military and space applications

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Abstract

Energetic materials used extensively both for civil and military applications. There are continuous research programmes worldwide to develop new materials with higher performance and enhanced insensitivity to thermal or shock insults than the existing ones in order to meet the requirements of future military and space applications. This review concentrates on recent advances in syntheses, potential formulations and space applications of potential compounds with respect to safety, performance and stability.
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Keywords: Advanced energetic materials; Heterocycles; High explosives; Thermally stable explosives; Insensitive explosives; Space and military applications of propellants and explosives

1. Introduction

Energetic materials (explosives, propellants and pyrotechnics) are used extensively for Civil as well as Military Applications. Today the variety and number of high energy materials for various applications have become innumerable of which chemistry, synthesis, properties and other salient features are available in the literature. In the past, common explosives hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6-trinitrotoluene (TNT) were considered adequate for all weapon applications. Because of many catastrophic explosions resulting from unintentional initiation of munition by either impact or shock, aboard ships, aircraft carriers, and munition trains, these explosives have become less attractive. Of course, higher performance has always been a prime requirement in the field of research and development of explosives and the quest for the most powerful high explosives still continues and this search seems to be never ending. The demand from the user for increased performance with reduced or low vulnerability could not be met with existing materials, and the need to control costs ensured that the processes for producing compositions

were also subject to rapid change. Thus, in modern ordnance there are strong requirements for explosives having both good thermal stability, impact and shock insensitivity and better performance. However, these requirements are somewhat mutually exclusive. The explosives having good thermal stability and impact insensitivity usually exhibit poorer explosive performance and vice versa. Therefore, the foremost objective at the stage of synthesis of new explosives consists of finding the molecule having both a good energy capability and optimal safety (reduced vulnerability, shock and impact insensitivity) to those in current use.

This review concentrates on the principal themes that have been pursued over the last few decades to synthesize new energetic compounds which exhibit high thermal stability, insensitivity and performance. The review is structured into three broad sections in order to achieve its aim and each section is sub-divided into more specific sections.

2. High performance (high VOD) explosives

It has always been an aim of explosives technologies to achieve higher performance for warhead applications. The "effectiveness" of an explosive is dependent on many things. The energy of the decomposition reactions and the number of moles and molecular weight of the gaseous products are among the critical factors [1]. Density is also crucial. The

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more moles of an explosives that can be packed into the limited volume of a shell the better. Less obvious, but more important is the velocity of propagation wave through an explosive i.e. rate of energy release which is proportional to the density squared. On the other hand, an increase in oxygen balance (OB) and heat of formation generally increases the sensitivity of an explosive as well as performance as the specific impulse of a propellant is proportional to the square root of its heat of formation.

In view of this, a brief review of organic energetic compounds typically have higher performance is mentioned in this section.

2.1. Polycyclic cage and small-ring energetic molecules

Energetic materials of the strained ring and cage families may constitute a promising new class of explosives. Recently, it was also predicted that caged structures and bicyclic heterocycles would give the best combinations of stability, oxygen balance, high heat of formation and predicted performance cage polycyclic hydrocarbons exhibit substantially increased densities (rigid highly compact structures) over their acyclic analogues while the strain inherent in many systems results in large positive heats of formation. Foremost in this regard is cubane, crystal density $1.29 \, g/cm^3$. Lawrence Livermore National Laboratory (LLNL) used molecular modeling and explosive performance prediction in which the target molecules were designed, then synthesized Then their physical properties were measured.

Cubane is a kinetically stable compound (decomposition only above $200 \, ^\circ C$), but a thermodynamic power house ($\Delta H_f \sim 620 \, kJ/mol$) corresponds to a total strain energy of $694.5 \, kJ/mol$ [2]. Cubane has also been reported as a binder for propellants that are reported to have high specific impulse (Cubane/AP/Al and Cubane HAP/Al) [3]. While such hydrocarbons represent high density fuels [4]. Highly nitrated cubane is predicted to be a very dense, have high energy, and to be shock insensitive, with great potential for explosives and propellants [5]. Unfortunately, these molecules can not generally be prepared directly, e.g. by nitration of the parent hydrocarbons, because the cage structures do not survive the reaction conditions. Consequently, elaborate multi-step reaction sequences are often required [6].

One of the principal target molecules, particularly of US researchers, is octanitrocubane (ONC). Recently, Zhang et al. [7] made successfully heptanitrocubane and the long sought ONC in 45–50% isolated yield over the last 18 years of synthesis efforts continued on the molecule.


Octa nitrocubane
(ONC)

Hepta nitrocubane
(HpNC)

$$C_8(NO_2)_8 \longrightarrow 8CO_2 + 4N_2$$

Energy Release ~ 3475 KJ. mol
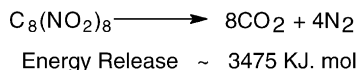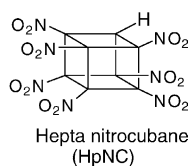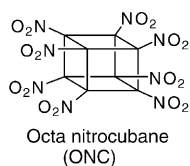
Both hepta- and octa-nitrocubane (HpNC and ONC) have decomposition temperatures well above $200 \, ^\circ C$. Samples were not detonated by hammer taps. HpNC is currently easier to make than ONC, an impressively high density ($2.028 \, g/cm^3$) was measured for HpNC. It may prove to be a more powerful explosive and/or monopropellant since it is more dense, has a calculated heat of formation only about 6% less than ONC. It will also produce some lighter gaseous products as it is not perfectly oxygen balanced [8,9].

The most recently published calculated value for heat of formation of solid ONC $[(CNO_2)_8]$ is $594 \, kJ/mol$, corresponding to $74 \, kJ/mol$ per (CNO_2) mole. The highest calculated ΔH_f of solid hexanitrobenzene $[(CNO_2)_6]$, one of the most energetic explosive known [10] is about $200 \, kJ/mol$ corresponding to $33 \, kJ/mol$ per (CNO_2)-molecule, less than half that of ONC [11]. The energy content of hexanitrobenzene is lowered by the stabilizing resonance energy of the aromatic systems. The energy content of octanitrocubane is increased by the strain energy of its unique carbon skeleton.

The X-ray crystal structures predicts a density of above $2.10 \, g/cm^3$ for the most stable polymorphs of ONC [12]. The significantly greater predicted density and detonation pressure indicate performance improvement >20% over HMX [13]. The most recent theoretical estimation of the detonation velocity for ONC is $9900 \, m/s$ [14]. The experimental value for hexanitrobenzene is $9500 \, m/s$ [10], for HMX, $9100 \, m/s$ and for CL-20, $9200 \, m/s$ [15].

Less nitrated cubanes such as tetranitrocubane (TNC) has recently been proved to be an extraordinary material as investigated by Eaton et al. [16]. It is a crystalline solid with high density ($1.814 \, g/cm^3$) and is kinetically quite stable, not melting until $270 \, ^\circ C$. Detonation has been achieved purposefully under controlled condition at US Army Armament Research & Development Command (now ARDEC); the explosive energy release exceeded expectation, but the quantitative results are not yet available publically. Calculations indicates that TNC may well prove to be a better monopropellant than ONC [17].

Tetranitrocubane
(TNC)

Tetra nitro adamantane(TNA)
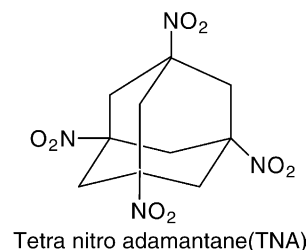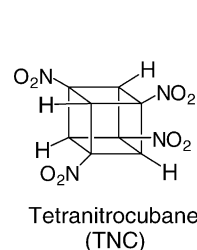
Another line of research in the field of cage compounds concerned the synthesis of nitroadamantane compounds. At the start, the preparation of 1,3,5,7-tetranitroadmantane (TNA) was reported by Sollott [18]. However, despite much optimism only a few adamantanes have been reported since that time and prove that these show no significant effect of adding nitrogoups in the ring. TNA with its high melting point of ca. $350 \, ^\circ C$, is likely to be of value as a heat resistant explosive. Similar to tetranitrodibenzo-1,3a,4,4a-tetraza-

pentalene (TACOT), it is very insensitive to impact [19]. Ionic salts of the cage molecules, adamantly tetrakis (ammonium nitrate), adamantine and cubyl poly (ammonium nitroformates) are high dense, energetic and water-soluble. They appear to be attractive in new hydroxyl ammonium nitrate (HAN) based liquid gun propellant formulations and are currently being investigated for such applications [20].

In 1987, a major scientific breakthrough came in the caged polycyclic compounds, when China Lake Researchers, Nielson and co-workers synthesized the energetic solid 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12 hexaazatetracyclo $(5.5.0.0^{5,9}.0^{3,11})$ dodecane (hexanitrohexaazaisowurtzitane (HNIW) or commonly called CL-20). HNIW is the most celebrated product of many years of research at the Naval Air Warfare Centre (NAWC) into the synthesis of novel nitramines and related energetic materials [21]. The compound has also been prepared in the Author's laboratory with high yield and high purity by the reported method [22] and is depicted further.

The Thiokol Corporation, USA, has modified the original route discovered by Nielsen and scaled upto pilot plant scale, and also currently at SNPE CL-20 is produced at the industrial pilot scale (50–100 kg by batch) [23]. Some of the properties of CL-20 are: density 2.04 g/cm^3, VOD 9380 m/s, ΔH_f +410 kJ/mol and DSC decomposition temperature 228 °C. It is reported to be compatible with nitramines, nitrate esters, azidopolymers, polyethylene glycol (PEG), hydroxyterminated polybutadiene (HTPB), ammonium perchlorate (AP), ammonium nitrate (AN) etc.


Ar = C$_6$H$_5$, Ac = CH$_3$CO
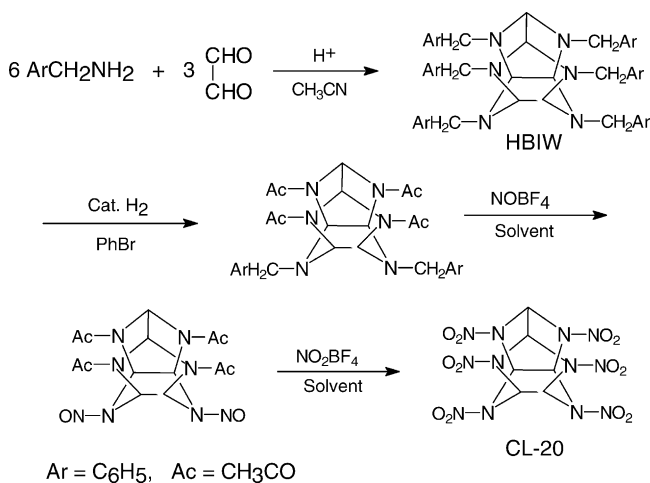
Because of its high chemical energy, propellants and explosives, using CL-20 deliver superior performance (up to 14% more than HMX) over conventional high energy propellants and explosives [24,25]. At the same time, propellant formulations containing CL-20 have the potential for remarkable stability, and resistance to external stimuli. It is likely to boost propulsion for strategic missile and space launches, and in special warheads for "Smart" or light weapons. It burns cleanly, making it more environment friendly as well as reducing a missiles' plume sig-

nature without encountering combustion stability problems [26,27]. Hence, CL-20 displays extraordinary attributes and has been described as the world's most powerful non-nuclear explosive and is the greatest promise for major technological advances in future weapon systems.

Another interesting polycyclic cage compound in the isowurtzitane series viz. 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo $(5.5.0.0^{5,9}.0^{3,11})$ dodecane (TEX). It emerged out of continuing research in the design and production of explosives to provide compositions which are highly energetic when intentionally initiated but in which the risk of unintentional detonation is minimized.

The synthesis of TEX reported by Boyer and co-workers in 1990 [28] is a two step process in which diformyltetrahydroxypiperazine (DFTHP) is formed by the reaction of formamide and glyoxal. DFTHP is then nitrated by sequential treatment with sulfuric acid and then nitric acid in presence of glyoxal to give TEX. Thiokol corporation has recently developed an improved two step synthetic route for the production of TEX which involves the use of readily available low cost materials. This new synthesis has resulted in sufficient quantity of material being available to allow some initial evaluation to be conducted.
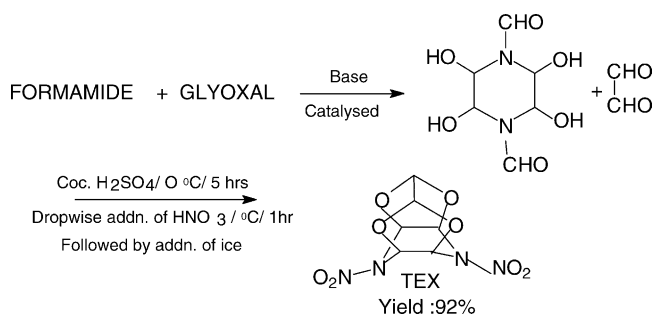
The high density of TEX can be attributed due to its three dimensional cage structure ($d = 1.99$ g/cm^3). TEX has excellent thermal stability (mp >240 °C), VOD, 8665 m/s, Detonation pressure 370 kbar and is compatible with common inert and energetic polymers systems. In castable and pressed explosives, and plasticizers, fuels and oxidizers: TEX is much less sensitive to friction and impact stimuli than RDX and HMX. It is planned to continue the development of TEX in new high performance insensitive munition (IM) explosives by US Army.

Highly nitrated small-ring heterocycles and carbocycles are interesting as energetic materials because of the increased performance expected from the additional energy release upon opening of the strained ring system during decomposition. The most widely studied energetic small-ring compound to date is 1,3,3-trinitroazetidine (TNAZ), a potentially melt-castable explosive that has been investigated as a possible replacement for TNT. TNAZ has a melting point of 101 °C, a crystal density of 1.84 g/cm^3 and thermal stability greater than 240 °C. It has excess oxygen available for the oxidation of fuel ingredients and has only half the impact sensitivity of HMX, meaning that it can sus-

tain twice the energy of impact as HMX without detonating. Unlike HMX, TNAZ is soluble in molten TNT, and is compatible with aluminium, steel, brass and glass. Also it is not hygroscopic and does not pose problems from a processing view point. It provides up to 10% increased energy relative to RDX in the low vulnerability ammunition (LOVA) XM-39 gun propellant formulations (RDX 1069 J/g, HMX 1063 J/g and TNAZ 1160 J/g) [29]. Its drawback at this moment is high production cost and slight volatility [25]. TNAZ was first synthesized by Archibald et al. [30] starting from tert-butylamine and epichlorohydrin. TNAZ has also been prepared in the author's laboratory via a five step synthetic route from an easily available raw material epichlorohydrin with good yield and high product purity. We followed the improved synthesis of Coburn et al. [31], who made it more amenable to scale up and ultimately prepared 450 kg. The synthesis of TNAZ involves the condensation of tris (hydroxy methyl) nitromethane with tertiary butylamine and formaldehyde to yield 3-tert-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-xoazine.
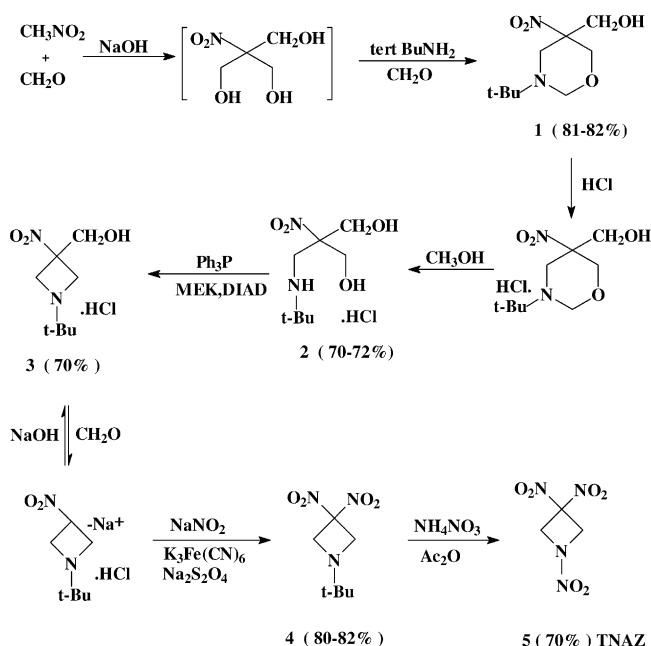

This was treated with methanolic HCl to yield 2-tert-butylamino methyl-2-nitro-1,3-propane diol hydrochloride. The cyclised azetidine ring was achieved with excellent reproducibility by the effect of diisopropyl azodicarboxylate (DIAD) – which subsequently treated with NaOH and oxidatively nitrated to yield 1-tert-butyl-3,3-dinitroazetidine (BDNA). The nitrolysis of BDNA with NH_4NO_3 and Ac_2O yielded TNAZ in 57% overall yield. TNAZ is now manufactured on a pilot plant scale at Morton Thiokol, USA and its cost continues to drop. Based on its properties, TNAZ is attractive as an explosive or as a near term candidate component for explosives/propellants with low sensitivity, good stability and enhanced performance (high energy and density) over existing military formulations.

2.2. Mono and dinitroureas

An alternative approach to increasing the performance of cyclic nitramines involves incorporating a carbonyl group in place of methylene group between two nitramines to generate a dinitrourea.

Several mono- and dinitroureas have been synthesized as energetic materials and have attractive densities and predicted performance. In general, both the mono- and dinitrourea explosives have very high densities (>1.90 g/cm^3) which has been attributed to the inherently high density of the urea framework. The dinitrourea explosives suffer from hydrolytic liability, restricting their use. However, the mono-nitrourea compounds are fairly stable to hydrolysis and are relatively insensitive to shock. The earliest and best known examples of mono- and dinitroureas were 1,3,4,6-tetranitroglycouril (TNGU) and 1,4-dinitroglycouril (DNGU) synthesized by Boileau et al. [32]. Both TNGU and DNGU were found to have high crystal densities (2.04 and 1.98 g/cm^3, respectively). A comparison of DNGU and TNGU with respect to their stability and sensitivity, is indicative of the general trend between mono- and dinitrourea explosives. TNGU is unstable to water while DNGU decomposes only slowly on treatment with boiling water. DNGU has a significantly higher drop hammer value than TNGU and better thermal stability. DNGU has been, in fact, investigated as an insensitive energetic material that was proposed to be an alternative to RDX and TNT [33].
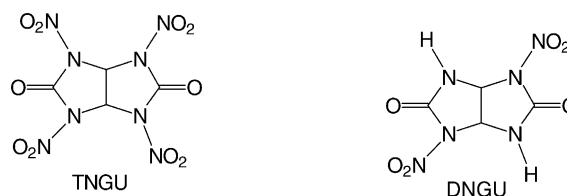
The DNGU based PBXs possess high explosion energy, good physico-chemical stability and outstanding low vulnerability, comparable to TATB-based PBXs [34]. As the method of preparation of DNGU is very simple and uses inexpensive starting materials as compared to TATB, the DNGU based plastic bonded explosives (PBXs) have a definite edge over TATB based PBXs.

Mitchell et al. [35] synthesized a number of cyclic nitrourea explosives with some attractive densities and performance. The most interesting is 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K-6) with a density of 1.932 g/cm^3, a DSC exotherm at 205 °C and measured performance 4% greater than HMX. K-6 was also synthesized in the Author's laboratory by reacting urea, formaldehyde and tert-butyl amine to yield 5-tert-butyl-2-oxo-1,3,5-hexahydrotriazine. Nitrolysis of the tert-butyl group and further nitration gave K-6 in 21–57% yield depending on the choice of the nitrolysis reagent. K-6 presumably because of the six-membered ring structure, has superior hydrolytic stability to other cyclic dinitroureas, including TNGU, K-55 and HK 55. Its

properties are; mp. 196 °C, DH$_{50}$, 61 cm and performance is equivalent to that of HMX.

K-55   HK-55   HK-56
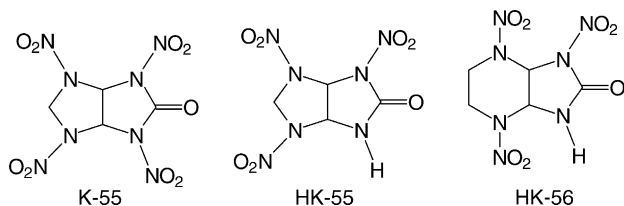
Pagoria et al. also prepared K-56 in a shorter synthesis route from 1,4-diformyl-2,3-dihydroxypiperazine which undergoes condensation reaction with urea (in aq. HCl) to yield 2,5,7,9-tetrahydro-2,5,7,9-tetrazabicyclo (4.3.0) nonane-8-one dilydrochloride, followed by nitration with fuming nitric acid and acetic anhydride. K-56 has a density of 1.969 g/cm^3 while HK-56 has a density of 1.84 g/cm^3.

Another interesting compound of this class is 2,4,6,8-tetranitro-2,4,6,8-tetra azabicyclo (3.3.1)-nonane-3,7-dione (TNPDU). This has been synthesized in the author's laboratory by a condensation reaction of tetramethoxy propane with urea according to the Mannich reaction, followed by the nitration with nitric acid–acetic anhydride medium [36].
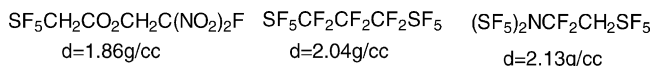

K-6

TNPDU

K-56
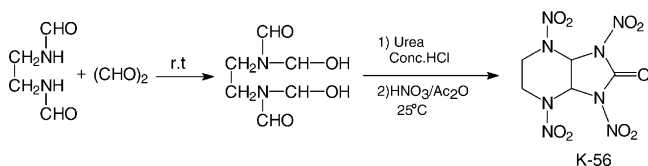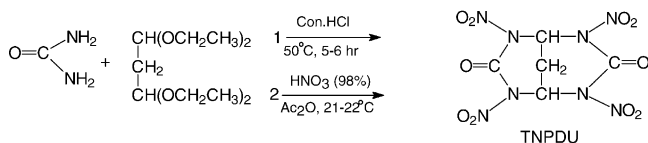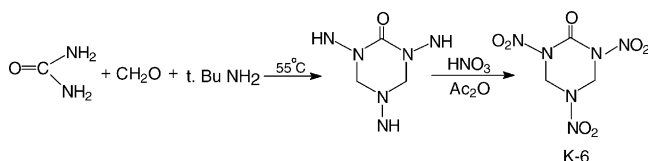
TNPDU is a powerful explosive with high density (1.93 g/cm^3), and high detonation velocity (9034 m/s). The compound is significantly more resistant to hydrolytic destruction than TNGU and has a higher oxygen balance (at –9.5%) than cyclotetramethylene tetra-nitramine, HMX (at –21%).

2.3. Polynitroaliphatic explosives containing the pentafluorosulphanyl (SF$_5$) group

As a part of continuing search for energetic materials that combine high performance with low vulnerability towards accidental detonation Sitzmann et al. [37] investigated extensively the effect of the pentafluorosulfonyl group on the

properties of explosive nitro compounds. The initial results supports that the SF$_5$ group can provide explosives with improved properties (increased density, greatly reduced impact, sensitivity and good thermal stability) relatively to very similar compounds that contain no SF$_5$ group. They also produce energy in the detonation due to formation of H–F in the detonation. The average S–F bond energy is 79 kcal/mole [38] as compared to that of H–F 136 kcal/mol, the predicted energy release, is much higher from SF$_5$ compounds in metallised composition as the Al–F bond energy is even higher at 158 kcal/mol [39]. Some examples of very dense, thermally stable insensitive polynitroaliphatic explosives containing SF$_5$ group are given below.

SF$_5$CH$_2$CO$_2$CH$_2$C(NO$_2$)$_2$F   SF$_5$CF$_2$CF$_2$CF$_2$SF$_5$ (SF$_5$)$_2$NCF$_2$CH$_2$SF$_5$
d=1.86g/cc   d=2.04g/cc   d=2.13g/cc

Further, two nitrated derivatives, 1a and 1b of the resulting cyclic amine have been prepared and both compounds have densities greater than 2.00 g/cm^3 [40].


1a   1b
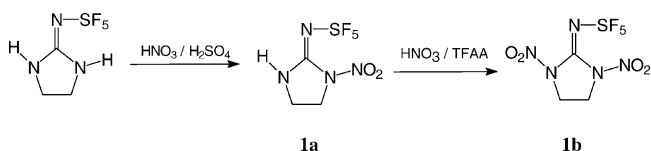
2.4. Furazans

Various synthesis routes were tested for synthesis of high energetic compounds with the use of aminofurazan as the basic precursor. Oxidation, nitration, diazotisation, condensation and nucleophilic displacement reactions were utilized in the investigation. As a result, number of prospective compounds, potential components of explosives, rocket propellants and pyrotechnics have been synthesized.

3,4-Diaminofurazan (DAF), first synthesized by Coburn in 1968 [41] has been an important precursor to a series of furazan-based energetic materials that are interesting as both propellant and explosive ingredients. DAF may be synthesized by the condensation of hydroxylamine with a variety of reagents including dithiooxamide, cyanogens, glyoxal and glyoxime to yield diaminoglyoxime followed by cyclization to DAF by treatment with aqueous base at 180 °C in a pressure vessel. Solodyuk et al. [42] reported the oxidation of DAF with H$_2$O$_2$ under various conditions to yield 4,4-diamino-3,3′-azoxyfurazan (DAAF) or 4,4′-diamino-3,3′-azofurazan (DAAzF). Chavez et al. [43] scaled up the synthesis of DAAF and performed measurement of explosive properties. DAAF has a crystal density of 1.747 g/cm^3, $\Delta H_f = 106$ kcal/mol and H$_{50}$ >320 cm (2.5 kg Type 12). Novikova et al. [44] reported the synthesis of 4,4′-dinitro-3,3′-azoxy bis (furazan) (DNABF) and 4,4′-dinitro,3,3′-azobis (furaza) (DNAzBF), all very energetic but shock sensitive compounds.

DAF DAAF

DAAzF

DNABF DNAzBF
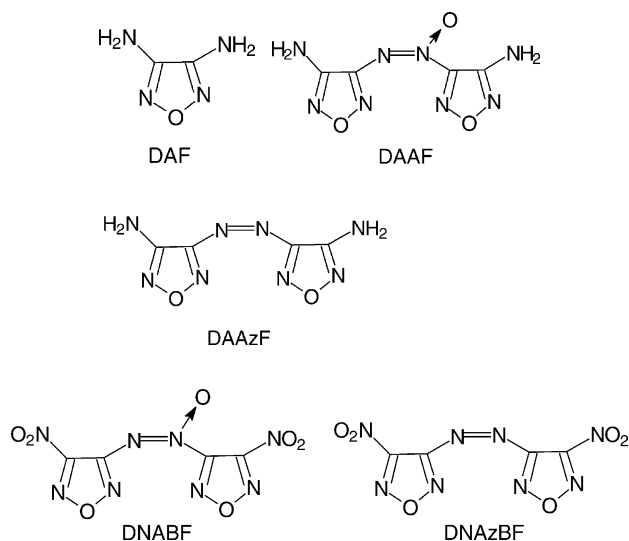
A structurally related explosive 1,4-dinitrofurazano [3,4b] piperazine has been prepared from the piperizene dione-dioxime by dehydration to the furazan followed by nitration [45].
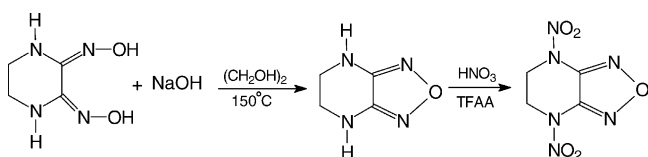
The compound has density, VOD, detonation pressure and specific impulse similar to RDX. The insensitiveness of the compound in combination with high Isp renders the compound excellent propellant properties (Imp. Sens. 162 cm, 12.5 kg wt).

Recently, Shermetev and Yudin [46] and then Tsel-niskii et al. [47] reported the synthesis of 4H, 8H-bis (furazano) [3,4:3′,4′] Pyrazine.(1a). Both syntheses used 4,5-dichlorofurazano [3,4b] pyrazine as the starting material. Fischer et al. [48] attempted the synthesis of the compound earlier but removal of the *N*-benzyl protecting groups from dibenzyl derivative proved problematic. Tselinskii et al. [47] found the dianion of 2a to be stable and reacted it with a variety of electrophiles including picryl chloride, acetic anhydride, methyl iodide and vinyl ketone. They synthe-sized the dinitro derivative (2b) by reacting the dianion (2a) with Nitrogen oxides in CH_3CN. The dinitro derivative was quite reactive but was isolated by column chromatography and the identity was confirmed by mass spectroscopy.


2a, R= H; 2b, R=NO2
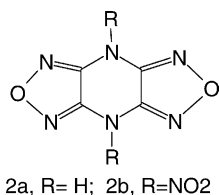
The predicted properties of 2b are density $2.00 \, g/cm^3$, VOD 9700 m/s, detonation pressure 450 kbar and specific impulse 266 s (HMX 263 s) [49].

2.5. Furoxans

A new area of interest and activity in the recent years is the development of new explosive replacing the nitro group by furoxan rings to achieve an increase in density, detonation velocity, stability and insensitivity. The benzofuroxan have been an extremely fruitful class of compounds in this con-text. The highly electrophilic nature of some benzofuroxans readily yields stable salts, a number of which show promise as primary (initiators) explosives [50,51].

By exploiting the concept, a few such explosives have also been prepared in the authors laboratory by the following scheme.


ADNBF

CI - 14
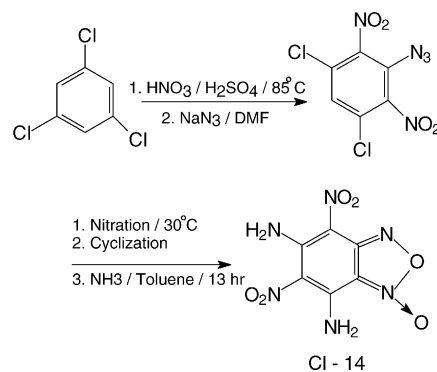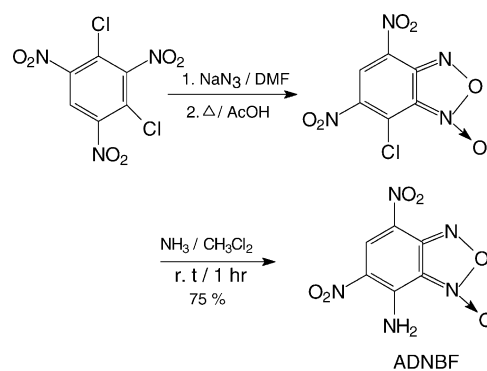
The promising explosive of this general class is 7-amino-4,6-dinitrobenzofuroxan, ADNBF which is under advanced development in the US. ADNBF has a crystal density of $1.90 \, g/cm^3$, mp 270 °C and VOD of 7900 m/s [52] whereas introduction of additional amino group in DANBF increases density $(1.91 \, g/cm^3)$ and makes it more powerful (VOD ∼8050 m/s) than TATB (VOD ∼8000 m/s) and, at the same time, it is insensitive [53]. A comparison with TATB and ADNBF shows that DANBF lies between these two explosives with respect to density and VOD. Sim-ilarly, the introduction of triazine ring in addition to NH_2 group further increases density $(2.02 \, g/cm^3)$, heat resistance

(336 °C) and promising level of insensitivity to friction (36 kg) and DH_{50} 170 cm (2.0 kg wt).

PL-1
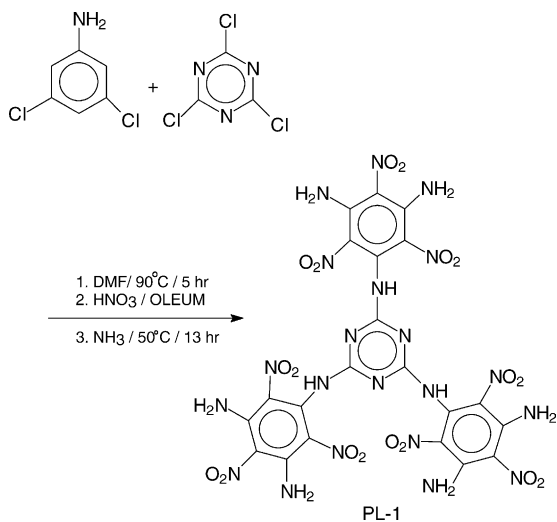
Makhov et al. [54] studied the explosion characteristic of super high energy of 4,4′-dinitro-3,3′-diazenofuroxan (DDF) of an empirical formula of $C_4N_8O_8$. It is connected with the presence of two active oxygen atoms inside of a furoxan cycle as well as with positive enthalpy of formation ($\Delta H_f = 159.6$ kcal/mol). At any density DDF has highest detonation velocity that reaches 10 km/s (measured experimentally) at the density of single crystal of 2.02 g/cm^3, very high calculated values are obtained for the heat of explosion hazard with respect to detonation capacity, sensitivity to thermal and mechanical actions. The high density value is connected with both high molecular packing rearrangement and high packing coefficient of this compound. There are 'herring-bone' motifs which are favourable from point of view of van der Waals as well as electrostatic interaction.

The compound was obtained using the step-wise transformation of functional groups in 4-amino-3-azido carbonyl furoxan as given further.


DDF
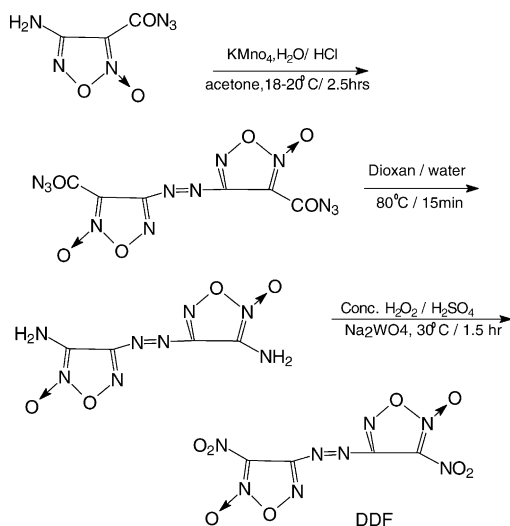
2.6. 1,2,4-Tetrazines

Chavez and Hiskey [55] have continued the research on 1,2,4,5-tetrazine based explosives and synthesized a number of derivatives which are interesting as propellants or smoke-free pyrotechnic ingredients because of their low carbon content and high heat of formation. Treatment of 1,2-dihydro-3,6-bis (3,5-dimethyl pyrazolyl)-1,2,4,5-tetrazine with hydrazine hydrate (2 eq. in acetonitrile) yielded 3,6-dihydrazino-1,2,4,5-tetrazine ($\Delta H_f = +128$ kcal/mol), an energetic fuel with a density of 1.61 g/cm^3 [56].
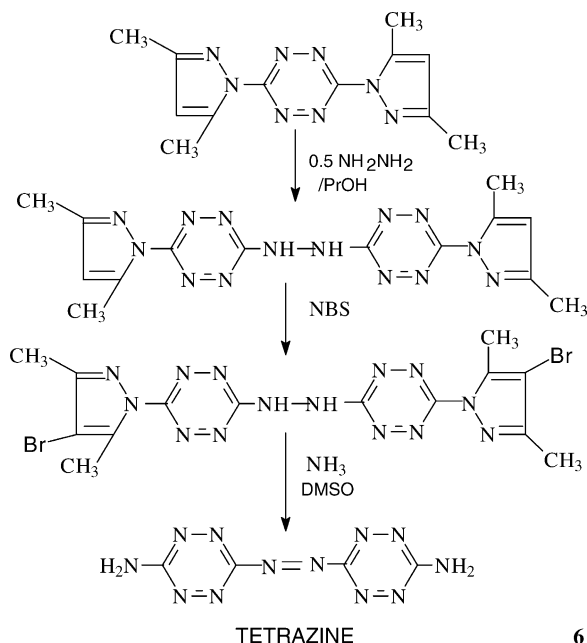

3
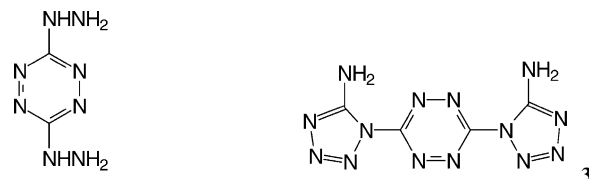
This compound was converted to 3,6-dichloro-1,2,4,5-tetrazine by treatment with Cl_2 (in CH_3CN) which then reacted with the sodium salt of 5-aminotetrazole to yield 3,6-bis (1H-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine, 3 (mp 264 °C and a measure $\Delta H_f = 211$ kcal/mol).

High nitrogen system extensively studied is the 1,2,4,5-tetrazine ring and also to some extent of oxadiazole. It has been found that 327 kJ/mol^{-1} of energy is gained in the transformation of 4,4′-hydrazobis-(1,2,5-oxadiazol-3-amine), 4 to 4,4′-azobis (1,2,5-oxadiazol-3-amine), 5. The latter material is a thermally stable, insensitive explosive [57].

4 $\Delta H_f = 209$ KJ/ mole   **5** $\Delta H_f = 536$ KJ/ mole
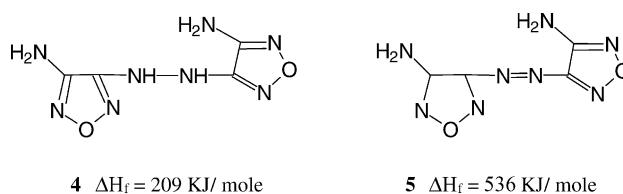
Extrapolating from these data, 3,3′-azobis (6-amino-1,2,4,5-tetrazine), 6 would give an even higher heat of formation due to the intrinsically large heat of formation of the 1,2,4,5-tetrazine ring. Chavez et al. [57] recently reported the synthesis of 6 by treatment of readily available 3,6-bis (3,5-dimethyl pyrazol-1-yl)-1,2,4,5-tetrazine with 0.5 eq. of hydrazine to yield hydrazo compound which on oxidation afforded azo compound. Treatment of azo compound with ammonia in dimethyl sulfoxide (DMSO) followed by treatment of the reaction mixture with 2-propanol, a red brown precipitate was isolated with 44% yield. The pure material is thermally stable to 252 °C and heat of formation is measured to be +862 kJ/mol. Some sensitivity properties include a drop weight impact value of 70 cm (HMX, 21 cm) despite the fact that there are no oxygen atoms in the molecule. The compound is insensitive to initiation by spark (>0.36 J) or friction (BAM >36 kg) [58] and the measured density is 1.84 g/cm^3. The compound is now being evaluated for the oxidation of NH_2 group with oxygen transfer reagents to

categorize as high performance (high VOD and high detonation pressure) explosives. The calculated density of the corresponding nitro compounds appears to be $2.26\,g/cm^3$ and that of detonation velocity and pressure are 10131 m/s and 580 kbar, respectively.

The synthesis of NTO is straightforward. Semicarbazide hydrochloride condenses directly with formic acid at $100\,^{\circ}C$ to give 1,2,4-triazol-5-one. Nitration of NTO occurs readily with a range of nitration media and conditions, best yields are obtained using those shown below.

The crystal density of NTO $\sim\!1.93\,g/cm^3$, and VOD and detonation pressure are equal to those of RDX. At the same time, it is far less sensitive than RDX and HMX. It is more stable than TNT and RDX, but its sensitivity to ignition is slightly higher than TNT.
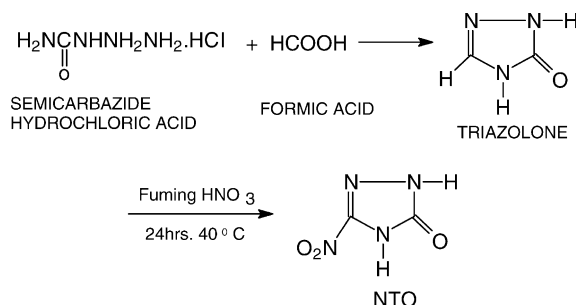
A comparison of PBXs based on TATB and NTO further confirms the same sensitivity levels, while the VOD of the NTO based PBX is slightly higher. The salient feature of NTO as a raw material for PBX is that it may be obtained in particle sizes much larger than TATB i.e. 300–500 μm as against 9–30 μm for TATB, which implies that NTO is suitable for processing by the casting technique also, whereas TATB has to be processed by the coating and pressing techniques [65].

The US AF compositon, AFX644 a low vulnerability GP bomb filling, is one example of this class. It is based on TNT and NTO with a performance matching that of TNT. The composition is based on poly-nitratomonomethyl-oxetane (NIMMO)/HMX/NTO/plasticizer, matched the performance goal of equaling composition B, while passing the UN series 7 Transport Test, ranking it as an extremely insensitive detonating substance (EIDS). The composition was not optimal but should prove a suitable candidate for further research [66].

The synthesis and structural characterization of metal salts of NTO i.e. K, Cu and Pb-NTO, reveal that they have special characteristics and may find applications in several fields [67].

Lee et al. [68] reported the preparation of 3-amino-5-nitro-1,2,4-triazole by an improved sequence where the dinitrotriazole salt was reduced with hydrazine, giving an almost quantitative conversion. The general interest in ANTA is because of amino-nitroheterocyclic compound as insensitive energetic material. The substituent combination of amino and nitro groups provides the inter and intramolecular hydrogen bonding that may stabilize the molecule and increase in density. The heterocyclic substrate is included to add density compared to the corresponding carbocyclic ma-
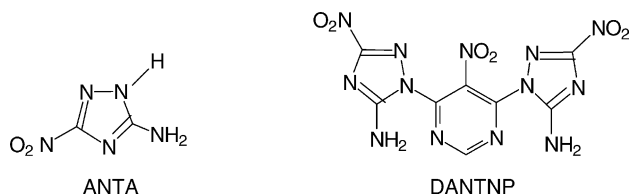
3. Insensitive high explosives based on heterocyclic nuclei

The conventional NC-NG based propellants are more sensitive than high explosive warheds, especially when they stored inside battle-tanks or other fighting vehicles. So in modern ordance there is strong requirement for explosives having both good thermal stability impact and shock insensitivity and better explosive performance. The requirement is to reduce the hazards to personnel and material on accidental initiation of a weapon due to environmental stimuli such as rough handling, fragment impact and thermal cook-off. One of the foremost objectives at the stage of the synthesis of new explosives consist in finding the molecules having a good energy capability of optimal safety.

The synthesis of nitrotriazoles as energetic materials and as intermediates to energetic materials has received a great deal of attention in the past 10 years [59]. The most studied nitrotriazole explosives, 3-nitro-1,2,4-triazole-5-one (NTO) was reported by Becuwe and Delclos [60]. NTO is currently being widely investigated in main charge warhead fillings for insensitive munition. First openly reported as an explosive in 1985 [61,62], it had obviously been discovered earlier by the French and developed into insensitive PBXs using NTO in conjunction with HMX [63]. A useful summary of the structural aspects, chemical and explosives properties and thermal behaviour, has been published [64].

terials and in many cases contribute more to positive heat of formation.

ANTA   DANTNP

ANTA has as potential a more energetic alternative to NTO, density (crystals) 1.82 g/cm³, a positive heat of formation (ΔH_f) of 21.0 kcal/mol and is thermally stable (mp 238 °C). The detonation velocity of ANTA (8460 m/s) calculated at a crystal density higher than that of TATB (performance 7% higher than TATB). The sodium salt of ANTA has been shown to be a versatile synthon to a range of explosives [68]. The most studied compound in this class is 4,6-bis (5-amino-3-nitro-1,2,4-triazolyl)-5-nitropyrimidine (DANTNP) reported by Laval and Vignane [69]. DANTNP was synthesized by reacting the sodium salt of 5-amino-3-nitro-1,2,4-triazole (ANTA) with commercially available 4,6-dichloro-5-nitropyridine (in EtOH). DANTNP (mp 330 °C) is an insensitive explosive with a density of 1.865 g/cm³ and is slightly more powerful while its impact insensitivity is of the order of that of TATB [70].
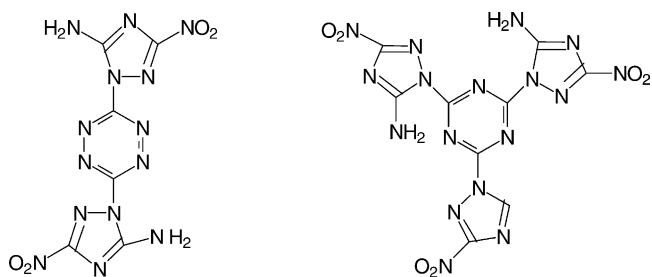

5-Amino-3-nitro-1,2,4-triazole (ANTA) based energetic compounds

Lee et al. [68] synthesized 3,6-bis (5-amino-3-nitro-1,2,4-triazolyl)-1,2,4,5-tetrazine and 2,4,6-tris (5-amino-3-nitro-1,2,4-triazoyl)-1,3,5-triazine by reacting the sodium salt of ANTA with 3,6-dichlorotetrazine and cyanuric chloride in refluxing CH₃CN. They have densities of 1.78 and 1.71 g/cm³. Although all these ANTA derivatives are thermally stable, insensitive energetic compounds they seem to hold no advantages over the current industry standard TATB.

Another energetic triazole investigated has been the 5,5'-dinitro-3,3'-azobis-(1,2,4-triazole) (DNA$_Z$T) prepared conveniently by the oxidation of K-salt of ANTA with potassium permanganate. However, when ANTA was oxidized with ammonium persulfate in aqueous medium one of the reaction product obtained was the azoxy molecule (DNA$_Z$T) of ANTA. DNA$_Z$T is a dense molecule ($d = 1.885$ g/cm³) with a calculated heat of formation is 100 kcal/mole and the specific impulse was calculated to be 244.8 s—while DNAT has a density 1.88 g/cm³, burns without smoke and solid residues, less sensitive to impact (69 cm, Type 12) than

HMX, and has a positive heat of formation (78 kcal/mol). These molecules offer unique features which are suitable for both explosives and propellants applications.

DNAT
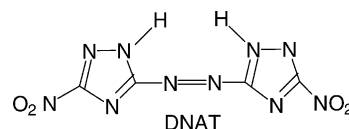
Polyamino-polynitro-pyridine-1-oxide is one such compound among several classes of heterocyclic compounds which have been investigated as potential new insensitive explosives. These compounds take the inherent stability of the aromatic hetrocyclic ring system and combine it with the insensitivity and stability associated with alternating amino and nitro groups, and supplement the performance with an energy contribution from the *N*-oxide functionality. Nissan and Wilson [71] prepared 2,6-diamino-3,5-dinitro pyridine-1-oxide, 7 by nitrating 2,6-diaminopyridine followed by its oxidation. It has a density of 1.88 g/cm³, mp >340 °C, oxygen balance −2.33% and its impact sensitivity is better than TNT. The predicted detonation velocity and pressure (7840 m/s and 275 k bar) do not match the performance desired and anticipated in the target compounds, but they do match those of TATB. In addition, the cost of 2,6-diamino pyridine is comparable with that of 1,3,5-trichlorobenzene from which TATB is prepared indicating that manufacture of 2,6-diamino 3,5-dinitropyridine-1-oxide may be a viable commercial possibility.

7   2,4-DNI   LLM - 105
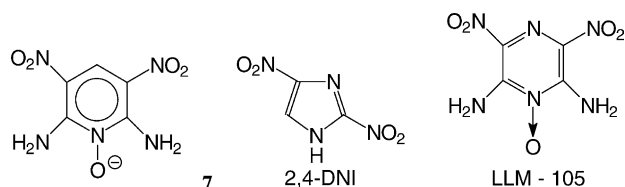
Simpson et al. [72] prepared another new shock insensitive explosive 2,4-dinitroimidazole (2,4-DNI), mp 264–267 °C that has moderate performance expected to be 60% greater than TNT and thus, can be a realistic alternative to TNT for mass use bombs. Lawrence Livermore National Laboratory (LLNL) is working together with the Army at ARDEC and Los Alamos National Laboratory (LANL) for optimizing the synthesis of this material and making it available at low cost. TNT is less expensive, HMX has higher performance, PETN has hotter detonation products, and TATB is less sensitive than 2,4-DNI. However, 2,4-DNI appears to beat them all in terms of a property compromise for real world applications.

The evaluation of the utility of 2,4-DNI in the joint LLNL-Air force Hard Structure Munition, high explosive programme is under progress [72].

Another novel insensitive high explosive 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) reported recently Pagoria and Trans [73] from Lawrence Livermore National Laboratory. The compound has performance and sensitivity

between those of HMX and TATB. Its calculated energy content is ∼85% that of HMX and 15% more than that of TATB. It is thermally stable, has a mp. 348 °C (decom.), insensitive to shock, spark and friction, and has an impact sensitivity level approaching to that of TATB. These combined properties makes it a realistic high performance high explosive material, attractive for application that require moderate performance and insensitivity [74].

4. Thermally stable explosives

Warhead fillings of modern weapons are expected to function under various environmental conditions. The requirements of an ideal high explosive composition for modern warheads are thus highly demanding [75,76]. Improved thermal stability generally simplify production procedures, increases shelf life of munition and weapons, and decrease their vulnerability to incidental initiation. They have benefited from the development of space programmes and down hole applications in oil-well exploration. Transportation of munitions by supersonic aircrafts etc. have resulted in the need for heat resistant or thermally stable explosive, that is explosives with improved high temperature properties. Thus, research of thermostable high energetic density material (HEDM) has extensively attracted world wide attention with the aim of producing explosive composition which are safe, reliable and stable at high temperatures.

In this area, nitro compounds have received special attention because of their ability to withstand the high temperature and low pressure encountered in space environments. Structural analysis shows that there are four general approaches to impact thermal stability of explosive molecules (i) introduction of an amino groups (ii) condensation with a triazole ring (iii) salt formation and (iv) introduction of conjugation. Some of the potential explosives in this class that have received special attention to service applications are mentioned below. It is worth mentioning that octahydro-1,3,5,9-tetranitro-1,3,5,7-tetrazocine (HMX), with a melting point of 291 °C, is also considered as a heat resistant explosive in some countries [75].

4.1. Polynitrophenyls and stilbenes

The introduction of an amino group into a benzene ring having a nitro group is one of the simplest approaches to enhance the thermal stability of explosives. This is evident from the study on mono-amino-2,4,6-trinitro benzene (MATB), 1,3-diamino-2,4,6-trinitrobenzene and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), where the order of thermal stability is MATB < DATB < TATB. DATB is fairly stable with a mp of 286 °C and has been qualified as heat resistant explosive and is of practical value in various space applications [77].

On the other hand, TATB has excellent thermal stability in the range 260–290 °C. TATB is an explosive with unusual insensitivity and heat resistance, and respectable performance, which places it first on the list of thermally stable and safe explosives. The structural features of TATB are (i) extremely long C–C bonds in the benzene ring (ii) very short C–N (amino) bands and (iii) six furcated hydrogen bonds. In addition, there is a evidence of strong inter and intramolecules hydrogen bonds in TATB. [78]. The net result is that TATB lacks an observable mp and has a low solubility in all solvents except H_2SO_4 [79]. TATB is the current industry standard and is used extensively in Military applications and in nuclear weapons. However, it has received limited use in civilian applications because of the cost of the materials. Recently a synthesis of TATB from picramide or1,3,5-trinitrobenzene was reported in three patents by Mitchell et al. [80–82] at LLNL which may significantly reduce the cost of TATB. The treatment of picramide, with 4-amino-1,2,4-triazole (ATA) [83] or with 1,1,1-trimethyl hydrazinium iodide (TMHI), as nucleophilic aminating agents, in DMSO in the presence of excess NaOMe yielded TATB also in excellent yield [84]. TATB with polymers compositions such as TATB/KeLF800 and TATB/Viton-A appear to be attractive for long term use.
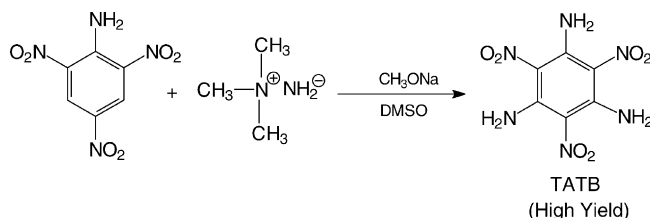
Higher molecular weight aromatics readily built by coupling of halobenzenes, exhibit increased thermal stability, while amine substitution decreases sensitivity. Molecules containing these features were very actively pursued over the 1960s and 1970s, but have received much reduced attention over the 1980s. One energetic material of this type is the 3,3′-diamino-2,2′4,4′,6,6′-hexanitrobiphenyl [85].
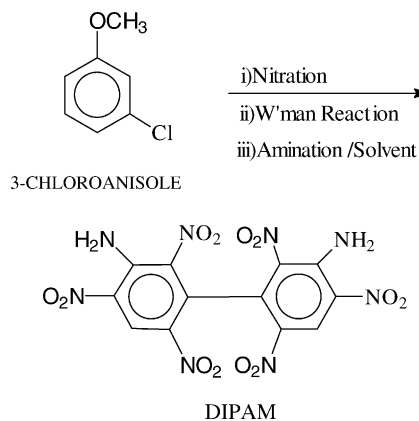
The density is high at 1.82 g/cm^3 and the predicted performance is significantly better. In addition to the ability of

the explosive to withstand high temperature (mp ca. 304 °C), it is extremely insensitive to electrostatic discharge, requiring more than 3200 J for initiation. DIPAM has been used to achieve stage separation in space rockets and for seismic experiments on the moon [86].

The concept of enhancing thermal stability by introduction of amino groups between two phenyl rings is further supported by Chinese workers C.X. Lu et al. [87]. And thermal stability is further enhanced by salt formation which may be illustrated by the following example.
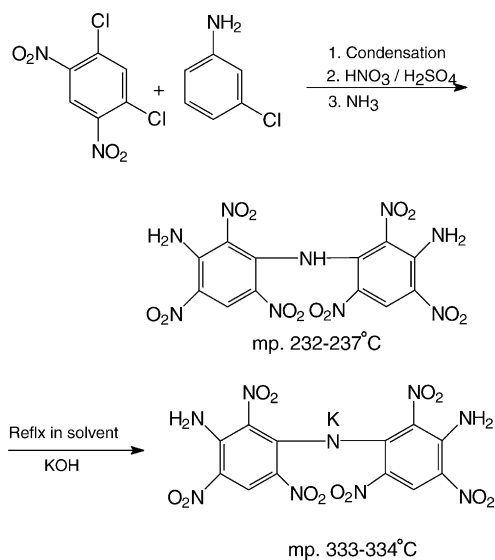
The best example of imparting higher thermal stability through the introduction of conjungation in explosive molecules is 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) (mp 316 °C) synthesized by Shipp [88] of American Naval Ordance Laboratory (NOL) in 1964. HNS is used increasingly in a wide range of explosives applications. Plants for full scale production exist in the UK and China based on the method of Shipp. HNS is in use for achieving stage separation in space rockets and for seismic experiments on the moon [89].
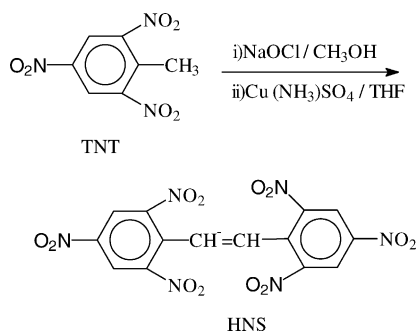

German workers Redecker and Higel [90] prepared polynitropolyphenylene (PNP) polymers by copper induced self coupling of 1,3-dichloro-2,4,6-trinitrobenzene.

(n = 11 to 19)
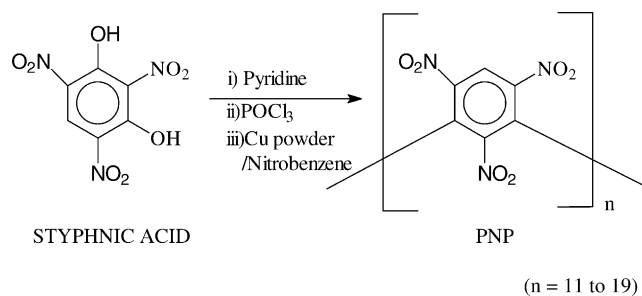
The properties of the compound are deflagration temperature 286–294 °C, explosion energy 3300 J/g, density 1.8–2.2 g/cm^3, VOD 7300 m/s. PNP is exceptionally thermally stable and is considered as high temperature resistance binders together with inert binders and/or softeners. Some pyrotechnic formulations which use PNP as a binder have been reported recently [91].

Another potential heat resistant explosives is 2,2′,2″,4,4′, 4″,6,6′6″ nona nitro terphenyl (NONA), resulted by the condensation reaction of picryl chloride with 1,3-dichloro-2,4, 6-trinitrobenzene in presence of Cu-dust at 210 °C. The compound has density of 1.78 g/cm^3 and exceptional heat stability, melting at 440–450 °C with decomposition, together with a low volume of split off gases rendered it an interesting material for booster explosion in space technology [92].
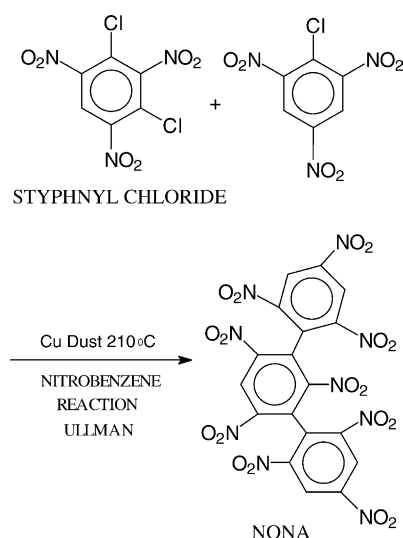
4.2. Thermally stable explosives of heterocyclic ring

Heterocyclic compounds have received a great amount of interest over the decades than their carboxylic analogues for the best combination of thermal stability, oxygen balance, heat of formation and predicted performance. The major approaches made in the recent years in the field of high temperature explosives in this class are reviewed further.

A special example was 3-picryl amino 1,2,4-triazole (PATO), which was reported by Coburn and Jackson in 1968 [93,94] based on thermal stability and impact sensitivity.

Its crystal density is 1.94 g/cm^3, calculated VOD 7850 m/s, detonation pressure 307 kbar, and impact sensitivity with 2.5 kg weight is >320 cm. It was considered as one of the potentially useful thermally stable (Thermolytic temperature up to 310 °C) explosives. Recently, PATO has been synthesized by a Chinese team with a modified route starting from Tetryl with 3-amino, 1,2,4-triazole in methanol under reflux in presence of sodium carbonate as catalyst with high yield [95]. PATO is relatively inexpensive and is at the same time, as insensitive as TATB. It was initially thought that it would replace TATB in future applications but its performance is inferior to TATB [96].


PATO
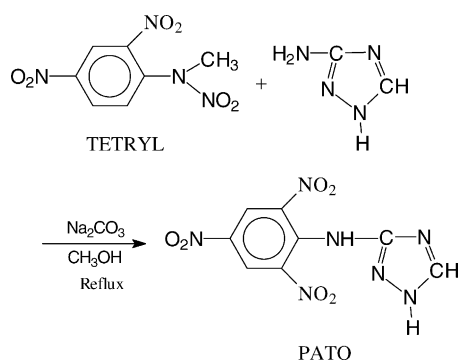
Another example of pyridine based heat resistant explosive is 2,6-bis (picrylamine)-3,5-dinitropyridine (PYX), prepared in high yields from relatively inexpensive starting materials. The compound has the properties like crystal-density of 1.75 g/cm^3, mp 460 °C, VOD 7450 m/s, detonation pressure 242 k bar and impact sensitivity 63 cm. PYX has been commercialized in America and Chemtronics Inc. is currently producing it under licence from Los Alamos for use in thermally stable perforations for oil and gas wells [97]. It is increasing being used as a substitute for HNS and is gradually replacing HNS for most commercially thermally stable explosive applications.


PYX
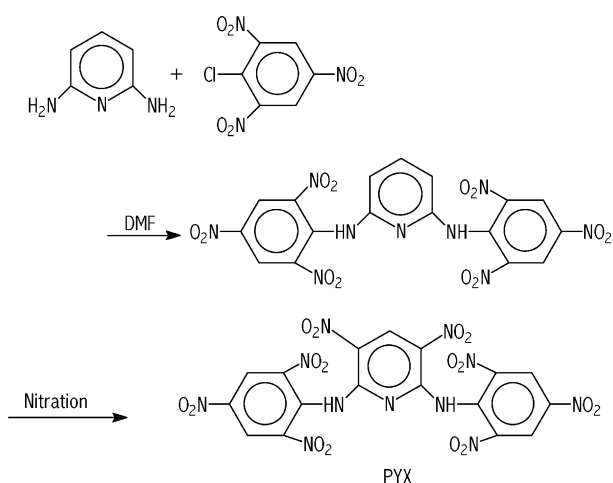
A triazine based insensitive compound 2,4,6-tris (3,5-diamino-2,4,6-trinitrophenylamino)-1,3,5-triazine (PL-1) was prepared in 50% yield in the author's laboratory [98] by amination of 2,4,6-tris (3,5-dichloro-2,4,6-trinitrophenyl amino)-1,3,5-triazine which, in turn, was prepared from condensation of cyanuric chloride and 3,5-dichloroaniline followed by nitration with mixed acid. PL-1 has considerably low hydrogen and high nitrogen content, and has good heat resistance with decomposition temperature 335 °C (DTA 10 °C/min). The compound has a density of 2.02 g/cm^3, detonation velocity, 7861 m/s and has the promising level of insensitiveness to friction (36 kg) and impact (height for 50% explosion 170 cm). The overall comprehensive properties of PL-1 are equivalent to that of TATB.


PL-1
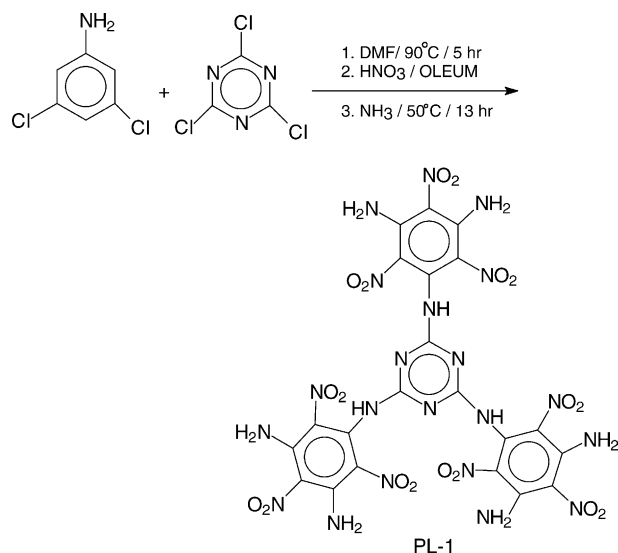
Carboni and Castle [99] synthesized a powerful explosives, tetranitrodibenzo-1,3a,4,4a-tetrazapentalene (TACOT) with unusual and outstanding high temperature stability. TACOT possesses several isomers depending on the position of the nitro groups (ortho, meta or para) in each individual benzene ring. But these isomers have found to have similar explosive and thermal properties. Therefore, the product which is a mixture of three isomers is used as such in explosive compositions. Its ignition temperature (ca. 494 °C) is the highest ever registered for explosives. However, its DTA curve shows that it is stable up to 354 °C, after which a slight exothermic reaction occurs, which builds into a very rapid deflagration exotherm at 381 °C. Its explosive power is equal to 96% and 80–85% to that of TNT and RDX respectively. It is highly insensitive to impact and electrostatic charge, but can be easily initiated by lead azide primer containing as little as 0.02–0.03 g grain of lead azide. TACOT continues to function effectively ever after long exposure to high temperature. TACOT is available in the form of high density charges, as a polymer bonded explosive (PBX) or core lead in explosive cords like mild detonating fuze and flexible linear shaped charge (FLSC). A comparison of properties between TACOT and PYX indicates that both have thermal stability, the former is slightly impact insensitive, whereas the latter is slightly impact

sensitive. Quality control of PYX during manufacture is much easier than TACOT as it consists of several mixtures.
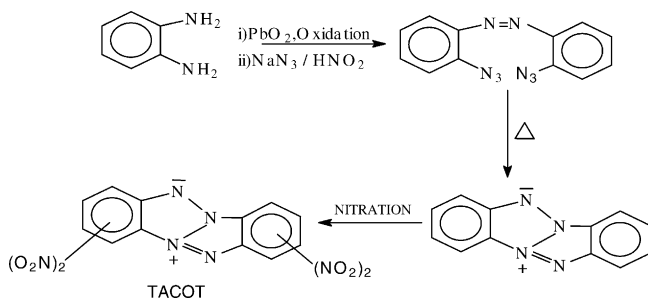
Two more insensitive energetic materials with structures similar to TACOT were synthesized by reacting 1,2,3-triazolo pyridine with 2-chloro-3-nitropyridine to yield 1-(3-nitro-2-pyridyl)-1,2,3-triazolo pyridine which was cyclized with triethyl phosphite to yield the dipyridotetraazapentalene. Subsequently this was nitrated (with HNO_3/H_2SO_4) at 60 °C to yield compounds. The compounds have decomposition temperature point of 340 and 396 °C respectively and both have a crystal density of $1.88 \, g/cm^3$. They are significantly more energetic than TACOT while retaining excellent thermal stability [100].
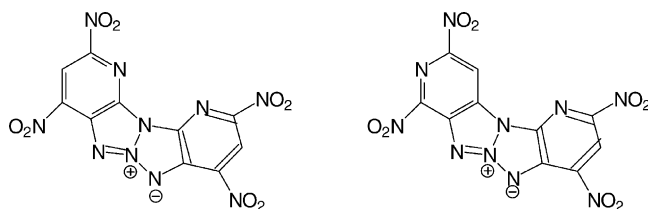
Pyridine- based TACOT analogues

5. Future options

The future of propulsion and ordnance technology holds many possibilities. Chemical explosives and propellants are likely to enjoy continued incremental improvements in density, energy and stability to the point where future materials are safer and superior.

The future agenda of energetic materials research will almost certainly pose four challenges: (1) to development of truly insensitive energetic oxidizer (2) an energetic fluorine containing oxidizer (3) an insensitive high energy explosive with a density $>2 \, g/cm^3$ and (4) high energy fuel technology. The first three goals are being promoted world wide, the fourth is largely a Russian endeavour which has so far yielded an unprecedented morphology of Aluminium hydride as a fuel for propellant applications.

The development of fluorine-laden oxidizers will enable the use of boron-laden fuels. Even in the realm of explosives, there is no reason why a formulation of appropriately encapsulated fuel and oxidizer can not surpass conventional nitro organics in both performance and economy.

The development of CPX 413 has demonstrated the potential in the binder system has proved to be successful. The aim of designing a formulation to meet a specific performance goal while being insensitive has been met. The composition based on an energetic binder, in combination with nitramine, insensitive high explosive and plasticizers, matched the performance goal of equaling composition B, while passing the UN series 7 transport tests, ranking it as an extremely insensitive detonating substance (EIDS). The composition was not optimal but should prove a suitable candidate for further research.

Attempts to match Octol performance are under way and early results are up to expectation. The combination of a higher energy binder and the range of energetic fillers now available should make it possible to go even further in designing for function. Whatever impact future technologies may have on the design of rocket motors and ordnance, chemical propellants and explosives will always have a place in the science of controlled kinetic energy release.

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