



Past, Present & Future of Thermally Stable Explosives^{*)}

Jai Prakash AGRAWAL

Directorate of Materials, DRDO HQ, New Delhi, India

E-mail: jpagra@gmail.com

Abstract: Explosives with improved high temperature properties are usually referred to as ‘thermally stable explosives’ or heat-resistant explosives. They are safer, more reliable and more stable at elevated temperatures and find applications in modern Ordnance, Space and Nuclear applications. This paper discusses general approaches for the synthesis of thermally stable explosives, their properties and specific applications. This paper also gives a comparative account of the properties of some of the most thermally stable explosives reported so far. Based on their ease of synthesis, properties (mainly stability at elevated temperatures and insensitivity to impact, friction and percussion) and cost, TATB is considered as a benchmark, thermally stable explosive which is discussed in detail. Furthermore, this review also describes the synthesis and properties of BTDAONAB which does not melt below 550 °C and is considered a better thermally stable explosive than TATB. Finally, a new line of research in this field in the years to come is also highlighted.

Keywords: explosives, thermally stable explosives, heat-resistant explosives

Introduction

High Energy Materials (HEMs) is a generic term which is used for explosives, propellants and pyrotechnics. These are generally perceived as the ‘devil’ during war and considered as an ‘evil’ during handling, transportation and storage, but have proved to be an ‘angel’ due to their innumerable applications in almost all walks of life. Explosives are used for civil as well as military applications. Of course, high performance has always been a prime requirement in the field of

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research and development of explosives. But more recently, research is in progress worldwide in the search for explosives with a combination of properties such as safety, reliability, stability, cost-effectiveness and eco-friendliness [1]. There are several methods for their classification [2]. While reviewing the research in the field of high energy materials (HEMs), Agrawal et.al. proposed an altogether different way for their classification which is based on one single, most important property – either thermal stability or high performance or insensitivity etc. [3], and accordingly, HEMs reported in the literature have been classified as:

- Thermally stable or heat-resistant explosives (DATB, TATB, HNS, PATO & its nitro derivatives, DIPAM, TPM, PYX, NONA, BTDAONAB etc.);
- High Performance (high density & high velocity of detonation) explosives (RDX, HMX, TNGU, TNPDU, HNIW/CL-20, TNABN, DNCC etc.);
- Melt-Castable Explosives (TNT, Tris-X, TNAZ, DNBF etc.);
- Insensitive High Explosives (IHEs – TATB, ADNBF, NTO, DINGU, ANTA, TNAD, FOX-7, FOX-12 etc.);
- Energetic Binders [PNP, GAP, NHTPB, Poly (NiMMO), Poly (GlyN) etc.] & Plasticizers [NG, EGDN, DEGDN, TEGDN, BTTN, BDNPF/A, Bu-NENA etc.] for explosives/propellants;
- Novel Energetic Materials synthesized with the use of dinitrogen pentoxide (N_2O_5) Technology [NHTPB, Poly (NiMMO), Poly (GlyN), ADN etc.].

Explosives with improved high temperature properties are usually referred to as thermally stable or heat-resistant explosives. These are safer, more reliable and more stable at elevated temperatures, and find applications in modern ordnance, space and nuclear applications [4]. This paper discusses the general approaches for the synthesis of thermally stable explosives, their properties and specific applications.

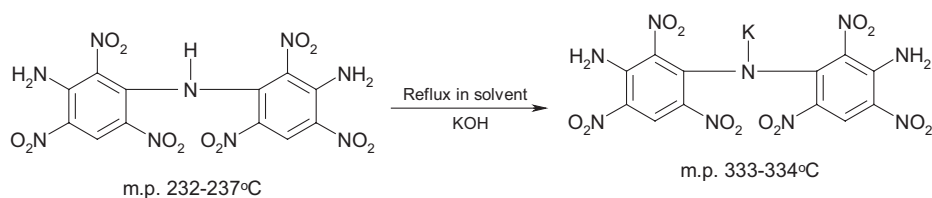
General Approaches for the Synthesis of Thermally Stable Explosives

For the synthesis of thermally stable explosives, nitro compounds have received special attention because of their ability to withstand high temperatures and the low pressures encountered in space environments. Research on heat-resistant explosives was reviewed first by Dunstan [5], followed by Urbański & Vasudeva [6], and Lu [7], and more recently by Agrawal [3, 4]. In some countries, cyclotetramethylene tetranitramine (HMX) with a melting point of 291 °C, is also regarded as a heat-resistant explosive and its safe working limit is 225 °C [8].

An analysis of the structures of well known, thermally stable explosives shows clearly that there are broadly four general approaches to impart thermal stability to explosive molecules [9, 10]:

- i) Salt formation;
- ii) Introduction of amino groups;
- iii) Introduction of conjugation;
- iv) Condensation with a triazole ring.

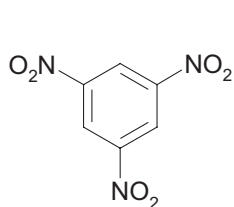
i) Salt formation: Thermal stability is enhanced by salt formation [11]. This may be illustrated by the following example:



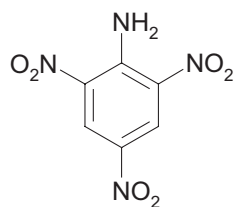
3,3'-Diamino-2,2',4,4',6,6'-
-hexanitrodiphenylamine

Potassium salt of 3,3'-diamino
-2,2',4,4',6,6'-hexanitrodiphenylamine

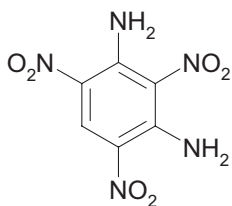
ii) Introduction of amino groups: The introduction of an amino (-NH₂) group (in the ortho position) into a benzene ring already having a nitro (-NO₂) group is one of the simplest and oldest approaches for enhancing the thermal stability of explosives. This is evident from the study of the effect of the introduction of amino groups in 1,3,5-trinitrobenzene [TNB] to form monoamino-2,4,6-trinitrobenzene [MATB], 1,3-diamino-2,4,6-trinitrobenzene [DATB] and 1,3,5-triamino-2,4,6-trinitrobenzene [TATB], where the order of thermal stability is MATB < DATB < TATB [12-14, Figure 1].



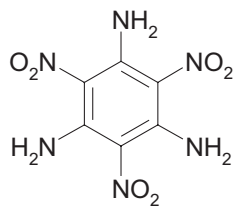
m.p. 122°C
Structure (2.18)



m.p. 192°C
Structure (2.19)



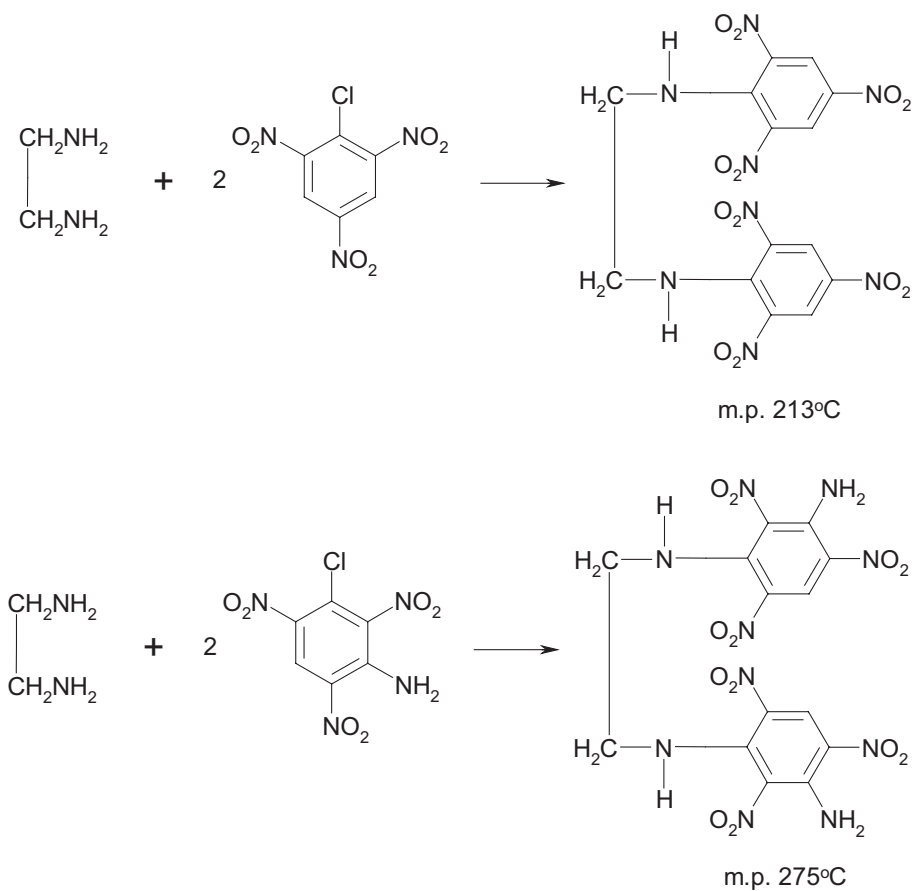
m.p. 286°C
Structure (2.20)



m.p. >350°C
Structure (2.21)

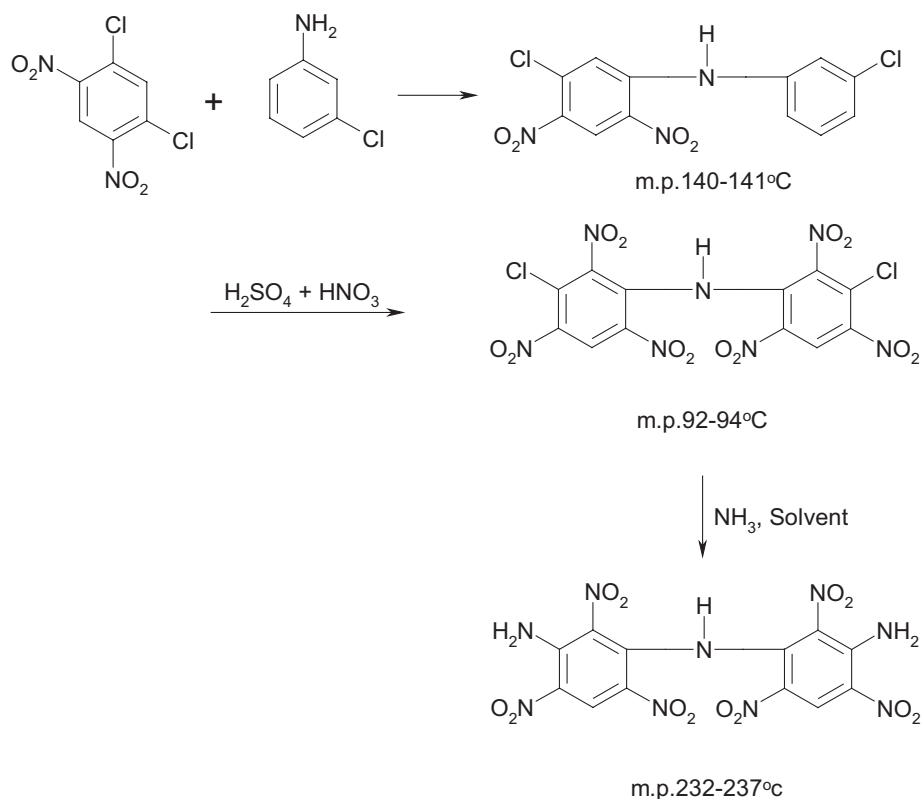
Figure 1. Structures of mono, di and tri amino derivatives of 1,3,5-trinitrobenzene (TNB).

The concept of enhancing thermal stability by the introduction of amino groups is further supported by the work of a Chinese team [7] and some typical examples are shown under Schemes 1 & 2.



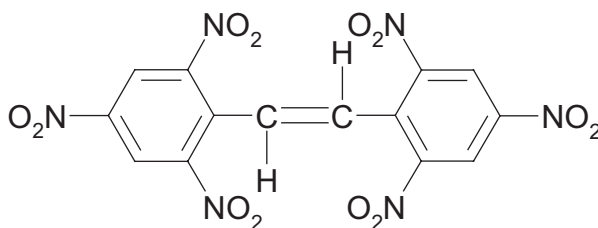
Scheme 1. Synthesis of bis-N,N'-(2,4,6-trinitrophenyl)ethylenediamine and its diamino derivative.

Similarly,



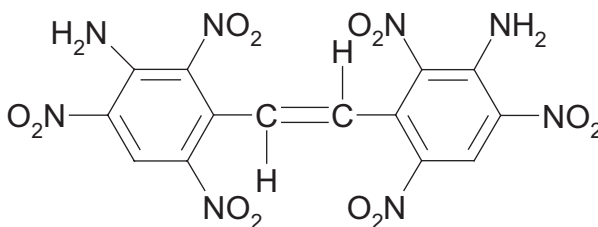
Scheme 2. Synthesis of 3,3'-diamino-2,2',4,4',6,6'-hexanitrodiphenylamine.

This aspect is also evident from the following example. 2,2',4,4',6,6'-Hexanitrostilbene (HNS) is an explosive with excellent heat resistance which is further enhanced by the introduction of amino groups.



m.p.316°C

2,2',4,4',6,6'-Hexanitrostilbene (HNS)



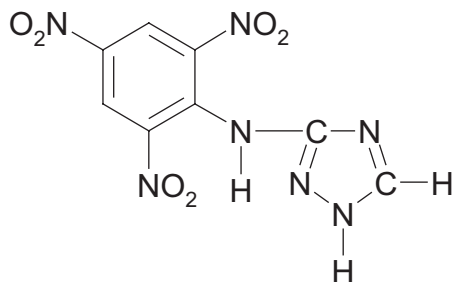
m.p.Very high

3,3'-Diamino- HNS

iii) Introduction of conjugation: The best example of how the introduction of conjugation in explosive molecules imparts higher thermal stability is hexanitrostilbene (HNS), synthesized by Shipp of the American Naval Ordnance Laboratory (NOL) in 1964 [15]. One method of synthesis of HNS ($\approx 50\%$ yield) involves reaction of 2,4,6-trinitrobenzyl chloride with sodium hydroxide in THF-methanol [16]. The yield of HNS could be increased to 70% by treating the same substrate with 2.4 mole equivalents of triethylamine in the same solvent mixture [17]. Plants for full-scale production based on the method of Shipp [18] exist in the UK and China. It has proved its efficiency as a heat-resistant explosive as well as a component of heat-resistant formulations employed in the Apollo spaceship and for seismic experiments on the moon. HNS has also been reported for use in achieving stage separation in space rockets [19]. In a similar manner to HNS, conjugation exists in hexanitroazobenzene (HNAB) and hexanitrotetrachloroazobenzene (HNTCAB), which are also interesting explosives from the point of view of thermal stability [20].

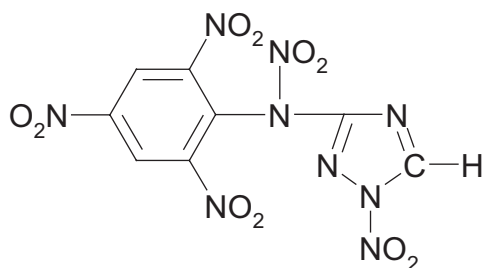
iv) **Condensation with triazole ring/s:** Coburn & Jackson [11, 21] studied in detail the synthesis of various picryl and picrylamino substituted 1,2,4-triazoles by condensing 1,2,4-triazole or amino-1,2,4-triazole with picryl chloride (1-chloro-2,4,6-trinitrobenzene) and established their structures by infrared (IR) & proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectroscopy. PATO (3-picrylamino-1,2,4-triazole) is a well known, thermally stable explosive and is obtained by the condensation of picryl chloride with 3-amino-1,2,4 triazole. It has a crystal density of 1.94 g cm^{-3} , a calculated velocity of detonation (VOD) 7850 ms^{-1} , a Chapman-Jouguet pressure (P_{CJ}) 30.7 GPa and impact sensitivity $> 320 \text{ cm}$ (2.5 kg weight). It is relatively inexpensive and was originally considered as one of the potentially useful thermally stable explosives. At the same time, it is as insensitive as TATB. It was initially thought that it would replace TATB in future applications but its performance is inferior to TATB.

PATO has also been synthesised by a Chinese team [22] through the condensation of tetryl with 3-amino-1,2,4-triazole and their data on its thermal stability is in agreement with the American investigators.

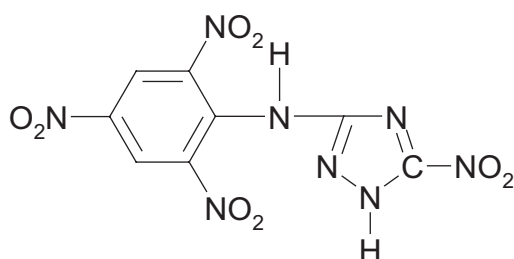


3-Picrylamino-1,2,4-triazole (PATO)

In addition to the Chinese investigators, Indian scientists have also reported two nitro derivatives of PATO and a comparison of their properties with PATO indicates that their thermal stability is not as good as that of the parent compound, i.e. PATO [10].

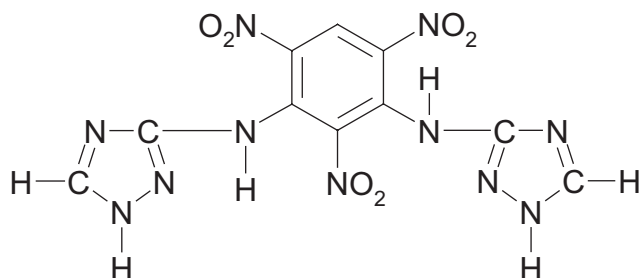


Nitro derivative of PATO-I



Nitro derivative of PATO-II

Similarly, a new explosive called 1,3-bis(1',2',4'-triazol-3'-ylamino)-2,4,6-trinitrobenzene [BTATNB] [previously named as 1,3-bis(1,2,4-triazolo-3-amino)-2,4,6-trinitrobenzene] has also been prepared by the condensation of styphnyl chloride (1,3-dichloro-2,4,6-trinitrobenzene) with 3-amino-1,2,4-triazole by Agrawal et al. [23] and characterized for its structural aspects, thermal and explosive properties.



1,3-Bis(1',2',4'-triazol-3'-ylamino)-2,4,6-trinitrobenzene (BTATNB)

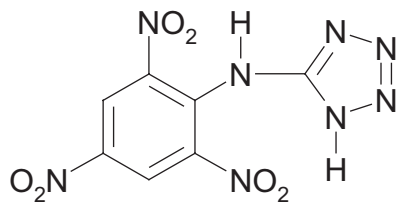
The data indicate that BTATNB is only slightly more thermally stable (m.p. 320 °C as compared to 310 °C for PATO), coupled with better insensitivity

towards impact and friction. But further research has not been pursued on this new explosive.

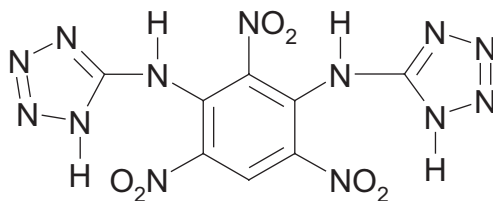
Agrawal et.al. have also developed two new explosives by condensation of:

- i) Picryl chloride with 5-amino-1,2,3,4-tetrazole, designated as 5-picrylamino-1,2,3,4-tetrazole (abbreviated as PAT) [24];
- ii) Styphnyl chloride with 5-amino-1,2,3,4-tetrazole, designated as 1,3-bis(1',2',3',4'-tetrazol-5'-ylamino)-2,4,6-trinitrobenzene [previously named as 5,5'-styphnylamino-1,2,3,4-tetrazole (abbreviated as SAT)] [25].

These have been characterized for structural aspects, thermal behaviour and explosive properties. The data, however, indicate that these are not thermally stable explosives.



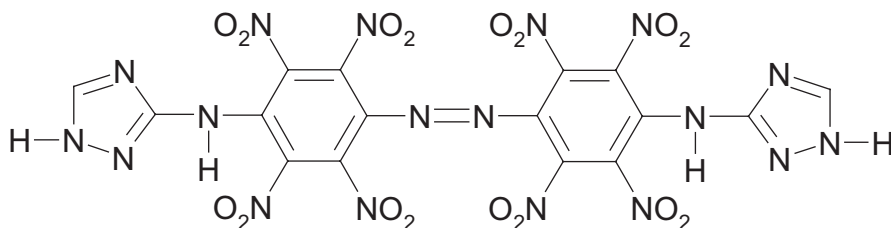
5-Picrylamino-1,2,3,4-tetrazole (PAT)



1,3-Bis(1',2',3',4'-tetrazol-5'-ylamino)-2,4,6-trinitrobenzene [previously named as 5,5'-styphnylamino-1,2,3,4-tetrazole (SAT)]

The proposal of concepts for imparting thermal stability to explosives by the four general approaches listed earlier is further supported by the synthesis of 4,4'-bis(1,2,4-triazol-3-ylamino)-2,2',3,3',5,5',6,6'-octanitroazobenzene [previously named as N,N'-bis(1,2,4-triazol-3-yl)-4,4'-diamino-2,2',3,3',5,5',6,6'-octanitroazobenzene (BTDAONAB)] via nitration-oxidative coupling of 4-chloro-3,5-dinitroaniline followed by nucleophilic displacement of the chloro groups with 3-amino-1,2,4-triazole [26]. This new explosive contains amino groups as well as conjugation and therefore has the unique distinction of being the most thermally stable explosive reported so far (DTA exotherm ~ 550 °C) as compared to well known thermally stable explosives

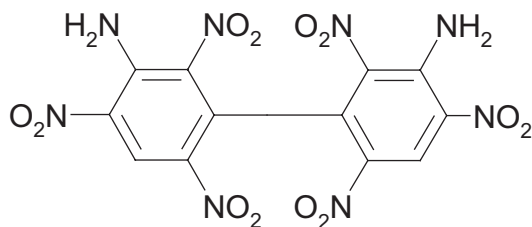
such as TATB (~ 360 °C), TACOT (~ 410 °C), NONA (~440 – 450 °C) and PYX (~ 460 °C).



4,4'-Bis(1,2,4-triazol-3-ylamino)-2,2',3,3',5,5',6,6'-octanitroazobenzene
[previously named as N,N'-bis(1,2,4-triazol-3-yl)-4,4'-diamino-
2,2',3,3',5,5',6,6'-octanitroazobenzene (BTDAONAB)]

In addition to the already mentioned thermally stable explosives, there are other well known, thermally stable explosives which have additional attractive features and are described below:

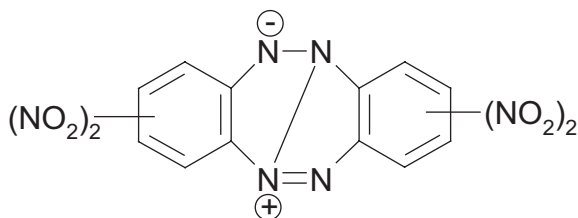
- **3,3'-Diamino-2,2',4,4',6,6'-hexanitrodiphenyl (DIPAM):** This is an explosive extremely insensitive to electrostatic discharge, requiring more than 32 kJ for initiation. Furthermore, it has good thermal stability and for these reasons, it has been used to achieve stage separation in space rockets and in seismic experiments on the moon in a manner similar to HNS [27].



3,3'-Diamino-2,2',4,4',6,6'-hexanitrodiphenyl (DIPAM)

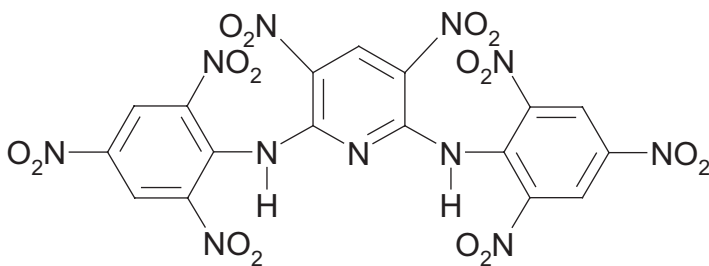
- **Tetranitro dibenzo-1,3a,4,4a-tetraazapentalene (TACOT):** This is an explosive from Du Pont and is a mixture of isomers with two nitro groups substituted in different positions in each benzene ring. As these isomers have similar explosive and thermal properties, they are not separated during the making of explosive formulations. It is an explosive with unusual and outstanding high temperature stability. Its ignition temperature (ca. 497 °C) is the highest registered for an explosive [28]. However, its differential thermal analysis (DTA) curve shows that it is stable up to 354 °C, after

which a slight exothermic reaction starts, which builds into a very rapid deflagration exotherm at 381 °C leading to explosion. As a result, its use is not recommended beyond 354 °C [29]. The VOD of TACOT is 7250 m s⁻¹ at a density of 1.64 g cm⁻³.



Tetranitro-2,3,5,6-dibenzo-1,3a,4,6a-tetraazapentalene, or its older name 1,3,7,9-tetranitrodibenzo-1,3a,4,6a-tetraazapentalene (TACOT Z)

- **2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX):** This is produced in high yields from relatively inexpensive starting materials [30, 31]. PYX has already been commercialized in America and Chemtronics Inc. is currently producing it under licence from Los Alamos National Laboratory, Los Alamos, for use in thermally stable perforators for oil and gas wells. Because of relative economics, PYX is increasingly being used as a substitute for HNS and it is gradually replacing HNS for most commercial applications where thermally stable explosives are required.



2,6- Bis(picrylamino)-3,5-dinitropyridine (PYX)

The most promising, thermally stable explosives and their properties are given in Table 1.

Table 1. Most promising thermally stable explosives and their properties

Name	Melting point (°C)	Density (g cm ⁻³)	Impact sensitivity for 50% probability (cm)	Detonation velocity (m s ⁻¹)
TATB	>350	1.94	very insensitive	8000
TACOT	494 (ignition)	1.85	very insensitive	7250
PYX	460	1.75	63	7450
BTDAONAB	does not melt or show any change; gives an exotherm at 550	1.97	87	8321

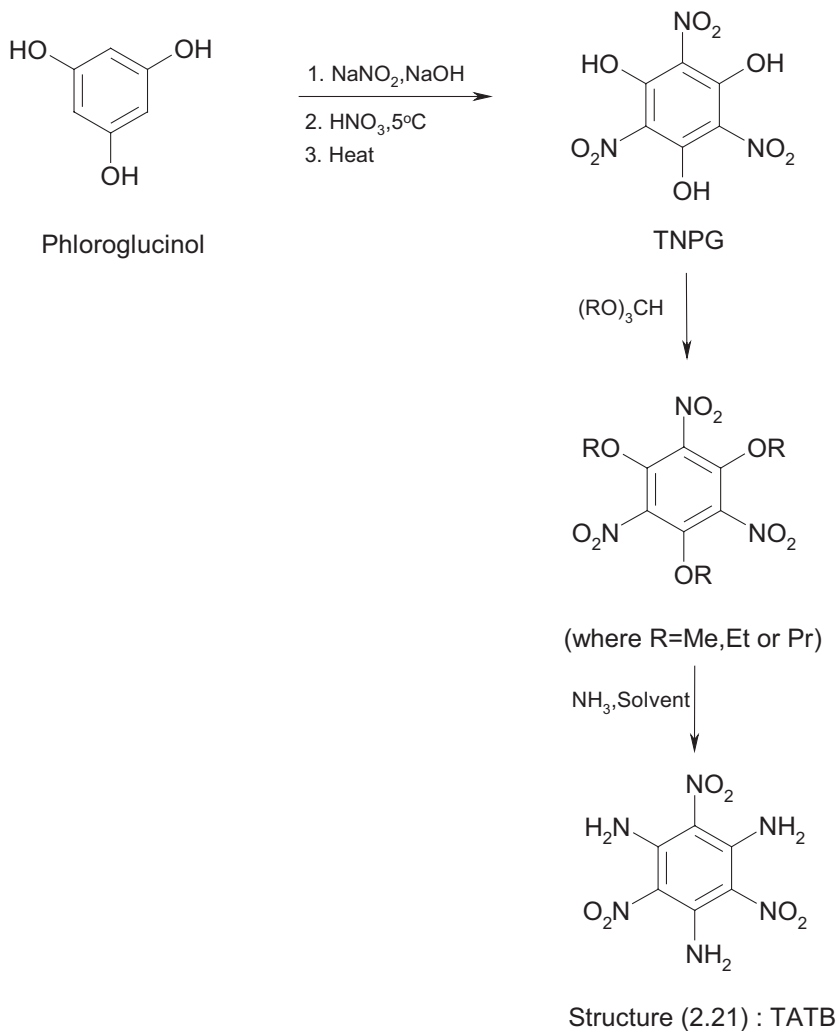
The data suggest that PYX is impact sensitive and is therefore not suitable. The synthesis of TACOT involves 5 steps and therefore it is very expensive. It is an explosive with unusual and outstanding high temperature stability but its performance is poor. On the other hand, TATB is the most thermally stable explosive of this group with excellent impact insensitivity and reasonable performance. The explosive BTDAONAB, reported recently by us, has the unique distinction of being the most thermally stable explosive reported so far. However, its synthesis has to be scaled-up and it needs to be exhaustively evaluated before it can be used for large-scale applications.

In view of the status of TATB among the most thermally stable explosives, it is considered worthwhile to discuss its synthesis, scale-up and other aspects in detail.

Several methods have been reported in the literature for the synthesis of TATB [32]. Considering the ease of synthesis, purity and yield of the resulting TATB, its synthesis from symmetrical trichlorobenzene (sym. TCB) is regarded as a method of choice for scaling-up and now almost all countries follow this method for its large scale manufacture. However, sym. TCB is a little expensive and also not domestically available in several countries. Furthermore, the use of sym. TCB also raises some environmental concerns. As a natural consequence, the following two methods are gaining in importance for the synthesis / manufacture of TATB.

- a) By the reaction of 1,1,1-trimethylhydrazinium iodide (TMHI obtained by the alkylation of UDMH (unsymmetrical dimethylhydrazine) with methyl iodide) and picramide (obtained from Explosive D, used as an explosive filling). American scientists at LLNL have studied all aspects related to the scale-up, followed by optimization of parameters, and it appears that TATB would be manufactured by them in future by the TMHI route [33].

b) 1,3,5-Trihydroxybenzene (phloroglucinol) as per Scheme 3 [34].



Scheme 3. Synthesis of TATB from phloroglucinol.

The process has been successfully scaled-up to pilot plant level and the product characteristics are: yield > 98%, purity \approx 95-99% and particle size \approx 40-60 μm . At the same time, this process reduces the environmental impact of TATB production as compared to the traditional TCB route. This method, proposed by UK scientists, is still at the laboratory scale in the UK. According to a recent report in the literature, ATK Thiokol, Inc, USA, has performed

considerable route development for an alternate TATB process starting with phloroglucinol [35].

DATB and TATB have already qualified as heat-resistant explosives among various nitro derivatives of benzene [36-40]. DATB is fairly stable with a m.p. of 286 °C, but it transforms into a crystalline form of lower density at 216 °C which represents the limit of its utility. The use of DATB in explosive formulations has been described in several American patents and it was of practical value for various space applications. On the other hand, TATB has excellent thermal stability in the range 260-290 °C which represents the upper temperature limit at which it may be used.

TATB is an explosive with unusual insensitivity, heat resistance and respectable performance, which puts it first in the list of thermally stable and safe explosives. These properties are attributed to several unusual features of its structure, i.e. extremely long C-C bonds in the -NO₂ & -NH₂ substituted benzene ring, very short C-N (amino) bonds and six branched hydrogen bonds. In addition, there is evidence of strong inter- and intra-molecular hydrogen bonds in TATB. The net result is that TATB lacks an observable m.p. and has a low solubility in all solvents except concentrated H₂SO₄. As a result of the discovery of TATB and its availability on a large scale, it is now preferred to DATB. It is of special interest for warheads of high velocity guided missiles. By using TATB, energy is sacrificed but handling safety is gained. TATB is extensively used in the US and a number of pilot plants are available for its manufacture in the US and other countries, including India.

Conclusions

TATB is a most thermally-stable and impact/friction insensitive explosive and it is reported that when it is incrementally replaced by RDX/HMX in formulations, all these properties are adversely affected. The laboratory scale studies on BTDAONAB (m.p. > 550 °C, density – 1.97 g/cm³, impact sensitivity – 87 cm & calculated VOD – 8321 m/s) indicate that it has a tremendous potential to replace TATB. However, it still requires detailed study of all aspects, including compatibility, stability, sensitivity and formulation, followed by their performance evaluation.

Acknowledgement

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References

- [1] Cumming A.S., New Directions in Energetic Materials, *J. Def. Sci.*, **1996**, 1(3), 319-321.
- [2] Plets V., Relation between Explosive Properties and Chemical Structure, *Zh. Obshch. Khim.*, **1935**, 5, 173-178; Urbański T., *Chemistry and Technology of Explosives*, Vol.1, Pergamon, Oxford, **1964**.
- [3] Agrawal J.P., Recent Trends in High Energy Materials, *Progress in Energy & Combustion Science*, USA, **1998**, 24, 1-30.
- [4] Agrawal J.P., Some New High Energy Materials and Their Formulations for Specialized Applications, *Propellants Explos. Pyrotech.*, **2005**, 30, 316-326.
- [5] Dunstan I., *Chem. Britain*, **1971**, 7(2), 62-69.
- [6] Urbański T., Vasudeva S.K., Heat Resistant Explosives, *J. Sci. Ind. Res.*, **1978**, 37(5), 250-255.
- [7] Lu C.X., Development and Present Situation of Heat-Resistant Explosives, *Kogyo Kayaku*, **1990**, 51(5), 275-279.
- [8] Gilbert E.E., The Preparation of Hexanitrobibenzyl from TNT with Sodium Hypochlorite, *Propellants & Explosives*, **1980**, 5(1), 15-19.
- [9] Agrawal J.P., Hodgson R.D., *Organic Chemistry of Explosives*, John Wiley & Sons, UK, **2007**.
- [10] Agrawal J.P., High Energy Materials, *Propellants Explos. Pyrotech.*, Wiley-VCH, Germany, **2010**.
- [11] Coburn M.D., Jackson T.E., Picrylamino-Substituted Heterocycles. III. 1,2,4-Triazoles, *J. Heterocycl. Chem.*, **1968**, 5(2), 199-203.
- [12] Ayres J.N., Montesi L.J., Bauer R.J., Small Scale Gap Test (SSGT) Data Compilation: 1959-1972. Vol. 1. *Unclassified Explosives*, Naval Ordnance Laboratory, Technical Report (NOLTR) No. 73-132, **1973**.
- [13] Gibbs T.R., Popolato A., *LASL Explosive Property Data*, University of California Press, Los Angeles, **1980**, pp. 38, 157.
- [14] Zeman S., The Thermoanalytical Study of some Amino Derivatives of 1,3,5-Trinitrobenzene, *Thermochim. Acta*, **1993**, 216, 157-168.
- [15] Shipp K.G., Reactions of α -Substituted Polynitrotoluenes. I. Synthesis of 2,2',4,4',6,6'-Hexanitrostilbene, *J. Org. Chem.*, **1964**, 29, 2620-23.
- [16] Shipp K.G., Kaplan L.A., Reactions of α -Substituted Polynitrotoluenes. II. The Generation and Reactions of 2,4,6-Trinitrobenzyl Anion, *J. Org. Chem.*, **1966**, 31, 857-861.
- [17] Sollott G.P., Conversion of 2,4,6-Trinitrobenzyl Chloride to 2,2',4,4',6,6'-Hexanitrostilbene by Nitrogen Bases, *J. Org. Chem.*, **1982**, 47, 2471-74.
- [18] Shipp K.G., Golding P., Hayes G.F., Studies on the Synthesis of 2,2',4,4',6,6'-Hexanitrostilbene, *Propellants & Explosives*, **1979**, 4, 115-120.
- [19] Bement L.J., Application of Temperature Resistant Explosives to NASA Missions, *Proc. Symp. on Thermally Stable Explosives*, Whiteoak, MD Naval Ordnance

Laboratory, **1970**.

- [20] O'Keefe D.M., *Hexanitrotetrachloroazobenzene Explosive and Method of Preparation*, US 4751289, **1988**; *Chem. Abstr.*, **1988**, 109, 152561r.
- [21] Coburn M.D., *PATO*, US 3483211, **1969**; *Chem. Abstr.*, **1970**, 72, 55458x.
- [22] Li J., Chen B., Ou Z., Modified Preparation and Nitration of 3-Picrylamino-1,2,4-triazole, *Proc. 17th Int. Pyrotech. Seminar* (Combined with the 2nd Beijing Inst. Symp. on Pyrotechnics and Explosives), Beijing Inst. Tech. Press, Beijing, Vol. 1, **1991**, pp. 196-199.
- [23] Agrawal J.P., Mehilal, Prasad U.S., Surve R.N., Synthesis of 1,3-Bis(1,2,4-triazol-3-amino)-2,4,6-trinitrobenzene and Its Thermal & Explosive Behaviour, *New Journal of Chemistry*, UK, **2000**, 24(8), 583-585.
- [24] Bapat V.K., Surve R.N., Agrawal J. P., Synthesis, Characterization and Evaluation of Explosive Properties of 5-Picrylamino-1,2,3,4-Tetrazole, *Proc. 2nd High Energy Materials Conference & Exhibits*, IIT, Madras, Dec. 8-10, **1998**, pp. 403-405.
- [25] Makashir P.S., Bapat V.K., Mahajan R.R., Mehilal, Agrawal J.P., A Comparative Study of Thermal & Explosive Behaviour of 5-Picrylamino-1,2,3,4-Tetrazole (PAT) and 5,5'-Styphnylamino-1,2,3,4-Tetrazole (SAT), *Proc. of International Workshop on Unsteady Combustion & Interior Ballistics*, Vol. 1, St. Petersburg, Russia, June 25-30, **2000**, pp 199-205.
- [26] Mehilal, Sikder N., Sikder A.K., Agrawal J.P., *N,N'*-Bis(1,2,4-triazol-3-yl)-4,4'-diamino-2,2',3,3',5,5',6,6'-octanitroazo-benzene (BTDAONAB): A New Thermally Stable Insensitive High Explosive, *Indian J. Eng. & Mater. Sci.*, **2004**, 11, 516-520.
- [27] Urbański T., *Chemistry and Technology of Explosives*, Vol. 4, Pergamon, Oxford, **1984**, p. 206.
- [28] Carboni R.A., Castle J.E., Dibenzo-1,3a, 4,6a-Tetraazapentalene: A New Heteroaromatic System, *J. Amer. Chem. Soc.*, **1962**, 84, 2453-2455.
- [29] Harder R.J., Carboni R.A., Castle J.E., Aromatic Azapentalenes V: 1,1'- and 2,2'-bibenzotriazoles and Their Conversion to Dibenzotetraazapentalenes, *J. Amer. Chem. Soc.*, **1967**, 89, 2643.
- [30] Coburn M.D., *2,6-Bis(picrylamino)-3,5-dinitropyridine and a Method for its Preparation*, US 3678061, **1972**; *Chem. Abstr.*, **1972**, 77, 139812z.
- [31] Pallanck R.G., *PYX Purification*, US 4564405, **1986**; *Chem. Abstr.*, **1986**, 104, 209534n.
- [32] Agrawal J.P., Surve R.N., Mehilal, Bapat V.K. et.al., *Development of High Density, High Velocity of Detonation and Thermally Stable Explosives*, HEMRL Report No. HEMRL/99/6, **1999**.
- [33] Mitchell A.R., Hsu P.C., Coburn M.D., Schmidt R.D., Pagoria P.F., Lee G.S., Kwak S.S.W., *Recent Progress on the Conversion of Surplus Picric Acid/Explosive 'D' to Higher Value Products*, UCRL-CONF-205236, July 14, **2004**.
- [34] Bellamy A.J., Ward S.J., Golding P., A new Synthetic Route to 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB), *Propellants Explos. Pyrotech.*, **2002**, 27, 49-58.
- [35] Dressen S., Merrill D., Sanderson A., Velarde S., Pilot Plant Synthesis of TATB from a Novel Proces, *IM/EM Technical Symposium*, San Fransisco, CA, Nov. 15-

- 17, **2004**.
- [36] Chaykovsky M., Adolph H.G., Synthesis and Properties of Some Trisubstituted Trinitrobenzenes: TATB Analogues, *J. Energ. Mater.*, **1990**, 8, 392-395.
- [37] Wright S.B., *Granular Explosive Molding Powder*, US 3173817, **1965**; *Chem. Abstr.*, **1965**, 62, 12968g.
- [38] Wright S.B., *Granulated Crystalline Plastic-Bonded Explosives*, US 3296041, **1967**; *Chem. Abstr.*, **1967**, 66, 87227p.
- [39] Jackson R.K., Weingart R.C., *Detonation Properties of the Insensitive Explosive TATB*, U.S. NTIS, AD Report (AD-A026051), **1976**; *Chem. Abstr.*, **1976**, 85, 179841.
- [40] Dobratz B.M., *Insensitive High Explosive Triaminotrinitrobenzene (TATB): Development and Characterization – 1888 to 1994*, Los Alamos National Lab. Report LA – 13014-H, (University of California Report, UC-741), **1995**.