

Review of some newly synthesized high energetic materials

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Abstract

Towards the end of the last millennium many new high energetic materials were developed. These materials may replace the presently used explosives, sooner or later. In this review, the authors try to explore some of these materials *viz.*, polynitropolycyclic cage explosives, cyclic nitramines, cage explosives, nitro derivatized heterocyclic compounds, nickel hydrazine nitrate (NHN) complex, nitrocubanes, hafnium explosives, heat-resistant explosives, new insensitive high explosives and some other novel high energetic materials. There is a need for the development of analytical methods for identification of these materials and their post explosion residues as these are likely to be encountered in crimes.

1. Introduction

During the nineteenth century the developing science of chemistry began to create molecular species with explosive properties. These molecules contain not only atoms that act as fuels, *i.e.* carbon and hydrogen, but also contain nitro groups (NO₂) similar to nitrates. There are three basic structural types: nitro compounds containing the C-NO₂ group; nitrate ester containing C-O-NO₂ and nitramines containing N-NO₂. Molecules that contain nitro groups are good candidates for explosives. The nitro group provides the essential oxygen for the combustion, and furthermore, the nitrogen atoms are converted to dinitrogen (N₂), increasing the volume of liberated gas. The advent of nitrated molecules opened the way to explosives with far better energetic properties but with the ability to create detonations.

However, at the turn of the nineteenth century, researchers were applying the concept of detonation to explosive molecules, some of which had been known for almost 100 years. One of the first to be developed into fillings for ordnance was picric acid (2,4,6-trinitrophenol), either as a pure material or mixed with dinitrophenol to lower the melting point of the mixture to aid melt casting¹. At the same time the explosive 2,4,6-trinitrotoluene (TNT) was also developed and found to be superior to explosives based on picric acid. The use of TNT was highly successful not only as a pure filling but, by the end of World War I, as a mixture with ammonium nitrate to give the explosive known as amatol which could contain as

much as 80% ammonium nitrate. By the beginning of World War II, the research to discover alternative explosives resulted in another group of explosive molecules that could be used for the filling of ordnance². After two major World Wars in twentieth century, picric acid, TNT, tetryl, RDX, NG, PETN, ammonium nitrate and potassium chlorate explosives were encountered in insurgent activities.

Experimental and theoretical studies on the pyrolysis mechanism, sensitivity and many aspects of organic explosives on this subject were described in the earlier literature³⁾⁻⁵. Polynitropolycyclic cage compounds, cyclic nitramines other than RDX and HMX, nitro derivatized heterocyclic compounds, nitro cubanes, hafnium explosives, heat-resistant explosives, a new primary explosive nickel hydrazine nitrate (NHN) complex, promising new insensitive high explosives and some other novel high energetic materials were developed recently. These high energetic materials have the potential to be used for insurgent activities by extremists groups in the coming years. The performance and other characteristic studies of these materials, reported recently show that some of them possess better potential than presently used explosives. This review paper examines them under several headings "thermally stable" or "heat-resistant", "high-performance", melt-castable, insensitive, energetic binders, and energetic materials synthesized using N₂O₅ and critically examines them from the point of view of stability, reliability, safety and specific application.

Problems associated with their processing are identified and suggestions are made to overcome them⁶.

Forensic scientists have to update their knowledge about the emerging high explosives, and develop systematic analytical procedures by including these materials so that no explosive residues would be left undetected. During seventies and eighties of last century analytical methods such as chemical spot tests, chromatographic and spectrometric techniques were developed for the trace analysis of explosives. Survey of available literature and proceedings of various conferences on detection of explosives do not indicate any significant work on detection of some of the newly emerged high energetic materials. Keeping this aspect in mind, with a view to explore the possibility of application of modern analytical methods for identification of the newly synthesized high energetic materials, the present paper highlights the importance of these compounds to the forensic community.

2. Chemistry of polynitropolycyclic cage explosives

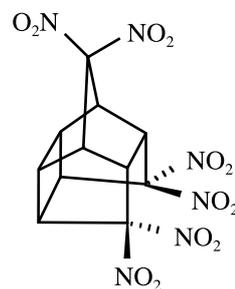
The performance of an explosive is determined by the amount of heat and gas produced in the initial reaction. Since the past decade many research groups are involved in an intensive effort to synthesize new polynitropolycyclic "Cage" compounds⁷. Such polycarbocyclic compounds, by virtue of their rigid compact structures, generally pack efficiently in the solid state and thus possess unusually high crystal densities. These classes of compounds having carbocyclic frame work often possess significant levels of steric strain, which correspondingly render them thermodynamically unstable relative to isomeric non-cage structure.

In recent years, attention has been focussed upon the potential use of polycarbocyclic cage compounds as a new class of energetic materials. Significant efforts have been made in several laboratories world-wide to introduce nitro groups as substituents into highly strained cage molecules in an effort to produce high density explosives and propellants. Compact three-dimensional cage compounds containing optimum numbers of nitro groups as determined in theory by thermodynamic calculations constitute a class of explosive compounds more powerful than HMX. This is due to direct result of high crystal densities, particularly in combination with high strain energies built in certain cage system. The synthesis of polynitrocage compounds has progressed on several fronts and is currently in the second stage of a three-stage effort. The first stage has seen the synthesis of forerunners of more highly nitrated cage compounds as

part of broad strategy to develop the methodology⁸.

The synthetic methodology, which has been utilised to prepare a number of polynitropolycyclic cage explosives, is presented by A.P. Marchand *et al.*⁹. The results of thermodynamic studies of several polynitropolycyclic systems are discussed along with preliminary results by explosives evaluation studies which have been performed on 4, 4, 7, 7, 11, 11-hexanitropentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane or D₃-hexanitrotrishomocubane¹⁰ and on 4, 4, 8, 8, 11, 11-hexanitropentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane¹¹. Thermodynamic parameters and explosive performance characteristics of hexanitro pentacyclo undecanes are given in Table 1.

2.1 4,4,7,7,11,11-hexanitropentacyclo [6.3.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane (or) D₃-hexanitrotrishomocubane



The density of this compound is 1.84 g cm⁻³. The detonation velocity is 7.95 km sec⁻¹ and the detonation pressure is 2838 × 10⁷ Pa. The heat of formation (ΔH_f) is -36.44 kcal mol⁻¹.

Shock sensitivity measurements on D₃-hexanitrotrishomocubane were performed by using the exploding foil slapper technique developed at the U.S. Army Armament Research Development and Engineering Center, by Velicky *et al.*¹². D₃-hexanitrotrishomocubane is less shock sensitive than TNT.

2.2 4,4,8,8,11,11-hexanitropentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane

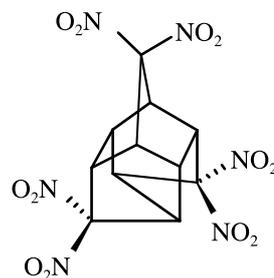


Table 1 Thermodynamic parameters and explosive performance characteristics of hexanitro pentacyclo undecanes¹¹.

Compound	Density (g cm ⁻³)	ΔH_f (kcal mol ⁻¹)	Detonation pressure (Pa)	Detonation velocity (km sec ⁻¹)
4,4,8,8,11,11-hexanitro pentacyclo [5.4.0.0 ^{2,6} .0 ^{3,10} .0 ^{5,9}] undecane	1.84	-22.5	2920 × 10 ⁷	7.87
4,4,7,7,11,11-hexanitro pentacyclo [5.4.0.0 ^{2,6} .0 ^{3,10} .0 ^{5,9}] undecane or D ₃ -hexanitrotrishomocubane	1.84	-36.44	2838 × 10 ⁷	7.95

The density of this compound is 1.84 g cm^{-3} . The detonation velocity is 7.87 km s^{-1} and the detonation pressure is $2920 \times 10^5 \text{ Pa}$. The heat of formation (ΔH_f) is $-22.5 \text{ k cal mol}^{-1}$. Shock sensitivity tests were also performed on 4, 4, 8, 8, 11, 11-hexanitropentacyclo [5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane as described above in the compound D₃-hexanitrotrishomocubane. The explosive performance of this compound could be compared with that of TNT¹¹⁾.

In comparison, the corresponding test results obtained for D₃-hexanitrotrishomocubane indicates that this material is slightly less powerful. Its explosive performance is 34% greater than that of TNT. Importantly, the D₃-hexanitrotrishomocubane compound is a considerably less sensitive explosive than this compound relative to TNT. The results of thermal analysis (DSC) and explosive performance evaluation tests on small quantities of materials suggest that D₃-Hexanitrotrishomocubane and 4, 4, 8, 8, 11, 11-hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}] undecane are both more powerful and less sensitive explosives than TNT.

3. Chemistry of cyclic nitramines

The cyclic nitramines, 1, 3, 5-trinitro-1, 3, 5-triazacyclo-

hexane (RDX) and 1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazacyclooctane (HMX) are high energy containing compounds that are used extensively as both propellant and explosive formulations. RDX (1.77 g cm^{-3}), HMX (1.89 g cm^{-3}) and PETN (1.77 g cm^{-3}) are all capable of providing very high shock pressures with HMX being the best. However, PETN is significantly more sensitive than RDX over PETN where safety is an issue in such uses as artillery and cannon rounds. As the performances of RDX and PETN are very similar, many countries have chosen to use RDX in preference to PETN in most other cases. HMX is slightly more sensitive than RDX but significantly more expensive. It is used where very high shock pressures are required. A thorough knowledge of the underlying complex physiochemical processes in the combustion of these materials is essential to develop methods to modify their formulations so as to obtain better ignition, combustion or sensitive properties. Thus military high explosives are based on RDX and HMX and to a lesser extent PETN to provide the necessary performance. Several other less known cyclic nitramines are also described in the literatures¹³⁾ which are structurally similar to RDX and HMX.

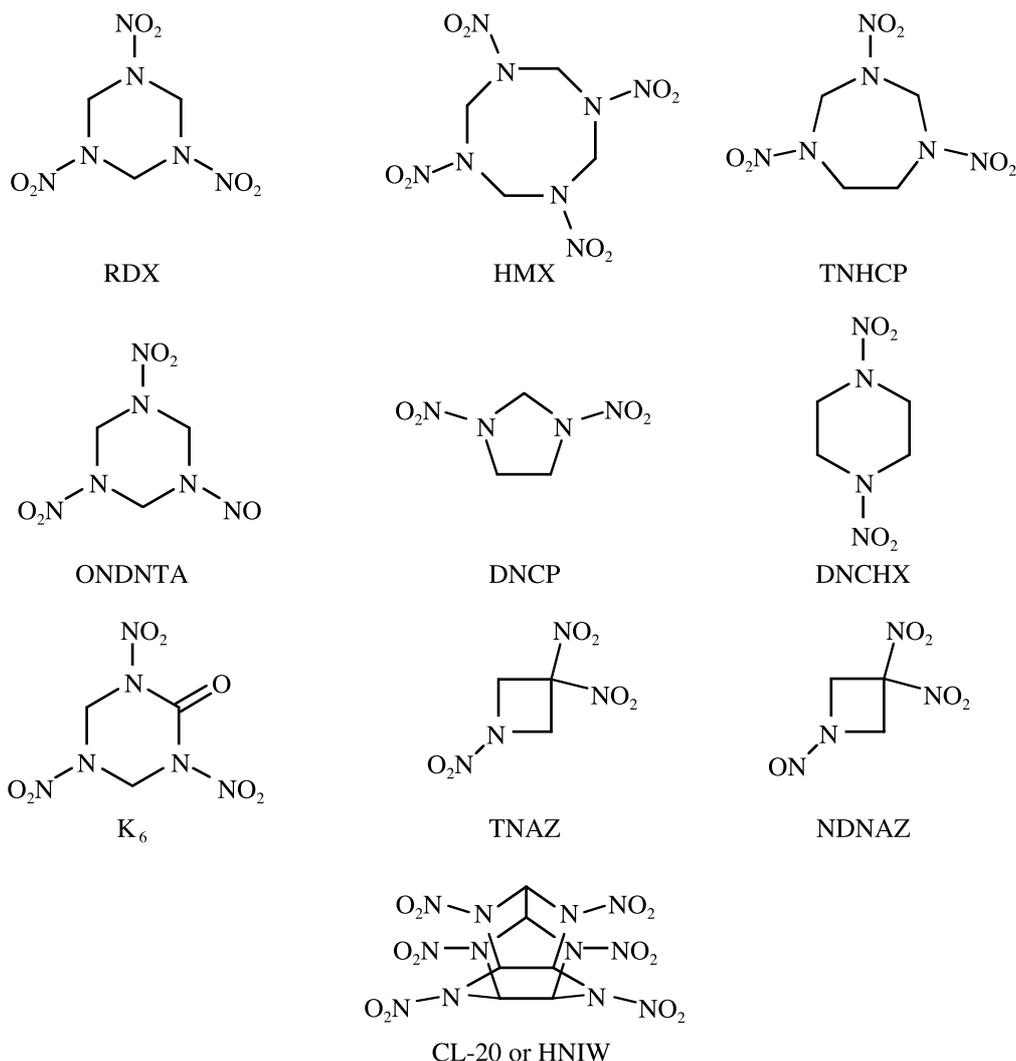


Fig. 1 Chemical structure of cyclic nitramines.

The highlights of the investigations on RDX, HMX and other cyclic nitramines given in Fig. 1 are discussed in this paper with the focus on the common features as well as the significant differences in their explosive properties and sensitivity. While RDX and HMX samples were obtained from military sources and purified by repeated crystallisation from acetone, their isotopic analogues and all the other nitramines were made in the laboratories by methods already known. The syntheses of the isotopic analogues of RDX and HMX have been described in the literature¹³. ONDNTA (1-nitroso-3, 5-dinitro-1, 3, 5-triazine) and its deuterium labelled analogue ONDNTA-*d*₆, which are intermediates in the decomposition of RDX-*d*₆, were prepared according to previously known methods starting with the corresponding hexahydro-1, 3, 5-trinitroso-*s*-triazine analogue.

The nitramines TNCHP (1, 3, 5-trinitro-1, 3, 5-triazacycloheptane), DNCP (1, 3-dinitro-1, 3-diazacyclopentane) and DNCHX (1, 4-dinitro-1, 4-diazacyclohexane) were synthesised according to the methods already described in the earlier literature. The methods of synthesis of K₆ (1, 3, 5-trinitro-1, 3, 5-triazacyclohexanone) and TNAZ (1, 3, 3-trinitroazetidine) have also been published^{14, 15}. TNCHP is more stable in the liquid phase than either RDX or HMX. DNCP is thermally much more stable in the molten state as compared to RDX and HMX while DNCHX begins to decompose in the solid state similar to the case of HMX.

TNAZ is a relatively new energetic material¹⁶ with a strained four membered ring and a *gem*-dinitro group in it. Because of its relatively low melting point (101°C), it is melt-castable using steam and is considered to be a useful explosive with valuable applications. NDNAZ (1-nitroso-3, 3-dinitroazetidine) plays an important role as an intermediate in the decomposition of TNAZ. Also, TNAZ and mixtures of TNAZ and NDNAZ are new energetic materials with high-energy contents, which are considered as possible replacement for HMX and TNT¹³.

Compared to thermal decomposition studies of the well known cyclic nitramines, RDX and HMX, studies on TNAZ have been new and limited. In the last several years new explosives have attracted attention as possible alternatives for the nitramines RDX & HMX. Some novel high energy compounds have been synthesized recently which may be used as explosives in future. Probably, some of the most important compounds are hexanitrohexaazaisowurtzitane (HNIW or CL-20), K₆, ONDNTA, TNCHP, DNCHX, DNCP, NDNAZ and TNAZ. These are currently being developed and tried in ordnance fillings.

The chemical structures of cyclic nitramines are shown in Fig. 1. HNIW also known as CL-20 is one of them. CL-20

is having higher energy value when compared with HMX & RDX. A new propellant¹⁷ was designed with CL-20 as main energetic compound, energy 1253 Jg⁻¹ and combustion temperature < 3700 K. It is the most powerful non-nuclear known explosive groups. The mean molecular weight of reaction gases is 24.8 g mol⁻¹ for this propellant type. The CL-20 crystal shape is different from that of RDX. The sensitivity tests and chemical stability tests are used for selecting the most promising propellant. CL-20 and mixtures of CL-20 with RDX are giving poor friction sensitivity (50 N) and impact sensitivity (2.5 Nm). CL-20 is predicted to significantly enhance performance in the areas of specific impulse or density in propellants and in detonation velocity and pressure in explosives¹⁸. The calculated detonation velocities and pressures are much higher than that of the classic C-nitro explosive TNT and also 15-30% greater than that of the N-nitro compound HMX. Presently it is the most energetic of standard military explosives and even better than that of the experimental polycyclic nitramine CL-20.

4. Nitro derivatized heterocyclic compounds

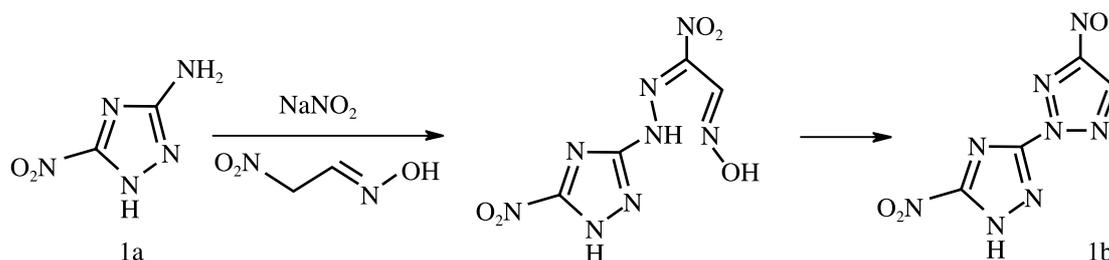
In this context, heterocyclic compounds like dinitrobitriazole¹⁹⁻²², 3-nitro-1, 2, 4-triazole-3-one (NTO)²³⁻²⁵, 3, 3-bis (difluoramino) octahydro-1, 5, 7, 7-tetranitro-1, 5-diazocine (TNFX), a diversified energetic heterocyclic compound²⁶⁻²⁸ and nitroimidazole derivatives are discussed in particular. The synthetic strategy of bitriazoles are given below to distinguish the C, C-dinitrobitriazole and C, N-dinitrobitriazole.

4.1 Chemistry of dinitrobitriazole

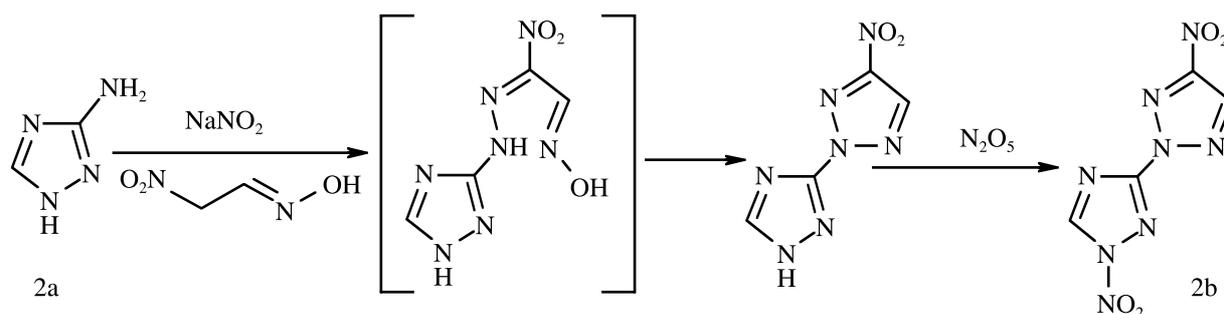
Basically dinitrobitriazole is a heterocyclic derivative. It is obtained from aminotriazoles by dinitro diazotization, coupling with methazonic acid and subsequent cyclization. It has been proved to be highly energetic material. The chemical and physical properties have been investigated by Licht and Ritter²⁰. To distinguish the two dinitrobitriazole, C, C-dinitrobitriazole and C, N-dinitrobitriazole the synthetic strategy is given in scheme 1 and scheme 2.

4.1.1 Synthetic strategy of bitriazoles

The explosive 3-amino-5-nitro-1*H*-1, 2, 4-triazole (ANTA) (1a) is a stable nitro compound of reduced reactivity²¹. ANTA was prepared and evaluated in terms of insensitivity and performance. The material is very insensitive to impact and moderately sensitive to thermal stimulus. Its performance was inferior to 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB). The best synthesis of ANTA is a three-step route using commercially available 3, 5-diamino-1, 2, 4-triazole¹⁹.



Scheme 1 Synthesis of C, C-dinitrobitriazole.



Scheme 2 Synthesis of C, N-dinitrobitriazole.

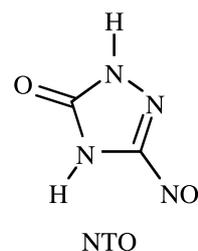
The primary amino group of ANTA is reactive to a greater extent. Diazotation and coupling with methanesulfonyl hydrazide followed by concurrent cyclization produced C, C-dinitro bitriazole (1b). This compound should be an explosive of greater performance than ANTA because of its more favourable oxygen balance. The explosive performance data of C, C-dinitro bitriazole (1b) are difficult to obtain, since the quantities needed to measure its detonation velocity are not easily accessible.

Browne²²⁾ reported the preparation of 2b from commercially available 3-amino-1,2,4-triazole (2a), following a similar synthetic sequence as above. In this reaction, standard nitration methods *i.e.*, $\text{HNO}_3 + \text{H}_2\text{SO}_4$ and $\text{HNO}_3 + (\text{CH}_3\text{CO})_2\text{O}$ failed. Hence, Browne used alternate solutions of dinitrogen pentoxide (N_2O_5) in methylene chloride (CH_2Cl_2) to obtain an isomeric C, N-dinitrobitriazole (2b).

The C, N-dinitrobitriazole (2b) has the lowest crystal density, it is the most energetic material because of its favourable heat of formation. Calculated performance data of triazole derivatives 1a, 2a and 2b at Theoretical Maximum Density given in Table 2.

4.2 NTO (3-nitro-1,2,4-triazole-5-one)

NTO is a potential high performance insensitive explosive, which is being explored as a substitute for popular high explosive like RDX in munitions²³⁾²⁴⁾. The structure of NTO is given below, the detonation performance of NTO was given, and compared with a foreign explosive composition based on NTO, and then compared with explosives based on HMX and TATB. The booster for initiating the composition based on NTO and its high explosive train were also described by W.Wendian²⁵⁾.



NTO

The density of compound NTO is 1.91 g cm^{-3} , the detonation velocity 8.12 km s^{-1} and the detonation pressure $307 \times 10^8 \text{ Pa}$. Its detonation velocity and pressure are equivalent to those of RDX. Owing to the unique characteristics of the compound, it finds application in plastic bonded explosives (PBX) automobile and air bags systems etc. in addition to the applications in military munitions. Results from initial small-scale sensitivity tests indicate that NTO is less sensitive than RDX and HMX in all respects²³⁾.

4.3 TNFX (3,3-bis (difluoramino) octahydro-1,5,7,7-tetranitro-1,5-diazocine)

Zheng and his co-workers²⁶⁾ studied *gem*-bis (difluoramino) substituted heterocyclic nitramines, such as HNFx and TNFX are of interest because of their potentially high density, high energy and superior properties as solid propellant oxidizers. TNFX is a diversified energetic heterocyclic compound. Chapman and his co-workers²⁷⁾ reported the first synthesis of *gem*-dinitro-substituted analog TNFX. The following steps are subjected to the preparation of TNFX; i). CH_2Cl_2 , O_3 , -78°C / Me_2S ; ii). EtOH , $\text{NH}_2\text{OH} \cdot \text{bul} \cdot \text{HCl}$, NaOAc , reflux; iii). CH_2Cl_2 , HNO_3 / NH_4NO_3 / urea, reflux; iv). CH_2Cl_2 , H_2SO_4 and v). CFCl_3 , H_2SO_2 , HNF_2 , -25°C ,

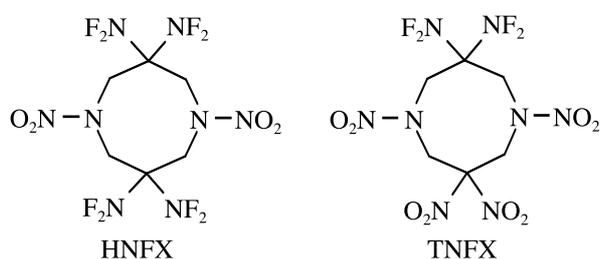
Table 2 Calculated performance data of triazole derivatives 1a, 2a, 2b at TMD (Theoretical Maximum Density)²⁰⁾.

Explosive	Density ρ (g cm^{-3})	Heat of combustion (J g^{-1})	Heat of formation (J g^{-1})	Detonation velocity (km sec^{-1})	Measured detonation velocity (km sec^{-1})	$\sqrt{2E_{\text{Gexp}}}$ Gurney-constant ($\text{mm } \mu\text{s}^{-1}$)
ANTA(1a)	1.82	-10018.9	70.10	8.336	7.710*	2.57
C,C-dinitrobitriazole(2a)	1.89	-10394.0	189.9	8.980	-----	2.61
C,N-dinitrobitriazole(2b)	1.82	-1054.6	515.6	8.980	7.767*	2.75

* Ref: 19

10°C–15°C, 3 hour to produce, after aqueous work-up. TNFX a difluoroamino component desired for energetic combustion of metalized-fuel propellant formulations, and the *gem*-dinitro component provides higher oxygen balance (for more-complete combustion) than analogous all-difluoroamino derivatives²⁸.

Highly deactivated precursor ketones hexahydro-7,7-dinitro-1,5-bis(2- and 4-nitrobenzenesulfonyl)-1,5-diazocin-3(2H)-ones were difluoraminated to the corresponding *gem*-bis (difluoroamino) diazocines. The 1,5-bis(4-nitrobenzenesulfonyl) diazocine derivative underwent N-nitrolysis with the protonitronium reagent formed in the nitric acid-trifluoromethanesulfonic acid-antimony pentafluoride system to produce 3,3-bis(difluoroamino) octahydro-1,5,7,7-tetraniro-1,5-diazocine (TNFX), containing nitramine, *gem*-dinitro, and *gem*-bis(difluoroamino) structural components²⁶.



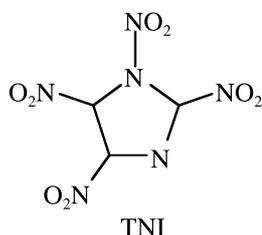
The asymmetric derivative TNFX incorporating both difluoroamino and C-nitro substituents in addition to nitramine may offer potentially superior propellant performance in certain formulations based either on argument involving qualitative chemical features of the ingredient or on computational estimates of its thermodynamic properties. TNFX is expected to be a relatively sensitive high explosive and should be synthesized and handled only by the experts.

4.4 Chemistry of nitroimidazole derivatives

Imidazole derivatives with more than two nitro groups are expected to be highly powerful, but these are insensitive explosives^{29–36}. So far numerous nitroimidazole derivatives including 2,4-dinitroimidazole^{29–31}, 4,5-dinitroimidazole³², 2,4,5-dinitroimidazole³³ and 4,4',5,5'-tetraniro-2,2'-imidazole^{34–35} have been studied. S. G. Cho *et al.*³⁶ have investigated the structure of 1,2,4,5-tetranitroimidazole (TNI) by using various levels of theories.

4.4.1 TNI (1,2,4,5-tetranitroimidazole)

One of the important geometric features in 1,2,4,5-tetranitroimidazole (TNI) is the orientation of nitro groups. Density is an important property in predicting performance of explosive molecules, and molecular packing may be altered significantly due to the orientation of these nitro groups.



S. G. Cho *et al.*³⁶ computed the gas phase heat of formation and molar volume of 1,2,4,5-tetranitroimidazole. These properties will be of importance in evaluating explosive performances. Furthermore, they have extended their study to calculate explosive performances *i.e.*, C-J pressure and detonation velocity of TNI with the molecular properties were estimated the solid phase heat of formation, 65 kcal mol⁻¹, density 2.02 g cm⁻³, the detonation pressure and detonation velocity of TNI to be 386 × 10⁸ Pa and 8.914 km s⁻¹, respectively. According to this result, explosive performances of TNI appear to be in a range of between HMX and RDX. These results predict that the performance of TNI far exceed to those of HMX and surprisingly are significantly different. S. G. Cho *et al.* are anticipating synthetic chemists to provide experimental results in the near future.

5. Nitro cubanes

High energy molecules are important not only for their obvious technological applications as explosives and propellants, but also for their inherently interesting molecular properties. The well known molecule cubane, C₈H₈, which was first synthesized by Eaton and Cole in 1964. As its name suggests, cubane is a molecule made up of eight carbons placed at the corners of a cube with a hydrogen atom covalently bound to each of the carbon atoms. The cubane molecule is so unusual, that its C-C-C bond angle is distorted to 90° thus giving the molecule an enormous amount of strain energy. In addition to being a very powerful explosive material, solid cubane may also have important antiviral and electro-optical properties³⁷.

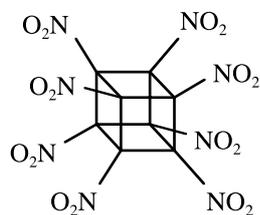
Highly nitrated cubanes and carboxylated cubanes cannot be synthesized because the conversion would proceed through intermediates that contain an electron donating group vicinal to a group that is electron withdrawing, this will cause unavoidable in highly strained cubane cage³⁷. Focus was on the use of 1,4-cubanedicarboxylic acid as a synthetic precursor due to its availability. The possibilities of introducing energetic substituents onto the cubane nucleus were examined with respect to the development of new explosives and energetic materials, and to the development of new methods for the synthetic organic chemistry of cubane. Highly nitrated cubanes are shock insensitive, very dense, high-energy compounds with great potential as explosives and propellants.

5.1 Heptanitrocubane

Heptanitrocubane³⁸ is easily soluble in polar solvents like acetone, tetrahydrofuran and dichloromethane. Solution of heptanitrocubane in methanol turns yellow the wavelength λ_{max} is 458 nm, but it could be colour of the anion. When it is added with trifluoroacetic acid, it will decolorize the solution, evaporation of the solvent returned colourless undecomposed material. It is sensitive to base. Sodium fluoride alone in methanol catalyzed its decomposition, as did amines like 2,2,6,6-tetramethyl piperidine. Powerful deflagrations will occur when a micro drop of pyridine was added to the dry solid.

5.2 Octanitrocubane

A new explosive octanitrocubane has been synthesized by chemists P. Eaton, R. Gilardi and M. X. Zhang³⁸⁾ at the University of Chicago and its structure proven by Richard Gilardi of the Naval Research Laboratory in Washington D.C. According to calculations, octanitrocubane could be more powerful than the best non-nuclear explosives. Oxygen atoms contained in the molecules of the explosive oxidize the other "combustible" parts of the molecule, in most cases carbon and hydrogen. This causes heat and hot gases to be released very quickly leading to an explosion. In a detonation, the most violent form of explosion, speeds up to 10 km s⁻¹, temperatures up to 6,000°C, and pressures up to 3 × 10¹⁰ Pa can be achieved in the shock wave. Synthesis of the new octanitrocubane explosive was tricky, because it is based on cubane, whose molecular "framework" consists of eight carbon atoms held rigidly at the corners of a cube. Such a frame is under high strain and can very easily burst, giving off energy. The researchers had to very cautiously attach a nitro group to each of the corners of the cube in order to make the desired product. Octanitrocubane is one of the most dense compounds built only of carbon, nitrogen and oxygen. Surprisingly, however, in its present crystal form it is significantly less dense than predicted by theory. High density is crucial to the strength of an explosive, because the pressure of the detonation increases tremendously with increasing density of the explosive.



Octanitrocubane

It is very stable compound kinetically. Such compounds need to be purposefully detonated and it could even become large constructions site regulars if it is cheap enough, P. Eaton and his co-workers³⁸⁾ took effort to synthesize a molecule even more energetic than cubane, they have successfully replaced all eight hydrogen atoms of cubane with nitro (NO₂) groups to form octanitrocubane, C₈N₈O₁₆.

Eaton credits scientists at the U S Army arsenal in Picatinny, New Jersey for coming to decades ago with the idea that led to the synthesis of octanitrocubane. Today, the standard military explosive HMX is less powerful than octanitrocubane and is difficult to safely manufacture because of shock sensitivity. Because of the strong electron-withdrawing properties of these nitro groups, octanitrocubane has been speculated to be even more energetic than the N-nitro compound HMX, which is one of the most energetic substances known till date. In fact we can hit octanitrocubane with a hammer and nothing happens. Part of the military's interest in the research stemmed from the belief that octanitrocubane would be insensitive to shock. As the detonation pressure at the shock wave front in an

explosion is thought to be proportional to the square of the density of the explosive.

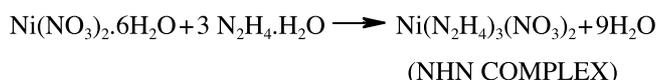
The predicted value for density of octanitrocubane is 1.9-2.2 g cm⁻³ and the heat of formation (ΔH_f) is 81-144 kcal mol⁻¹. This leads to calculated detonation velocities and pressures much higher than that of the classic C-nitro explosive TNT and also 15-30% greater than that of N-nitro compound HMX, presently the most energetic of standard military explosives and even better than that of experimental the polycyclic nitramine.

6. Nickel hydrazine nitrate (NHN) complex

NHN complex is a new primary explosive³⁹⁾. It is a thermally and hydrolytically stable solid. It can easily be prepared from available raw materials. Its preparation liquor can be used repeatedly, which means no waste water pollution in industrial manufacture.

NHN complex is not sensitive to impact, friction or electrostatic charge, but is more sensitive to flame. Its preparation is much safer than other initiators so does its handling. One of the critical factors is its crystal shape polycrystal which is similar to the diazodinitrophenol (DDNP). It is demonstrated that NHN complex is suitable as a replacement for lead azide as an intermediate charge in commercial detonators.

Lead azide is a main primary explosive, which is very important for civil or military purpose. It can be easily obtained by the reaction between sodium azide and aqueous lead salt. But the manufacture of sodium azide will cause inevitable harms to person because of its toxic gases (hydrazoic acid fumes). Although NHN complex has been reported in the middle of the century it has not as yet found application. In fact, some properties of NHN complex are much better than that of lead azide, because of its low mechanical sensitivity, good stability and no effect to light. The preparation of NHN complex is also very simple in laboratory, which makes it easy for perpetrators of crime to have ready accessibility. The reaction can be represented as;



The heat of explosion, Q, is 1014 cal g⁻¹ in 1 atm of air. NHN complex gets burning on reaction with 96% sulphuric acid at room temperature and the weak solution of acid only makes its decomposition gently. NHN complex reacts mildly with 10% sodium hydroxide and this can be used as a method of disposal. Unlike other primary explosives, NHN does not change its characters on prolonged exposure to sunlight, neither to the X-ray. In the approaching electrostatic test, NHN appears considerably less sensitive than other primary explosives.

The sensitivity of the NHN complex to the mechanical action is also very weak. The detonation character of NHN complex under different pressure, NHN complex will display different performance to the normal ignition of safety fuse. The detonation velocity and sensitivity data of NHN complex in comparison with other explosives is given in Table 3. NHN complex after washing with ethanol, filtered and dried in vacuum, could be ignited with safety fuse and deflagrated rapidly.

Table 3 Detonation velocity and sensitivity data of NHN in comparison with other explosives³⁹⁾.

Compound	Detonation velocity km sec ⁻¹	Density g cm ⁻³	Electrostatic (Joule)	Friction ^a (%)	Impact ^b [cm]	Five-second explosion ^c temperature [°C]
Lead azide	4.630	3.0	0.003	100	24	345
Lead-styphnate	4.900	2.6	0.0009	70	36	282
DDNP	6.600	1.5	0.012	25	40	172
NHN	7.000	1.7	0.02	12	26	167

^a Explosion percentage of 25 samples under 588.40 kpa and 80° swinging angle.

^b Drop-hammer test, height to give 100 % fire.

^c The five-second explosion temperature test is run with 20 mg of NHN. At this dosage, NHN showed extensive disruption of the containing blasting cap and splashing of the wood's metal from the test vessel.

7. Hafnium explosives

Hafnium Explosive is an exotic kind of nuclear explosive being developed by the US Department of Defence that could trigger the next arms race, says a report in *New Scientist*⁴⁰⁾. It could make the critical distinction between conventional and nuclear weapons. The explosive works by stimulating the release of energy from the nuclei of certain elements but does not involve nuclear fission or fusion. The energy, emitted as gamma radiation, is thousands of times greater than that from conventional chemical explosives. The explosive consolidation method, developed to prepare combustion synthesized TiC and TiB₂, was applied to Hafnium Carbide (HfC). This method results in a moderately dense HfC product. Sample confinement and configuration, explosive loading, and total heat available for the combustion-synthesis process affected product characteristics. Kecskes *et al.*⁴¹⁾ described the key features of the process as well as some of the properties of the HfC ceramics.

Scientists have known for many years that the nuclei of some elements, such as hafnium, can exist in a high-energy state, or nuclear isomer, that slowly decays to a low energy state by emitting gamma rays. Before hafnium can be used as an explosive, energy has to be "pumped" into its nuclei. Just as the electrons in atoms can be excited when the atom absorbs a photon, hafnium nuclei can become excited by absorbing high energy photons. This process could be explosive, was discovered when Carl Collins and colleagues at the University of Texas at Dallas demonstrated that they could artificially trigger the decay of the hafnium isomer by bombarding it with low-energy X-rays. The hafnium explosive could be extremely powerful. One gram of fully charged hafnium isomer could store more energy than 50 kilograms of TNT. Miniature missiles could be made with warheads that are far more powerful than existing conventional weapons, giving massively enhanced firepower to the armed forces.

8. Heat-resistant explosives

Based on experimental research, some synthetic methods for a new type of heat-resistant explosives were suggested

by Lu Chunxu⁴²⁾. More recent development in explosives have seen the production of hexanitrostilbene (HNS). The compound HNS is an extremely thermally stable explosive that was first invented at the United States of America naval logistic laboratory in 1964 and triaminotrinitrobenzene (TATB, 1, 3, 5-triamino-2, 4, 6-trinitrobenzene), in 1978 by Adkins and Norris. Both of these materials are able to withstand relatively high temperatures compared with other explosives.

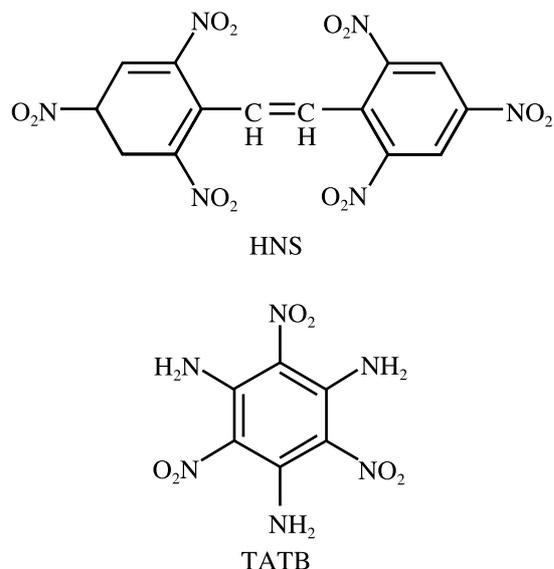
8.1 TATB (1,3,5-triamino-2,4,6-trinitrobenzene)

TATB was first prepared in 1888 by Jackson and Wing, who also determined its solubility characteristics. In the 1950s, the USA Naval Ordnance Laboratories recognized TATB as a heat-resistant explosive, and successful small-scale preparations and synthetic routes for large-scale production were achieved to give high yields. TATB forms an unusually stable free radical upon irradiation with UV light. Extension with DMSO yields a liquid solution. ESR spectrum which is, apparently, due to a TATB-H adduct⁴³⁾.

TATB was prepared from trichlorobenzene by nitration and then amination by V. H. Evans⁴⁴⁾. A new, three-stage synthesis of TATB was developed which avoids the use of halogenated precursors or reagents. The starting material, 1, 3, 5-trihydroxy-benzene, is converted via the sequence nitration-alkylation-amination to TATB in an overall yield of 87%. The product, when 1, 3, 5-tripropoxy-2, 4, 6-trinitrobenzene is the intermediate subjected to amination, is directly comparable, in terms of purity and thermal stability, to TATB synthesized from trichlorobenzene. An analogous route was used to convert 1, 3-dihydroxybenzene to 1, 3-diamino-2, 4, 6-trinitrobenzene (DATB), and phenol to picramide via picric acid⁴⁵⁾. Xing *et al.*⁴⁶⁾ described a method for synthesizing TATB by condensation reaction of 3, 5-dichloroaniline and tricyanogen chloride, the condensation product is then nitrated and aminated with a yield of 80% compared with the traditional method, this procedure is easy to realize and the cost of starting materials is relatively inexpensive.

8.2 Hexanitrostilbene (HNS) explosive

HNS is a well known heat resistant explosive. A new method for synthesizing a heat-resistant explosive HNS or HNS-I (recrystallised HNS) in two steps from TNT starting material through hexanitrobibenzyl (HNBB) intermediate was examined by Ming *et al.*⁴⁷⁾. HNS can be prepared directly from HNBB by oxidation with Br₂. The overall yield based on TNT was >65% for HNS, and is >59% for HNS-I. Achuthan *et al.*⁴⁸⁾ reviewed, with 55 references on the preparation, properties, and uses of HNS.



The HNS has specific applications in military industries, ballistic missile systems, shuttles, and explosive fuse⁴⁹⁾. The performance of ignition and combustion of HNS explosive was studied through a series of small igniting devices in which B/KNO₃ ignition composition was used as igniting energy of HNS explosive. Some important factors which affected ignition and combustion of HNS explosive were pointed out and analyzed, and the igniting mechanism of HNS explosive is discussed by Meilin *et al.*⁵⁰⁾ [50]. A review of properties, production methods, and technology of hexanitrostilbene explosive and a comparative study of existing production methods and perspectives of this explosive usage is reviewed by Zhilin *et al.*⁵¹⁾. Also Rieckmann *et al.*⁵²⁾ studied the thermal decomposition of HNS.

HNS was investigated by simultaneous TGA/DTA at heating rates between 0.05–40°C min⁻¹. Depending on the temperature and time history, the reaction takes place either in the solid phase or in the liquid phase after melting of the sample. In order to observe the solid phase reaction, experiments with

constant heating rates well below 2.5°C min⁻¹ have to be performed. Therefore, it is impossible to judge the thermal stability of solid HNS by using kinetic models derived from DSC experiments at heating rates of 10–20°C min⁻¹, as is the standard procedure. Poly-HNS, as a HNS-based new booster explosive, is characterized by higher heat resistant and safety in processing. The manufacturing process of the poly-HNS-based explosive was discussed by Cao and Fengying⁵³⁾ in relation to the bonding mechanism and effects of processing conditions, such as temperature, stirring rate, etc.

Hexanitrostilbene (HNS) is added to trinitrotoluene (TNT) in order to improve the grain structure of cast munitions⁵⁴⁾. The formation and composition of the nucleant material was investigated by thermal methods using mixtures of HNS and TNT, with composition in the range 0.5 %, the normal casting level, to 50 % HNS to TNT. These were cycled between ambient and upper temperatures of 160°–235°C. Endotherms in the DSC traces, due to nucleant decomposition, were observed *in-situ* without the need for separation and purification DSC enthalpy measurements, before and after thermal decomposition, and were used to determine the composition of separated nucleant. Nucleant regeneration after decomposition was investigated by thermal methods. The nucleant could not be recrystallised from solvents. The results were interpreted based on the formation of a solid solution of TNT in HNS, rather than a complex of formula (TNT)₂-HNS. David and Louis⁵⁵⁾ analyzed 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB), a non-volatile explosive used in some weapon high-explosive formulations.

The safety during storage, transportation and use, long shelf life, reliability and ease of filling into ordnance are very important requirements for military explosives. These requirements have led to a series of compositions capable of fulfilling all of these requirements based almost on the explosive molecules RDX, HMX and TNT together with a limited use of PETN and a few highly specialized compounds such as HNS, TATB, 2, 4, 6-tripicryl-5-triazine (TPT) and 1, 3, 3, 5, 7, 7-hexanitro-1, 5-diaza cyclooctane (HCO). The performance of these as pure compounds together with some safety related data are given in Table 4.

8.3 HTX (High-Temperature Explosive)

The explosive, called HTX (high-temperature explosive), is formulated from TATB and HNS, which are known for their high thermal stability⁵⁶⁾. The combination has performance that is superior to shaped charges made with either of its individual constituents. This particular formulation was also easier to use in the manufacture of shaped charges than other com-

Table 4 Performance data for some high temperature stable explosives^{45) 48) 50) 54)}.

Compound	Melting point (°C)	Density (g cm ⁻³)	Detonation velocity (km s ⁻¹)	Detonation pressure (Pa)
HNS	316	1.70	7.000	21 × 10 ⁹
TATB	340	1.87	7.610	27 × 10 ⁹
HCO	250	1.84	8.800	36 × 10 ⁹

mon high-temperature explosives, such as HNS, because of its better filling and pressing properties. The data were presented for shaped charge performance that compares HTX to other common explosives commonly used in oil-well perforating. HTX offers about a 5-10% increase in penetration over HNS.

8.4 TAAP and TAAT

TAAP and TAAT are thermally stable new explosives⁵⁷. In the synthesis of the new explosives, 2, 6-bis (2, 4, 6-trinitroanilinoacetamido) pyridine (TAAP), and 3, 5-bis (2, 4, 6-trinitroanilinoacetamido)-4*H*-1, 2, 4-triazole (TAAT), trinitroanilinoacetic acid chloride was used as a building block. A successful strategy for the synthesis of thermally stable explosives is the condensation of aromatic amino compounds with picryl chloride, producing 3, 5-dinitro-*N,N'*-bis (2, 4, 6-trinitrophenyl)-2, 6-pyrimidinediamine (PYX) and 3-(2, 4, 6-trinitrophenylamino)-1, 2, 4-triazole (PATO). It was also well known that the amide group imparts thermal stability. Thus, a combination of these two approaches was adopted to synthesize two new explosives. TAAP and TAAT were characterized from the IR and NMR spectroscopy. Differential thermal analysis showed the onset of decomposition initiation temperature of 195°C for TAAP and 310°C for TAAT.

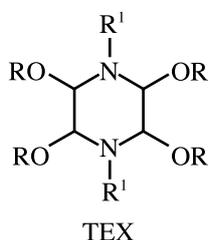
8.5 Heat-resistant industrial explosives

When explosives are heated under acidic environment, due to metal sulfide and sulphuric acid, their decomposition temperature falls remarkably and decomposition reaction occurs quickly, and then explosives have the risk of the deflagration to the detonation transition. Heat resistant industrial explosives which can be used under condition of high temperature of 200°C and acidic environment were studied by Kenji *et al.*⁵⁸. The explosive composition consisted of ammonium perchlorate as oxidizer saturated hydrocarbon oil as fuel and binder, and calcium carbonate as decomposition inhibitor is developed. The characteristics of this explosive composition show the heat resistance for > 24 h at 200°C, and the detonation velocity > 2.5 km s⁻¹. This explosive composition has a cap-sensitivity at temperature > 80°C.

9. New insensitive high explosives

9.1 TEX (4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo.5.0.0^{5,9}.0^{3,11}]dodecane)

TEX is a promising new insensitive high explosive⁵⁹. A series of new explosives were developed based on the new insensitive high explosive TEX. The Thiokol Corporation (USA) had developed an improved 2 step synthetic route for the production of TEX which involved the use of readily available, low cost materials. Characteristics of TEX were studied.



- (1). R (as part of the -OR leaving group) is R¹, -CR¹O, -COOR¹, SO₃R¹, NO, -NO₂, acetal and cycloacetal, and
- (2). R¹ is a nitrolyzable group, such as H, C1-10-alkyl, branched alkyl, cycloalkyl, Ph, substituted Ph, and monocyclic heterocyclic moieties.

S. Andrew *et al.*⁶⁰ synthesized the explosive TEX, by reacting a hexa-substituted piperazine with a nitrate source and a strong acid, such that the reaction proceeds through 3 stages: (1) a highly exothermic stage which requires cooling to maintain a reaction temperature of 80°C, (2) an intermediate non-exothermic stage to maintain the above reaction temperature and (3) an undesired autocatalytic and exothermic NO_x-generation stage. At the end of step (2), the reaction is cooled to about 0°C to prevent initiation of the unwanted step (3) (to prevent step (3) from reaching an exothermic stage).

TEX is more thermally stable and less sensitive to shock, impact, and friction than conventional solid nitramines like RDX, HMX, or CL-20. The density of compound TEX 1.99 g cm⁻³, the detonation velocity 8.665 km s⁻¹ and the detonation pressure 37 × 10⁹ Pa. It proceeds from deflagration to detonation less probably than conventional nitramines. Theoretical performance calculations of TEX revealed increased performance relative to NTO, due to its high density. The problems are analyzed of setting new explosives and explosive compounds with classification of low vulnerable ammunition (LOVA) explosives. Vagenknecht⁶¹ made a brief analysis of known characteristics of explosives is realized with TEX as the low vulnerable explosive.

9.2 PADNT (4-picrylamino-2,6-dinitrotoluene)

PADNT is a new insensitive explosive. A chemoselective reductive method has been achieved for the preparation of PADNT, which has been characterized by spectral data and elemental analysis. Some explosive properties of the compound have also been determined by Mehilal *et al.*⁶². The results indicate that PADNT is quite safe to impact and friction.

9.3 DANTNP (5-nitro, 4,6-bis (5-amino-3-nitro-1*H*-1,2,4-triazole-1-yl) pyrimidine)

DANTNP is also a new insensitive high explosive. The synthesis of DANTNP was synthesized by Wartenberg *et al.*⁶³. The reaction of the sodium salt of 5-amino-3-nitro-1, 2, 4-triazole with 4, 6-dichloro-5-nitropyrimidine was characterized by ¹⁵N and ¹³C-NMR spectroscopy. DANTNP had a density of 1.810 g cm⁻³ and detonation velocity of 8.2 km s⁻¹.

10. DNNC, HCO and TNAD: New high-energy materials

DNNC (1, 1, 3, 5-tetranitrohexahydropyrimidine), HCO (1, 3, 3, 5, 7, 7-hexanitrooctahydro-1, 5-diazocine and TNAD (*trans*-1, 4, 5, 8-tetranitro-1, 4, 5, 8-tetraazadecalin) are three new high energetic materials. The synthetic technology of TNAD and the effects of reaction parameters and reactant introduction on the yields were studied and discussed by Yunyang *et al.*⁶⁴. Cheng-Shyong and Tschau-Gan reviewed⁶⁵, with 47 references of the preparation, characterization, and properties of these three novel high-energy materials.

11. Conclusion

To contain terrorism and to keep pace with the know how attained by various terrorist groups world over, using new technologies, it is imperative that forensic scientists are required to equip themselves with the latest knowledge in the field of development of new explosives. Some of the explosives discussed above could be prepared by simple chemical reactions and therefore the chance of them being prepared by insurgent groups cannot be ignored. High energy molecules continue to play an important technological applications as well as fundamental scientific interest. For these forensic scientists should be constantly in touch with the latest literature and should have close interaction with other scientists working in the field of synthetic chemistry. New analytical methods should either be developed or existing methods be suitably modified for trace identification of newly developed explosives and post blast residues.

The forensic scientist faces difficulty in identification of explosives in post blast cases because the amount of explosion residue available for analysis is meagre. To add his hardship, new explosives are being used for which analytical methods are not available. Some of the high energy materials under research do not leave any residue. This gives incomplete and sometimes incorrect inferences that affect proper disposal of justice. Hence testing procedures should be modified to include a wider list of newly emerging high energetic materials.

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