

## A review of energetic materials synthesis

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### Abstract

Energetic materials (explosives, propellants and pyrotechnics) are used extensively for both civilian and military applications. There are ongoing research programs worldwide to develop pyrotechnics with reduced smoke and new explosives and propellants with higher performance or enhanced insensitivity to thermal or shock insults. In recent years, the synthesis of energetic, heterocyclic compounds have received a great amount of interest. Heterocycles generally have a higher heat of formation, density, and oxygen balance than their carbocyclic analogues. This review will concentrate on recent advances in the synthesis of heterocycles as energetic materials and will complement the excellent review of recent advances in energetic materials published in 1998 by Agrawal [Prog. Energy Combust. Sci. 24 (1998) 1]. © 2002 Elsevier Science B.V. All rights reserved.

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### 1. 3,6-Dinitropyrazolo[4,3-*c*]pyrazoles (DNPPs)

Recently, at Lawrence Livermore National Laboratory (LLNL), we have used molecular modeling and explosive performance prediction codes to guide the synthesis of new energetic materials based on the pyrazolo[4,3-*c*]pyrazole ring system with energies greater than HMX. This is one of the few examples in which target molecules were designed by a set of predictive codes, were then synthesized, and their physical properties were measured. It was predicted that caged structures and bicyclic heterocycles would give the best combination of stability, oxygen balance, high heat of formation and predicted performance. In 1993, Shevelev et al. [2] reported the synthesis of DNPP from 3,5-dimethylpyrazole. Pagoria et al. [3]

recently developed an alternative synthesis of DNPP, shown in Fig. 1, which had several advantages over the Shevelev synthesis, namely, ease of synthesis scale-up and improved product yield. The most significant improvement was the combination of the decarboxylation and nitration steps into a single nitrative decarboxylation step. Therefore, 3-carboxy-6-nitropyrazolo[4,3-*c*]pyrazole was treated with 98% HNO<sub>3</sub> at 45 °C to give DNPP in 70% yield. The overall yield of DNPP from acetylacetone was 21%, which represents a significant increase from the Shevelev synthesis. The physical and safety properties of DNPP were measured. DNPP has a peak exotherm on the DSC at 330 °C, a drop hammer weight (5 kg, 50% value) (DH<sub>50</sub>) of 68 cm (HMX = 32 cm), a measured  $\Delta H_f$  of +65 kcal/mol, a X-ray crystal density ( $\rho$ ) of 1.865 g/ml [4], and is not friction or spark sensitive as tested. The performance of DNPP is predicted to be 85% of HMX (CHEETAH calculation) using the experimental values for density and heat of formation. The good thermal stability and performance of DNPP

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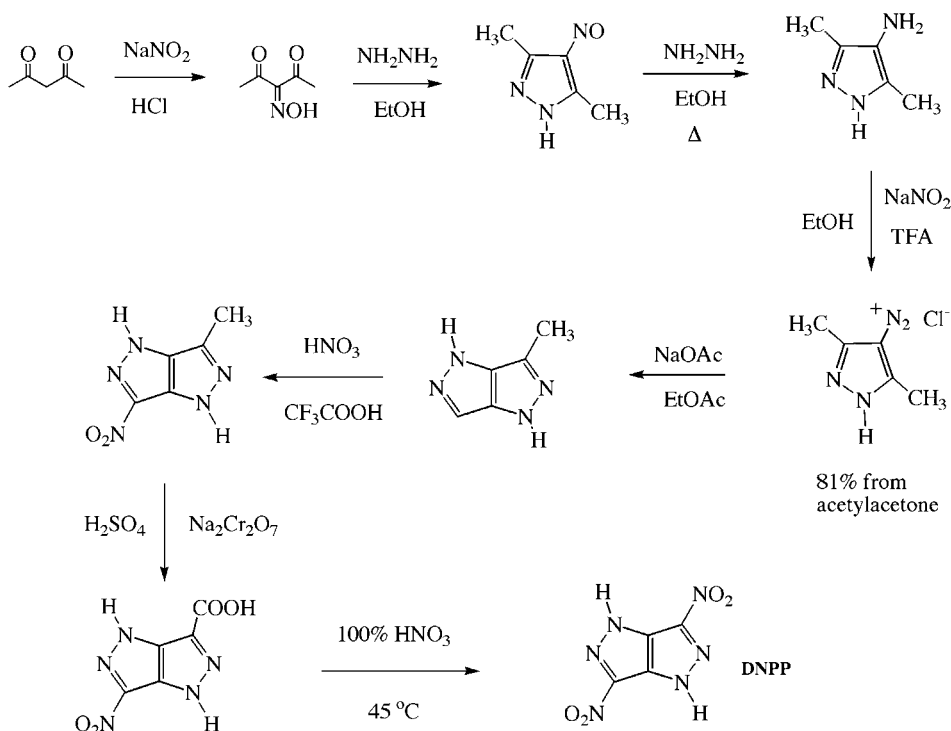


Fig. 1. LLNL synthesis of DNPP.

make this compound an attractive explosive ingredient.

DNPP was also used as a precursor to 1,4-diamino-3,6-dinitropyrazolo[4,3-*c*]pyrazole (LLM-119). LLM-119 was synthesized by amination of DNPP using either hydroxylamine-*O*-sulfonic acid in aqueous base [5] or *O*-(mesitylenesulfonyl)hydroxylamine [6] in THF in the presence of NaOH as the base. The latter method gives the best yields and product purity. LLM-119 has a density of 1.845 g/ml as determined by X-ray crystallography [4], which is significantly lower than predicted. The low density may be attributed to the fact that the crystal structure shows the amino groups are orthogonal to the plane of the molecule. We predicted that the amino groups would be in the same plane as the rest of the molecule to both maximize lone pair delocalization with the heterocyclic  $\pi$ -electron system and maximize hydrogen bonding with the nitro-groups. The predicted geometry was that of a planar molecule, similar to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). In actuality, the repulsion energy

between the lone pairs on the amino-nitrogen and the ring nitrogen must be significantly greater than the energy gains via lone pair-ring system and in maximizing hydrogen bonding. Gilardi [4], who has determined the crystal structures of similar compounds possessing the *N*-amino moiety, has noted amino groups orthogonal to the plane of these molecules. Even with lower than anticipated density, the LLM-119 still has a predicted performance 104% that of HMX, based on a predicted  $\Delta H_f$  of +114 kcal/mol. Bottaro at SRI International [7] has previously reported the synthesis of *N*-amino derivatives of nitroheterocycles, and has noted that in comparison to the parent compounds, they have increased heat of formation and predicted performance and possess no acidic protons (considered problematic in some formulations). LLM-119 has a peak exotherm at 253 °C as determined by DSC, good thermal stability for *N*-amino compound. LLM-119 has a  $DH_{50}$  value of 24 cm (HMX = 32 cm) and is not friction or spark sensitive as tested (Fig. 2).

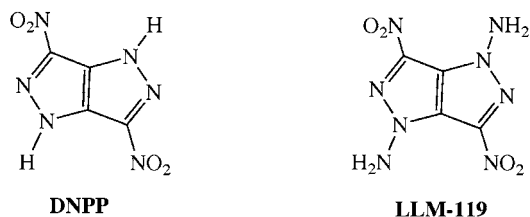


Fig. 2. DNPP and LLM-119.

## 2. New TATB synthesis

TATB is the current industry standard for heat-resistant, insensitive explosives [8]. It is used extensively in military applications but has received limited use in civilian applications, mainly because of the cost of the material. Recently a synthesis of TATB from picramide or 1,3,5-trinitrobenzene was reported in three patents by Mitchell et al. [9–11] at LLNL which may significantly reduce the cost of TATB. The treatment of picramide with 4-amino-1,2,4-triazole (ATA) [12] or 1,1,1-trimethylhydrazinium iodide (TMHI), as nucleophilic aminating reagents, in DMSO in the presence of excess NaOMe yielded TATB in excellent yields [10]. Pagoria et al. [13] previously reported the first example of TMHI as a nucleophilic aminating reagent in the amination of a series of 3-substituted nitrobenzenes. This method uses chemistry coined by Makosza and Winiarski [14] as the “vicarious nucleophilic substitution (VNS) of hydrogen” in which an amino-group formally replaces a hydrogen atom on an electrophilic aromatic ring. Mitchell et al. also found hydroxylamine hydrochloride acts as a nucleophilic aminating reagent (in DMSO in the presence of NaOMe) to convert picramide to TATB but requires elevated temperatures [11].

TMHI and ATA were also used as nucleophilic aminating reagents in the synthesis of 4-amino-3,5-

dinitropyrazole (LLM-116) and 3,5-diamino-2,4,6-trinitrotoluene (DATNT). 3,5-Dinitropyrazole was treated with TMHI (in DMSO) in the presence of potassium *tert*-butoxide to yield LLM-116 in 70% yield [15]. LLM-116 has a density of 1.90 g/ml [4], a decomposition point of 178 °C and has a  $DH_{50} = 165$  cm. The synthesis of DATNT was first reported by Iyer [16], and later by Marchand and Reddy [17], but both syntheses involved multi-step processes with low overall yields. Pagoria et al. [15] found treatment of commercially available 2,4,6-trinitrotoluene (TNT) with ATA (in DMSO) in the presence of NaOMe gave DATNT in 65% yield. DATNT is more thermally stable than TNT and has slightly more power. Both of these compounds are good examples of a general structure–property relationship found among energetic ingredients, that the addition of amino-groups to a polynitroaromatic increases the density and thermal stability and decreases the sensitivity compared to the corresponding H-atom-substituted material. In general, the density increase outweighs the concomitant decrease in oxygen balance and heat of formation that accompanies the addition of amino groups, resulting in better performance. Also, the decrease in oxygen balance and heat of formation, along with increased hydrogen bonding between the amino group and the nitro-groups, decreases sensitivity and increases thermal stability (Fig. 3).

## 3. Pyrazines and pyridines

The difficulty of synthesizing some nitroheteroaromatic systems may be attributed to their electron deficiency, making electrophilic aromatic substitution problematic. By the addition of electron donating substituents to the heteroaromatic ring, nitration

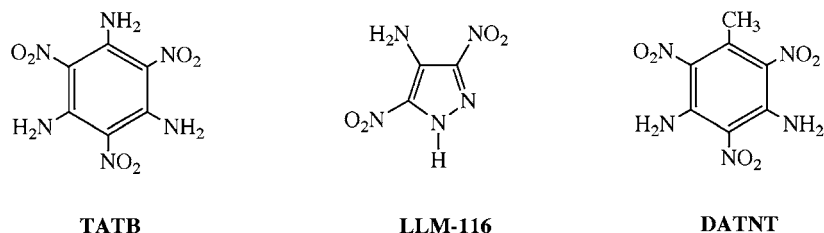


Fig. 3. Insensitive amino- and nitro-substituted energetic compounds.

may proceed more readily. This is illustrated in the next few examples in which activated pyridine and pyrazine precursors are nitrated to yield the desired dinitro-substituted heterocycles. These examples also illustrate the concept of increasing density and thermal stability by the use of an alternating array of amino- and nitro-groups. Pagoria et al. [3] synthesized 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) by reacting commercially available 2,6-dichloropyrazine with sodium methoxide to yield 2-methoxy-6-chloropyrazine. This compound was nitrated with mixed acid at 70 °C, then treated with NH<sub>4</sub>OH in CH<sub>3</sub>CN at 60 °C to yield 2,6-diamino-3,5-dinitropyrazine (ANPZ) [18]. Oxidation of ANPZ with a mixture of trifluoroacetic acid and 30% H<sub>2</sub>O<sub>2</sub> yielded LLM-105 (in 48% overall yield) from 2,6-dichloropyrazine. LLM-105 has a density of 1.918 g/ml [4] and a decomposition point of 354 °C. This work also illustrated another method to increase density and oxygen balance in heterocyclic systems, i.e. through the conversion of tertiary amines to their corresponding *N*-oxides. The N–O bond of a tertiary *N*-oxide is a relatively strong bond possessing significant double bond character owing to  $\pi$ -back bonding by the lone oxygen pair [19]. The formation of a heterocyclic *N*-oxide also changes the charge distribution of the heterocyclic ring and leads to, in some cases, an increase in the aromaticity of the heterocyclic ring, thus stabilizing the ring system [19]. It should be noted that ANPZ has a crystal density of 1.84 g/ml [4], whereas LLM-105 has a crystal density of 1.918 g/ml. Thus, the *N*-oxide functionality not only increases oxygen balance but also allows better crystal packing (Fig. 4).

Ritter and Licht [20] reported the synthesis of 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) by the nitration (with mixed acid at 60–65 °C) of 2,6-diaminopyridine to yield 2,6-diamino-3,5-dinitropyridine (ANPy) [21], followed by oxidation with a mixture

of acetic acid and 30% H<sub>2</sub>O<sub>2</sub>. ANPyO has a density of 1.878 g/ml and an mp of >340 °C (dec). Hollins et al. [22,23] extended this work and synthesized 2,4,6-triamino-3,5-dinitropyridine-1-oxide (**1**) by the amination of ANPyO with hydroxylamine (in aq. KOH) in 39% yield. Compound **1** is an insensitive energetic material with a density of 1.876 g/ml and an mp of 308 °C (dec). Hollins et al. [23] also synthesized 3,5-dimethoxy-2,6-dinitropyridine-1-oxide by the nitration of 3,5-dimethoxypyridine-1-oxide, but treatment of this compound with ammonia (in EtOH) yielded 2-amino-3,5-dimethoxy-6-nitropyridine-1-oxide instead of the desired 3,5-diamino-2,6-dinitropyridine-1-oxide.

Licht and Ritter [24] also reported the syntheses of 2,4,6-trinitropyridine (TNP<sub>y</sub>) and 2,4,6-trinitropyridine-1-oxide (TNP<sub>y</sub>O<sub>x</sub>) with densities of 1.77 and 1.86 g/ml, respectively. TNP<sub>y</sub>O<sub>x</sub> was synthesized by the acid catalyzed cyclization of potassium acid-2,2-dinitroethanol. De-oxygenation of TNP<sub>y</sub>O<sub>x</sub> was accomplished by the treatment with NaNO<sub>2</sub> (in dilute H<sub>2</sub>SO<sub>4</sub>) to yield TNP<sub>y</sub> in 46% yield. The 2,6-positions of TNP<sub>y</sub>O<sub>x</sub> are very reactive to nucleophiles and can be easily transformed into the 2,6-dichloro- and 2,6-diazido-derivatives by reaction with PCl<sub>3</sub> and NaN<sub>3</sub>, respectively. This reactivity has also precluded attempts at the synthesis of 3,5-diamino-2,4,6-trinitropyridine-1-oxide, a potentially insensitive target molecule, by nucleophilic amination with ATA via the VNS of hydrogen, yielding only unidentified, water soluble products [25] (Fig. 5).

Trudell and coworkers [26,27] reported the synthesis of 2,4,8,10-tetranitro-5*H*-pyrido[3'',4'':4',5']-[1,2,3]-triazolo[1',2':1,2][1,2,3]-triazolo[5,4-*b*]-pyridin-6-ium inner salt (**2**) and 2,4,8,10-tetranitro-5*H*-pyrido[3'',2'':4',5']-[1,2,3]-triazolo[1',2':1,2][1,2,3]-triazolo[5,4-*b*]-pyridin-6-ium inner salt (**3**), two insensitive energetic materials with structures similar to the commercial product, TACOT [28]. Compound **2** was synthesized by reacting 1,2,3-triazolo[4,5-*c*]pyridine with 2-chloro-3-nitropyridine to yield 1-(3-nitro-2-pyridyl)-1,2,3-triazolo[4,5-*c*]pyridine which was cyclized with triethyl phosphite to yield the dipyridotetraazapentalene (**4**). Compound **4** was nitrated (with HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> at 60 °C) to yield **2**. Compound **3** was made similarly using 1,2,3-triazolo[4,5-*b*]pyridine as the starting material. Compounds **2** and **3** have decomposition points of 340 and 396 °C, respectively; and both have a crystal

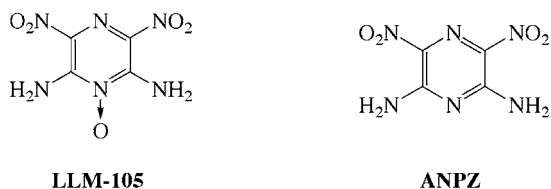


Fig. 4. Energetic pyrazine explosives.

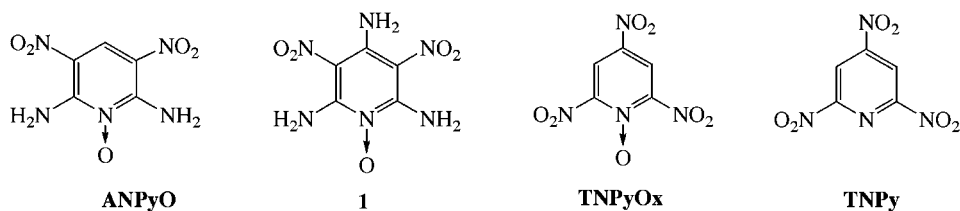


Fig. 5. Energetic pyridine derivatives.

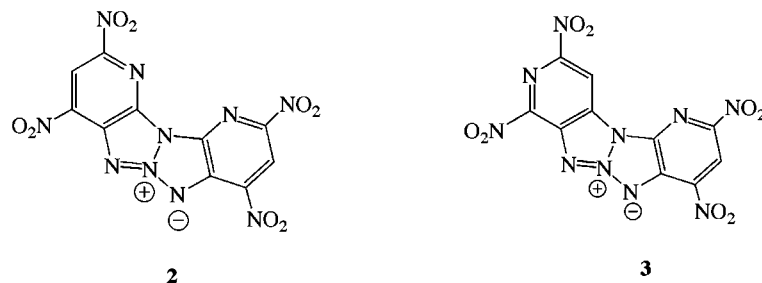


Fig. 6. Pyridine-based TACOT analogues.

density of 1.88 g/ml. They are significantly more energetic than TACOT while retaining excellent thermal stability (Fig. 6).

#### 4. 1,2,4,5-Tetrazines

In 1993, Coburn et al. [29] reported the synthesis of 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (LAX-112), an example of a cycloaromatic energetic material without a nitro-group as an oxidizing group. LAX-112 was synthesized by the treatment of 3,6-bis(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine with ammonia (at 90 °C in a pressure vessel) to yield 3,6-diamino-1,2,4,5-tetrazine [30], followed by oxidation with OXONE<sup>®</sup> (in water or glacial acetic acid and 84% H<sub>2</sub>O<sub>2</sub>) [31]. LAX-112 has a relatively high heat of formation and detonation velocity and good density that initially led to a much higher predicted performance than measured. They were able to oxidize 3,6-diamino-1,2,4,5-tetrazine further (with trifluoroacetic acid and 90% H<sub>2</sub>O<sub>2</sub>) to yield 3-amino-6-nitro-1,2,4,5-tetrazine-2,4-dioxide, a sensitive, energetic compound that decomposes at 110 °C [29] (Fig. 7).

Hiskey and Chavez [32] have continued the research on 1,2,4,5-tetrazine-based explosives and synthesized a number of derivatives which are interesting as

propellant 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-dimethylpyrazolyl)-1,2,4,5-tetrazine with hydrazine hydrate (2 eq. in acetonitrile in air) yielded 3,6-dihydrazino-1,2,4,5-tetrazine (**5**) [33] ( $\Delta H_f = +128$  kcal/mol), an energetic fuel with a density of 1.61 g/ml. Several energetic salts of **5** were synthesized including the bis-dinitramide, diperchlorate, dinitrate, and 4,4',5,5'-tetranitro-2,2'-biimidazolate, all having fairly low drop weight impact values and decomposition points. Compound **5** was converted to 3,6-dichloro-1,2,4,5-tetrazine by treatment with Cl<sub>2</sub> (in CH<sub>3</sub>CN) which then reacted with the sodium salt of 5-aminotetrazole to yield 3,6-bis(1*H*-1,2,3,4-tetrazol-5-ylamino)-1,2,4,5-tetrazine (**6**) (mp=264 °C and a measured  $\Delta H_f = 211$  kcal/mol).

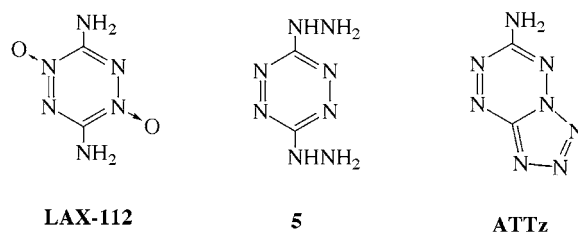


Fig. 7. Energetic tetrazine derivatives.

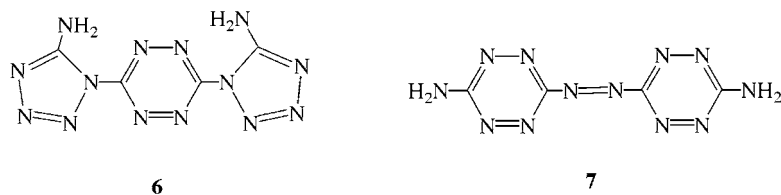


Fig. 8. High-nitrogen tetrazine derivatives.

Hiskey and coworkers [34] recently reported the synthesis of 3,3'-azo-bis(6-amino-1,2,4,5-tetrazine) (7), a high-nitrogen propellant ingredient with a density of 1.84 g/ml, an mp of 252 °C and a  $\Delta H_f = +862$  kJ/mol. The synthesis involved reacting hydrazine hydrate (0.5 eq.) with 3,6-bis(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine (in *i*-PrOH) to yield 3,3'-hydrazo-bis-6-(3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine (8). Treatment of 8 with *N*-bromosuccinimide gave 3,3'-azo-bis-6-(4-bromo-3,5-dimethylpyrazolyl)-1,2,4,5-tetrazine which was subsequently reacted with ammonia (in DMSO) to yield 6 (Fig. 8).

Licht and Ritter [35] synthesized 6-amino-tetrazolo[1,5-*b*]-1,2,4,5-tetrazine (ATTz) (decreasing point = 200 °C), by the diazotization of 3,6-diamino-1,2,4,5-tetrazine with  $\text{NaNO}_2$ , followed by reacting the non-isolated diazonium salt compound with  $\text{NaN}_3$ .

## 5. Furazans

3,4-Diaminofurazan (DAF), first synthesized by Coburn in 1968 [36], 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 [37], cyanogen [38], glyoxal [39], and glyoxime [40], to yield diaminoglyoxime followed by cyclization to DAF by treatment with aqueous base at 180 °C in a pressure vessel. Solodyuk et al. [41] reported the oxidation of DAF with hydrogen peroxide under various conditions yields 3-amino-4-nitrofurazan (ANF); 4,4'-diamino-3,3'-azoxyfurazan (DAAF); or 4,4'-diamino-3,3'-azofurazan (DAAzF). Chavez et al. [42] scaled-up the synthesis of DAAF and performed measurements of its explosive properties including a poly- $\rho$  test, mini-wedge test and a standard

1 in. cylinder test. The  $E_{19}$  (cylinder energy) for DAAF was measured at 1.22 kJ/g compared to values of 1.04 and 1.58 kJ/g for similar TATB and HMX formulations, respectively. DAAF has a crystal density of 1.747 g/ml, a  $\Delta H_f$  of 106 kcal/mol and  $\text{DH}_{50} > 320$  cm (2.5 kg, Type 12). Schmidt [43] optimized the synthesis of ANF (mp = 122 °C), using a modification of Novikova et al. procedure [44], in which DAF was oxidized (with a mixture of 30%  $\text{H}_2\text{O}_2$ ,  $\text{Na}_2\text{WO}_4$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and conc.  $\text{H}_2\text{SO}_4$ ) to yield ANF in 70% yield. Novikova et al. [44] reported the synthesis of 3,4-dinitrofurazan (DNF), 4,4'-dinitro-3,3'-azoxy-bis(furazan) (DNABF) and 4,4'-dinitro-3,3'-azo-bis(furazan) (DNAzBF), all very energetic but shock sensitive compounds, using the above procedure with more concentrated  $\text{H}_2\text{O}_2$  solutions. DNF was reported to have a crystal density of 1.62 g/ml, a mp of 15 °C, and a boiling point of 168 °C. Sheremetev et al. [45] have exploited the high reactivity of the nitro-groups of DNF, DNAF, and DNAzF to nucleophiles in the synthesis of a large number of 3-substituted-4-nitrofurazan derivatives (Fig. 9).

Zelenin et al. [46] reported the synthesis of 4-amino-4'-nitro-3,3'-azoxy-bis(furazan) by the oxidation of DAAzF (30%  $\text{H}_2\text{O}_2$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and conc.  $\text{H}_2\text{SO}_4$  at 50 °C) in 25% yield. Gunasekaran and Boyer [47] synthesized an interesting new, highly energetic liquid (bp = 160–165 °C), 5-(4-nitro-(1,2,5)oxadiazolyl)-5H-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazole (NOTO) from DAAF. The synthesis involved treatment of DAAF with  $\text{NaNO}_2$  (in conc.  $\text{H}_2\text{SO}_4$  and AcOH), followed by  $\text{NaN}_3$ , to yield the diazide. Heating the diazide in  $\text{CH}_3\text{CN}$  yielded 5-(4-azido-(1,2,5)oxadiazolyl)-5H-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazole. This was reduced to the amine with  $\text{SnCl}_2$  (in MeOH) and then oxidized (30%  $\text{H}_2\text{O}_2$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and conc.  $\text{H}_2\text{SO}_4$  at 35 °C) to NOTO (Fig. 10).

Recently, Sheremetev and Yudin [48] and then Tselinskii et al. [49] reported the synthesis of

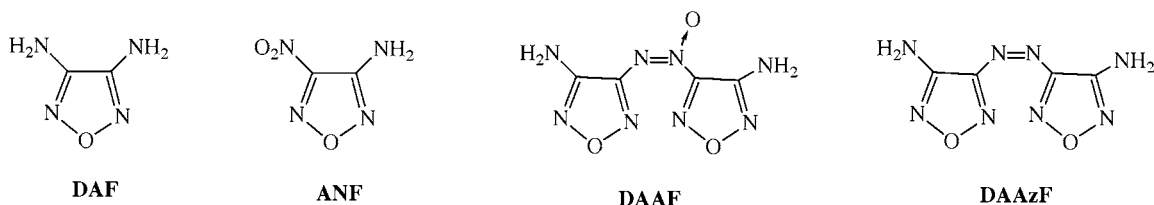


Fig. 9. 3,4-Diaminofurazan-based energetic compounds.

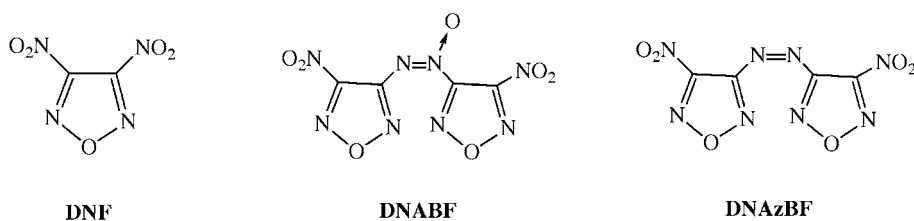


Fig. 10. Nitro-substituted furazan derivatives.

4*H*,8*H*-bis(furazano)[3,4:3',4']pyrazine (**9**). Both syntheses used 4,5-dichlorofurazano[3,4-*b*]pyrazine as the starting material. Fischer et al. [50] attempted the synthesis of **9** earlier but removal of the *N*-benzyl protecting groups from the dibenzyl derivative proved problematic. Tselinskii et al. [49] found the dianion of **9** to be stable and reacted it with a variety of electrophiles including picryl chloride, acetic anhydride, methyl iodide and methyl vinyl ketone. They synthesized the dinitro-derivative (**10**) by reacting the dianion of **9** with nitrogen oxides in  $\text{CH}_3\text{CN}$ . The dinitro-derivative was quite reactive but was isolated by column chromatography and the identity was confirmed by mass spectroscopy.

Earlier, Coburn [36] synthesized 3,4-bis(picrylamino)furazan (BPAF) by reacting dichloroglyoxime with aniline, followed by heating the dianilino-glyoxime with NaOH in ethylene glycol to yield the dianilino-furazan. Nitration with conc.  $\text{HNO}_3$  (at 25 °C) yielded

BPAF in 86% yield. He also reported the synthesis of 4-(picrylamino)-3,3'-bifurazan and 4,4'-bis(picrylamino)-3,3'-bifurazan (BPABF) (mp = 315 °C) by treatment of 4,4'-diamino-3,3'-bifurazan (DABF) with picryl fluoride (1 or 2 eq.). Recently, Sheremetev and Mantseva [51] reported an improved synthesis of DABF (14% overall yield from  $\text{CH}_3\text{NO}_2$ ) by reacting 3,4-bis(hydroxyiminomethyl)furoxan with hydroxylamine. 4,4'-Dinitro-3,3'-bifurazan (DNBF) was synthesized by the oxidation of DABF with TFA/90%  $\text{H}_2\text{O}_2$ . DNBF has an mp of 85 °C and a density of 1.85 g/ml but has a  $\text{DH}_{50}$  value similar to pentaerythritol tetranitrate (PETN). The treatment of DAF with 1 eq. of picryl fluoride yielded 3-(picrylamino)-4-aminofurazan which was oxidized with TFA/90%  $\text{H}_2\text{O}_2$  to yield 3-nitro-4-(picrylamino)furazan (Fig. 11).

Khmelnitskii and coworkers [52,53] reported the synthesis of 3,4-dinitrofuroxan (DNFX), a highly oxidized, fully nitrated heterocycle. It was synthesized

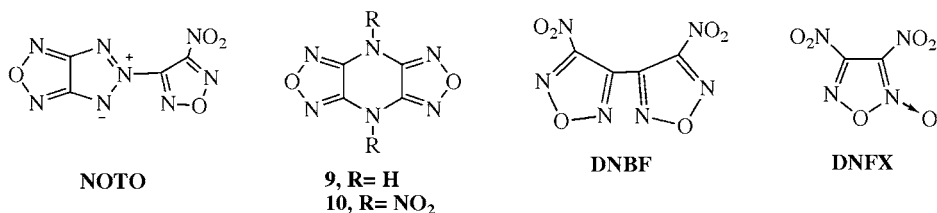


Fig. 11. Furazans and furoxans.

by the nitration of glyoxime followed by cyclization of the resulting dinitroglyoxime with  $N_2O_4$ . DNFx is a mobile liquid that decomposes slowly at room temperature but is stable at  $-15$  to  $-20$  °C. It is a sensitive explosive that must be handled with care. The nitro-group of DNFx is very reactive to nucleophilic substitution, leading to the synthesis of the 3-amino-3-azido, and 3-methoxy-4-nitrofuraxans from DNFx [53].

### 6. 2,3,4-Trinitropyrrole and 2,3,4,5-tetranitropyrrole

The synthesis of nitropyrroles has been studied extensively over the years. Pyrrole, an electron-rich heterocycle, undergoes nitration with acetyl nitrate (at  $-10$  °C) to yield 2-nitropyrrole and a small amount of 3-nitropyrrole with a substantial amount of carbonaceous material [54]. Further treatment with acetyl nitrate gives a mixture of 2,4- and 2,5-dinitropyrrole in 48 and 15% yield, respectively [55]. The synthesis of 1-alkyl-substituted 2,4-dinitro-, 2,5-dinitro- and 3,4-dinitropyrroles have been reported by several methods: (1) the alkylation of the corresponding unsubstituted pyrroles [55]; (2) the condensation of primary alkyl amines, formaldehyde and the dipotassium salt of 2,3,3-trinitropropanal [56] and (3) the nitration of 1-alkyl-3-nitropyrroles with conc.  $H_2SO_4$  and 100%  $HNO_3$  (at  $0$ – $25$  °C) [57]. Pagoria [25] synthesized 1-*tert*-butyl-2,3,4-trinitropyrrole (**11**) (in 40% overall yield from 1-*tert*-butylpyrrole) by treatment first with a mixture of  $Cu(NO_3)_2$ , silica gel and  $CH_3NO_2$ , followed with acetyl nitrate (at room temperature) and finally with conc.  $H_2SO_4$  and 100%  $HNO_3$  (at  $0$  °C). Hinshaw et al. [58] reported the de-*tert*-butylation of **11** with  $CF_3COOH$  to yield 2,3,4-trinitropyrrole (**12**) and the subsequent nitration

(conc.  $H_2SO_4$  and 100%  $HNO_3$  at  $60$  °C) to yield 2,3,4,5-tetranitropyrrole (**13**). 2,3,4,5-tetranitropyrrole (mp =  $156$ – $158$  °C) is unstable at ambient temperature upon storage (Fig. 12).

### 7. 1,3,3-Trinitroazetidine (TNAZ) and small-ring energetic materials

Highly nitrated small ring heterocycles and carbocycles are interesting as energetic materials because of the increased performance expected from the additional energy release (manifested in a higher heat of formation) upon opening of the strained ring system during decomposition. The most widely studied energetic small-ring compound to date is TNAZ, a potentially melt-castable explosive that has been investigated as a possible replacement for TNT. TNAZ has a melting point of  $103$ – $104$  °C, a crystal density of  $1.84$  g/ml and thermal stability of  $>240$  °C. TNAZ was first synthesized by Archibald et al. [59], with entry into the azetidine ring system accomplished by reacting *tert*-butylamine and epichlorohydrin to yield 1-*tert*-butyl-4-hydroxyazetidine. Subsequently, Coburn et al. [60] improved the synthesis, making it more amenable to scale-up, and ultimately prepared 450 kg. Their synthesis involved the condensation of tris(hydroxymethyl)nitromethane with *tert*-butylamine and formaldehyde to yield 3-*tert*-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine. This was treated with aq. HCl to yield 2-*tert*-butylaminomethyl-2-nitro-1,3-propanediol hydrochloride which was cyclized under Mitsunobu conditions to 1-*tert*-butyl-3-hydroxymethyl-3-nitroazetidine hydrochloride. This was 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. Recently, Nagao and coworkers [61] reported the synthesis of TNAZ from 1,2-dibromo-propyl-3-amine hydrobromide and proceeding through 1-azabicyclo[1.1.0]butane, but the yields were inferior to the Coburn method. This procedure was similar to Marchand et al. [62] procedure which used 2-amino-1,3-propanediol as the starting material and also proceeded through 1-azabicyclo[1.1.0]butane.

Hiskey et al. [63] effected the de-*tert*-butylation of BDNA by reacting it with benzyl chloroformate to yield the 1-(benzyloxycarbonyl)-3,3-dinitroazetidine.

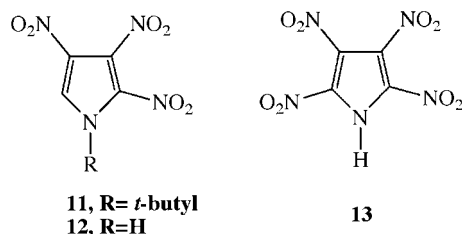


Fig. 12. Polynitropyrroles.



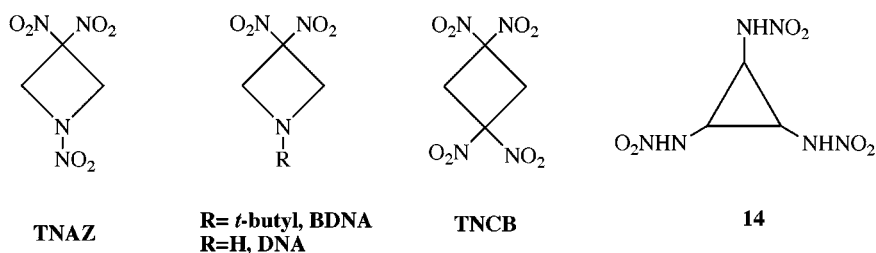


Fig. 13. Small ring energetic compounds.

Removal of the benzyloxy carbonyl protecting group with trifluoromethanesulfonic acid yielded 3,3-dinitroazetididine trifluoromethanesulfonate. This was neutralized with aq. NaHCO<sub>3</sub> to yield 3,3-dinitroazetine (DNA), an energetic material with a  $pK_a$  of 6.5. Hiskey et al. [64] exploited this basicity and synthesized a number of energetic salts of dinitroazetididine, including the nitrate, dinitramide, 3,5-dinitrotriazolate, 4,4',5,5'-tetranitro-biimidazolate, 2,4-dinitroimidazolate and 3-nitro-5-hydroxytriazolate. These salts have a drop weight heights between 14 and 71 cm (RDX = 23 cm) and a fairly low DTA exotherms (140–160 °C).

Earlier, Baum and coworkers reported the synthesis of 1,1,3,3-tetranitrocyclobutane (TNCB) [65] by the oxidative nitration of 1,3-dinitrocyclobutane with AgNO<sub>3</sub> and NaNO<sub>2</sub>. TNCB (mp = 165 °C) has a density of 1.83 g/ml.

Recently, Tartakovskii and coworkers [66] synthesized *trans*-1,2,3-tris(nitramino)cyclopropane (**14**) by the nitration of 1,2,3-tris(acetamido)cyclopropane with Ac<sub>2</sub>O/HNO<sub>3</sub> or TFAA/HNO<sub>3</sub>, followed by ammonolysis of the amide groups, and subsequent acidification of the tris-ammonium salt (Fig. 13).

## 8. Mono- and dinitroureas

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/ml) which has been attributed to the inherently high density of the urea framework. However, the dinitrourea explosives suffer from hydrolytic lability, restricting their use; but the mono-nitrourea compounds are fairly stable to hydrolysis and are relatively insensitive to shock. The ear-

liest 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. [67]. Both TNGU and DNGU were found to have a high crystal densities (2.04 and 1.98 g/ml, 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 [1].

Pagoria and coworkers [68] synthesized a number of cyclic nitrourea explosives with some attractive densities and performance. The most interesting was 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (K-6), with a density of 1.932 g/ml, DSC exotherm at 205 °C and measured performance 4% greater than HMX. K-6 was synthesized 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 and K-55 (Fig. 14).

Pagoria et al. [69] also reported the synthesis of 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (K-56) and 6-oxo-2,5,7-trinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (HK-56) from 1,3-diacetyl-2-imidazolone. Graindorge et al. [70] subsequently reported a shorter synthesis of K-56 from 1,4-diformyl-2,3-dihydroxypiperazine (**15**). This

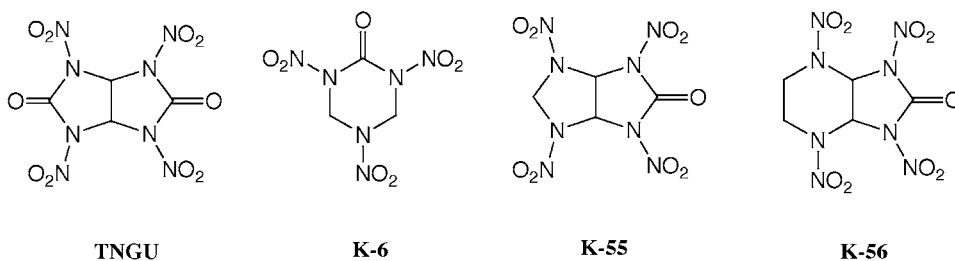


Fig. 14. Dinitroureas.

involved the condensation of **15** with urea (in aq. HCl) to yield 2,5,7,9-tetrahydro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one dihydrochloride, followed by nitration with 20%  $\text{N}_2\text{O}_5/\text{HNO}_3$ . K-56 has a density of 1.969 g/ml while HK-56 has a density of 1.84 g/ml.

Pagoria et al. [69] also synthesized 2,4,6,8-tetra-nitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one (K-55) and 2,4,6-trinitro-2,4,6,8-tetraazabicyclo[3.3.0]nonane-3-one (HK-55) by nitration of 2,4,6,8-tetrahydro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one dihydrochloride. Nitration with 100%  $\text{HNO}_3/\text{Ac}_2\text{O}$  (at 20–50 °C) yielded K-55 in 49% yield while nitration with 90%  $\text{HNO}_3$  and  $\text{Ac}_2\text{O}$  (at <10 °C) yielded HK-55 in 72% yield. Interestingly, HK-55 has approximately the same density (1.905 g/ml) as K-55 (crystal density = 1.91 g/ml). HK-55 (mp = 196 °C) has a  $\text{DH}_{50}$  of 61 cm (vs. 32 cm for HMX) and predictive codes suggest it has similar performance to HMX (Fig. 15).

Boyer and coworkers [71] reported the synthesis of *cis-syn-cis*-2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine (**16**) and *cis-syn-cis*-2,6-dioxo-1,4,7,8-tetra-nitrodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine (**17**) by nitration of the parent dihydrochloride salt with 20%  $\text{N}_2\text{O}_5/\text{HNO}_3$  or  $\text{Ac}_2\text{O}/\text{HNO}_3$ , respectively. Compound **16** which has a

crystal density of 2.07 g/ml, the highest density recorded for a C, H, N, O explosive, decomposes explosively at 210 °C and is decomposed easily with water [72]. Compound **16** is probably the most powerful explosive synthesized to date. Compound **17** (mp = 225 °C) has a density of 1.970 g/ml, and is stable to water and decomposes very slowly in boiling MeOH (Fig. 16).

Fischer et al. [73] synthesized octahydro-1,3,4,6-tetra-nitro-3 $\alpha$ ,3 $\beta$ ,6 $\alpha$ ,6 $\beta$ -cyclobuta[1,2-*d*:3,4-*d'*]-diimidazole-2,5-dione (**18**) by the nitration of octahydro-3 $\alpha$ ,3 $\beta$ ,6 $\alpha$ ,6 $\beta$ -cyclobuta[1,2-*d*:3,4-*d'*]-diimidazole-2,5-dione with 100%  $\text{HNO}_3$  in 97% yield. Compound **18** is a sensitive energetic material with good thermal stability (DSC exotherm at 232 °C) and is stable to dilute sulfuric acid at room temperature. It was converted to 1,2,3,4-cyclobutanetetranitramine (CBTN) by refluxing in dilute sulfuric acid for 6–8 h. CBTN is a quite sensitive energetic material that does not melt but detonates at 156 °C. Treatment of CBTN with *para*-formaldehyde in 80% aq.  $\text{H}_2\text{SO}_4$  yields octahydro-1,3,4,6-tetra-nitro-3 $\alpha$ , 3 $\beta$ ,6 $\alpha$ ,6 $\beta$ -cyclobuta[1,2-*d*:3,4-*d'*]diimidazole (**19**), which is similar in energy and sensitivity to HMX (Fig. 17).

Dagley et al. [74] have synthesized a number of cyclic nitramines containing the nitroguanidine group and measured their physical properties and shock and

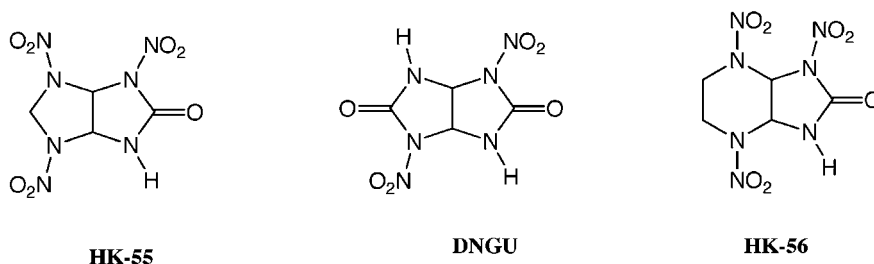


Fig. 15. Nitroureas as energetic compounds.

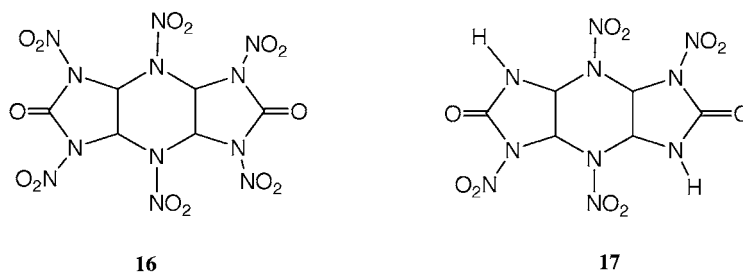


Fig. 16. Highly energetic nitroureas.

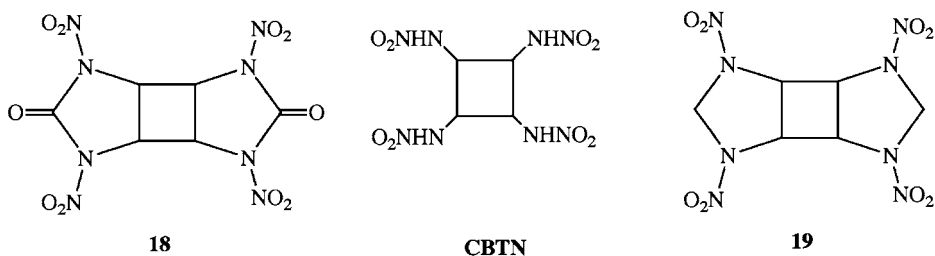


Fig. 17. Cyclobutane-1,2,3,4-tetraamine-based energetic materials.

friction sensitivities. In general, these nitroguanidine derivatives were more sensitive to shock and less thermally stable than anticipated. They conclude that the nitroguanidine and dinitrourea groups confer similar sensitiveness and are more sensitive trigger linkages than secondary nitramines. Compound **20**, the most promising of the reported compounds, was first reported in a patent by Huang and Rindone [75] and investigated as an insensitive energetic material. It has an mp of 207 °C and a drop hammer value of 80 cm (RDX = 32 cm). Dagley and coworkers [76] reported an improved synthesis of **20** by the chloride assisted nitrolysis of 2-nitrimino-5-*tert*-butyl-hexahydro-1,3,5-triazine (obtained from the condensation of nitroguanidine and formaldehyde with *tert*-butylamine). The addition of NH<sub>4</sub>Cl to the nitrolysis mixture improved the yield and eliminated an ensuing exotherm that occurred when NH<sub>4</sub>Cl was not used. This was the first reported example of a chloride-assisted nitrolysis of a tertiary amine.

Recently, Syczewski et al. [77] reported the synthesis of *N,N'*-dinitrourea (DNU) and its diammonium and dipotassium salts. DNU is unstable at room temperature and may undergo decomposition that may lead to spontaneous ignition. The diammonium

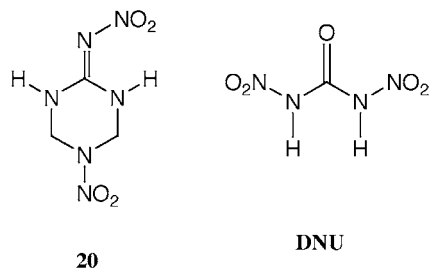


Fig. 18. Dinitrourea and nitrimine-based energetic compounds.

and dipotassium salts are stable at room temperature but start to decompose at 110 and 135 °C, respectively (Fig. 18).

## 9. Nitrotriazoles

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 [78]. The most studied nitrotriazole explosive, 4,6-bis(5-amino-3-nitro-1,2,4-triazolyl)-5-nitropyrimidine (DANTNP), was reported by Laval and coworkers [79]. The

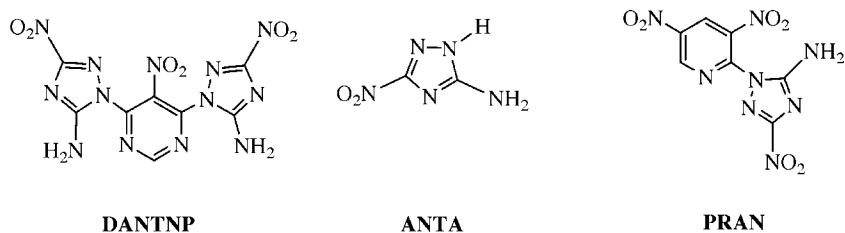


Fig. 19. 5-Amino-3-nitro-1,2,4-triazole (ANTA)-based energetic compounds.

conception and synthesis of DANTNP was an example of theoreticians and modelers guiding the organic chemists in the synthesis of new energetic materials. 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-nitropyrimidine (in EtOH). DANTNP (mp = 330 °C) is an insensitive explosive with a density of 1.865 g/ml and performance 10% greater than TATB.

ANTA was first prepared in 20% overall yield by Pevzner et al. [80] and involved first, the nitration of 3-acetyl-1,2,4-triazole with  $\text{Ac}_2\text{O}/\text{HNO}_3$  (at  $-25^\circ\text{C}$ ), followed by hydrolysis of the acetyl group. Lee et al. [81] subsequently reported an improved synthesis of ANTA that involved the treatment of 3,5-diamino-1,2,4-triazole with  $\text{NaNO}_2$  in sulfuric acid and heating to  $60^\circ\text{C}$  to yield 3,5-dinitro-1,2,4-triazole. This was converted to the ammonium salt, and one of the nitro-groups was reduced with refluxing hydrazine hydrate to give ANTA in 50% overall yield. Simpson et al. [82] used a modification of this synthetic method to scale-up the synthesis of ANTA and perform a 1-in. cylinder shot performance measurement. ANTA was found to be an insensitive energetic material with a density of 1.819 g/ml,  $\Delta H_f = 61$  kcal/mol, mp =  $238^\circ\text{C}$ , and performance 7% less than TATB.

Pagoria [25] synthesized a number of thermally stable, insensitive energetic materials by reacting the sodium salt of ANTA with a variety of mono- and dichloro-substituted nitroheterocyclic substrates in a polar, aprotic solvent. 1-(2,4,6-Trinitrophenyl)-5-amino-3-nitro-1,2,4-triazole, 2-(5-amino-3-nitro-1,2,4-triazolyl)-3,5-dinitropyridine (PRAN), 2,4-bis(5-amino-3-nitro-1,2,4-triazolyl)pyrimidine (IHNX), 1,5-bis(5-amino-3-nitro-1,2,4-triazolyl) 2,4-dinitrobenzene, and 4-(5-amino-3-nitro-1,2,4-triazolyl)-6-(3-nitro-1,2,4-triazolyl)-5-nitropyrimidine were all prepared and their structures were confirmed by

X-ray crystallographic analysis. The two most interesting, PRAN and IHNX, have densities of 1.815 and 1.865 g/ml, and mp = 289 and  $336^\circ\text{C}$ , respectively (Fig. 19).

Lee et al. [81] synthesized 3,6-bis(5-amino-3-nitro-1,2,4-triazolyl)-1,2,4,5-tetrazine (**21**) and 2,4,6-tris(5-amino-3-nitro-1,2,4-triazolyl)-1,3,5-triazine (**22**) by reacting the sodium salt of ANTA with 3,6-dichlorotetrazine and cyanuric chloride in refluxing  $\text{CH}_3\text{CN}$ . They have densities of 1.78 and 1.71 g/ml, respectively, and both have DTA exotherms at  $240^\circ\text{C}$ . Although all these ANTA derivatives are thermally stable, insensitive energetic compounds they seem to hold no advantages over the current industry standard, TATB (Fig. 20).

Baryshnikov et al. [83] synthesized several 4-nitro-1,2,3-triazoles by reacting sodium azide with a variety of 1,1-dinitroethylene synthons, including 2,2-dinitroethyl acetate, 1,1,1-trinitroalkanes and 1,1-dimethyl-2,2-dinitroethylamine. 3-Methyl-4-nitro-1,2,3-triazole was synthesized by the condensation of acetaldehyde with ethyl-2,2-dinitroacetate and  $\text{NaN}_3$ . This was converted to the insensitive explosive, 4-amino-5-nitro-1,2,3-triazole (ANTZ) (mp =  $290^\circ\text{C}$ ), by oxidation of the methyl group with  $\text{KMnO}_4$  to the 4-carboxy-derivative, followed by conversion of the acid to an amino group using classical methods. The amino group of ANTZ was oxidized with  $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$  to yield 4,5-dinitro-1,2,3-triazole (DNTZ), which was isolated as its sodium or potassium salt. Earlier, Neuman [84] synthesized 4-picrylamino-5-nitro-1,2,3-triazole (PANT) by reacting 4-amino-1,2,3-triazole with picryl chloride followed by nitration with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  at  $20^\circ\text{C}$ . PANT (mp =  $236^\circ\text{C}$ ) has a crystal density of 1.82 g/ml.

Baryshnikov et al. [85] also reported the synthesis of 5,5'-dinitro-4,4'-bi-1,2,3-triazole (DNBT) by the condensation of 1,1,4,4-tetranitrobutane-2,3-diacetate

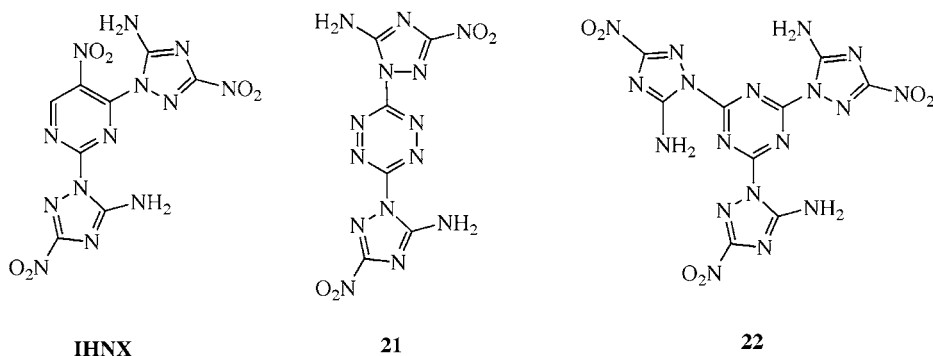


Fig. 20. ANTA-substituted energetic compounds.

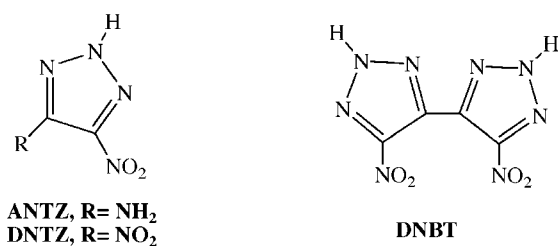


Fig. 21. Energetic 4-Nitro-1,2,3-triazole explosives.

with  $\text{NaN}_3$  in aq. MeOH. DNBT is a sensitive energetic material with an mp of  $155^\circ\text{C}$  and two acidic protons (Fig. 21).

## 10. Ammonium dinitramide (AND)

Bottaro et al. [86] in 1991 reported the synthesis of ADN, an interesting new oxidizer that may have potential uses in environmentally benign rocket propellant ingredient and as a cationic phase transfer agent. Following this paper, Tartakovsky and coworkers [87–93] published a number of articles on their independent research on the synthesis and use of dinitramide salts. A significant number of salts of the dinitramide anion have been synthesized, including the alkali salts, guanidinium, hydroxylammonium, aminoguanidinium, cubane-1,4-diammonium, cubane-1,2,4,7-tetraammonium, biguanidinium, 1,2-ethylenediammonium and many others [86]. There have been several reported syntheses of ADN including the nitration of nitramide and even ammonia, although the reported yields from ammonia thus far have been

<15% using these methods. Dinitramide salts were first synthesized by the  $\beta$ -elimination reaction of 1-(*N,N*-dinitramino)-2-trimethylsilylethane with CsF, yielding the cesium salt of ADN. Ion-exchange of the cesium cation was the expedient route into the synthesis of the large number of dinitramide salts reported. The synthesis routes currently used for the large scale production of ADN involves either: (1) the nitration of ammonium nitrourethane with  $\text{N}_2\text{O}_5$  in  $\text{CH}_2\text{Cl}_2$  to yield the non-isolated dinitrourethane followed by treated with ammonia to yield ADN and ammonium nitrourethane [94]; or (2) nitration of sulfonamide derivatives followed by treatment with metal hydroxides and ion-exchange [95].

ADN has some interesting chemical properties. It is a very strong acid with a  $pK_a \approx -5$ , is stable between pH 3 and 15, but slowly decomposes in concentrated acid. It has an mp of  $92^\circ\text{C}$ , a DTA exotherm which leaves the baseline at  $130^\circ\text{C}$  and peaks at  $198^\circ\text{C}$  and a density of  $1.801\text{ g/ml}$  [96]. ADN is stable compared to alkyl dinitramines [97] which are unstable, sensitive energetic materials. This stability has been attributed to the delocalized negative charge that stabilizes those  $\text{N}-\text{NO}_2$  bonds of ADN most susceptible to rupture (Fig. 22).

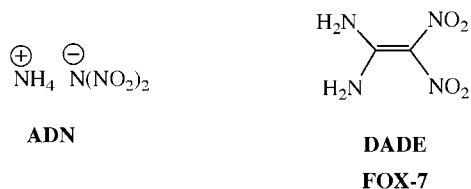


Fig. 22. Ammonium dinitramide (ADN) and 1,1-diamino-2,2-dinitroethylene (DADE, FOX-7).

### 11. 1,1-Diamino-2,2-dinitroethylene (FOX-7, DADE)

Recently, Latypov et al. [98] reported the synthesis of 1,1-diamino-2,2-dinitroethylene (FOX-7 or DADE), an interesting new energetic material with a density of 1.885 g/ml,  $\Delta H_f = 32$  kcal/mol, and a drop hammer height value of 72 cm (HMX = 32 cm). It has the same oxygen balance as HMX and is predicted to have 85% of its performance. The first synthesis of FOX-7 involved the nitration of 2-methyl-4-nitroimidazole with conc.  $H_2SO_4$  and  $HNO_3$  to give a mixture of parabanic acid and 2-(dinitromethylene)-4,5-imidazolidinedione. The latter product was treated with ammonium hydroxide at pH 8–9 to yield FOX-7 as an insoluble yellow solid. FOX-7 may be recrystallized from water to yield yellow plates with an mp of 289 °C. A synthesis more amenable to scale-up involves the condensation of acetamidine hydrochloride and diethyl oxalate in MeOH to yield a mixture of 2-methylene-4,5-imidazolidinedione and 2-methoxy-2-methyl-4,5-imidazolidinedione (**23**). Recrystallization of the mixture from MeOH yields **23** which was nitrated and treated with ammonium hydroxide as above to yield FOX-7 in 50% overall yield. Earlier, Baum et al. [99] synthesized several 1,1-bis(alkylamino)-2,2-dinitroethylenes by reacting 2,2-diiodo-2,2-dinitroethylene (DIDN) with alkylamines, but when DIDN was reacted with ammonia FOX-7 was not formed, the major product being  $NH_4^+C(NO_2)_2CN^-$  (Fig. 22).

### 12. Highly nitrated cage compounds

Highly nitrated cage compounds constitute a new class of energetic materials that have received a substantial amount of interest in the past 10 years. The great promise of this new class of energetic materials is based on the premise that the combination of the strained rings of cage compounds (with concomitant increase in the heat of formation) and the rigid, highly compact cage structure should result in a highly dense, more powerful explosive. A major drawback has been the corresponding increase in the difficulty in synthesis of these caged structures. The most studied example of highly nitrated cage compounds has been CL-20, first synthesized by Nielsen et al. [100] at NAWC,

China Lake. Nielsen et al. [101] reported the first synthesis of the 2,4,6,8,10,12-hexabenzyl-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0.5.9.0.3,11]dodecane(hexabenzyl-hexaazaisowurtzitane, HBIW) structure in 1985 when he condensed benzylamine with glyoxal in  $CH_3CN$  to yield HBIW. HBIW was further elaborated to CL-20 in three synthetic steps [101,102]. CL-20 is the most powerful explosive currently being investigated at the pilot plant scale or larger [103]. CL-20, in its  $\epsilon$ -crystal polymorph, has a density of 2.04 g/ml, a decomposition temperature of 228 °C and a drop hammer height of 12–18 cm (PETN = 10 cm).

Highly nitrated cubanes were predicted to be very dense, highly energetic compounds with explosive performance greater than CL-20. Recently, Eaton and coworkers [104] reported the synthesis of heptanitrocubane (**24**) and octanitrocubane (**25**), the culmination of an ongoing project in the synthesis of nitrocubanes as energetic materials. Previously, Eaton et al. [105] reported the synthesis of 1,3,5,7-tetranitrocubane (**26**) (mp = 202 °C,  $\rho = 1.814$  g/ml) by the oxidation of the tetraamino derivative with dimethyldioxirane. The more highly nitrated species proved to be more difficult to synthesize. The pentanitrocubanes ( $\rho = 1.959$  g/ml) and hexanitrocubanes [106] were synthesized by the treatment of the anion of tetranitrocubane with  $N_2O_4$  at the interface between frozen THF and  $N_2O_4$ . Heptanitrocubane ( $\rho = 2.028$  g/ml) was synthesized by the treatment of tetranitrocubane with 4 eq. of  $NaN(TMS)_2$  followed by reacting the resulting anionic species with frozen  $N_2O_4$  in THF/isopentane. Octanitrocubane ( $\rho = 1.979$  g/ml) was synthesized by the treatment of heptanitrocubane with  $LiN(TMS)_2$  in  $CH_2Cl_2$  at  $-78$  °C with  $NOCl$  followed by ozonation until the blue color disappeared (Fig. 23).

Marchand et al. have synthesized a number of polynitro-caged compounds including compounds **27** [107], **28** [108], and **29** [109], mainly from elaboration of the corresponding di- and triketone derivatives. Zajac [110] reported the synthesis of 3,7,9-trinitronoradamantane (**30**) by the conversion of 9,9-dimethoxy[3.3.1]nonane-3,7-dione to the Trisoxime and subsequent oxidation. Sollot and Gilbert [111] reported the synthesis of 1,3,5,7-tetranitroadamantane (TNA), a thermally stable energetic material with an mp of 361 °C, by the oxidation of 1,3,5,7-tetraaminoadamantane with  $KMnO_4$  in aqueous acetone.

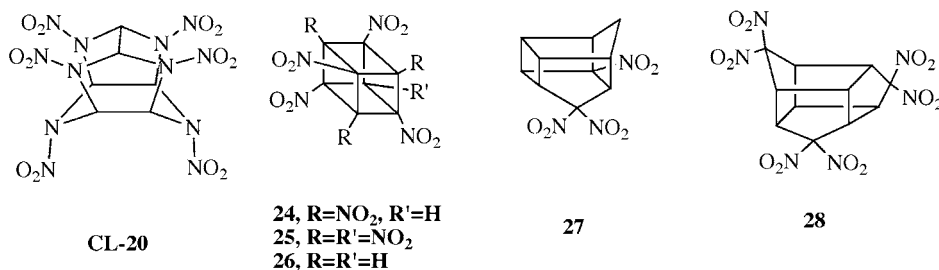


Fig. 23. Highly energetic caged compounds.

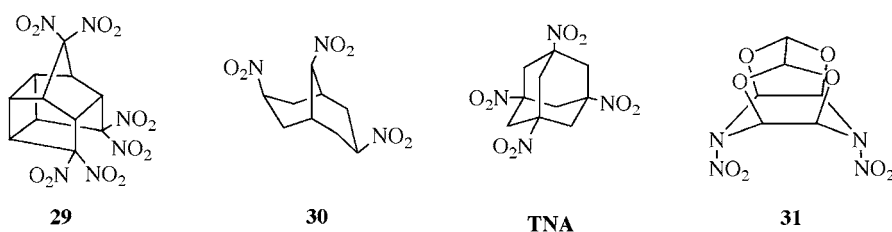


Fig. 24. Polynitro-substituted cage compounds.

Boyer and coworkers [112] reported the synthesis of 4,10-dinitro-2,6,8,12-teraoxo-4,10-diazatetracyclo[5.5.0.0.5,9.03,11]dodecane (**31**) by the condensation of 1,4-diformyl-2,3,5,6-tetrahydropiperazine with glyoxal in the presence of acid. The surprisingly high density of compound **31** (1.99 g/ml), considering it possesses only two nitramine moieties, was attributed to the caged structure. It is thermally stable with an mp of >250 °C and has been investigated as an insensitive energetic material [1] (Fig. 24).

### 13. Difluoramines

Recently, there has been renewed interest in the synthesis of difluoramines as energetic materials, especially for weapon systems containing aluminum and boron [113]. The difluoramine group, because on decomposition yields HF in the presence of a hydrogen source, is quite energetic, but all difluoramines with good oxygen balance synthesized thus far have been quite sensitive to shock and have relatively poor thermal stability. Recently there have been two main approaches to the synthesis of energetic difluoramines,

the difluoroamination of heterocyclic [114] and dinitromethyl anions [115] with NF<sub>2</sub>OSO<sub>2</sub>F and the formation of geminal difluoramino groups by reacting ketones with difluoramine in fuming sulfuric acid. The two most interesting energetic materials containing the difluoramino group synthesized recently are 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-dinitro-1,5-diazocine (HNFX) [116] and 1,1,3,5,5-pentanitro-1,5-bis(difluoramino)-3-azapentane (DFAP) [115]. HNFX was synthesized by the nitrolysis of 3,3,7,7-tetrakis(difluoramino)octahydro-1,5-bis(4-nitrobenzenesulfonyl)-1,5-diazocine with HNO<sub>3</sub>/CF<sub>3</sub>SO<sub>3</sub>H at 55 °C for 40 h. HNFX has a density of 1.807 g/ml, the low density attributed to solvent channels in the crystal structure formed during crystallization. Chapman et al. [116] note that more dense polymorphs may be found in the future, in a manner similar to both CL-20 and HMX which had low-density polymorphs isolated initially. DFAP was synthesized by the alkylation of bis(2,2-dinitroethyl)nitramine with NF<sub>2</sub>OSO<sub>2</sub>F in CH<sub>3</sub>CN. DFAP (mp = 103 °C) has an extremely high density for an acyclic compound of 2.045 g/ml (Fig. 25). All difluoramines are shown in Figs. 23–25.

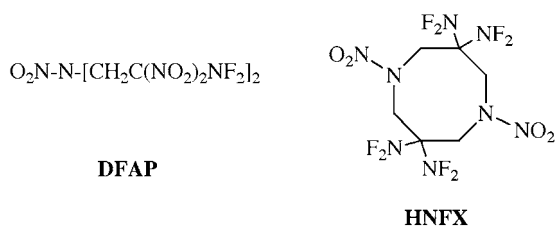


Fig. 25. Difluoramines as energetic compounds.

#### 14. $\text{N}_5^+\text{AsF}_6^-$

Polynitrogen compounds are of significant interest as high energy density materials as described earlier in this review. Recently, Christie and coworkers [117] synthesized  $\text{N}_5^+\text{AsF}_6^-$ , the first example of a new homoleptic polynitrogen ion since the discovery of the azide ion in 1890.  $\text{N}_5^+\text{AsF}_6^-$  was synthesized by the condensation of  $\text{N}_2\text{F}^+\text{AsF}_6^-$  with  $\text{HN}_3$  at  $-78^\circ\text{C}$  in anhydrous HF.  $\text{N}_5^+\text{AsF}_6^-$  is a white solid that is marginally stable at room temperature but can be stored for weeks at  $-78^\circ\text{C}$ .

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