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# Advanced energetic materials: novel strategies and versatile applications

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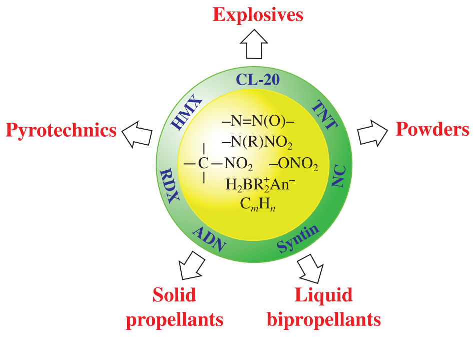
**Novel efficient synthetic strategies, including green methodologies, to basic and perspective high-energy density compounds, bearing active oxygen sources (*C*-, *N*- and *O*-nitro groups and *N*-oxide fragments) and high-enthalpy polynitrogen heterocycles, are briefly overviewed. Recently developed synthetic approaches to nitro group-free hypergolic ionic liquids (HILs) and strained 1,5-diazabicyclo[3.1.0]hexane derivatives capable of ultrafast ignition upon mixing with an oxidizer, and to high-energy liquid hydrocarbons with strained cyclopropane fragments are also considered. Physicochemical properties, energetic performances and potential applications of energetic compounds and composites as key components of explosives, powders and solid or liquid rocket propellants are critically discussed with a focus on original reports published in the period 2016–2021.**



*Keywords*: energetic materials, energetic compounds, explosives, powders, propellants, hypergolic fuels, nitro compounds, *N*-oxides, strained hydrocarbons, green chemistry.

*Dedicated to memory of Professor Nina Makhova*

## 1. Introduction

Creation of new materials with unique properties and modification of known ones aimed at significant improving their performance and/or attaining ecological or any other desirable benefit are the main goals of chemistry and material sciences.[1–3] Energetic materials (EMs), key integral parts of mixed solid propellants, explosives, powders and pyrotechnical compositions, and important ingredients of civil industries (mining, fracking, aerospacing industries),[4–6] are considered as advanced high technology products which adequately indicate scientific and technological level of a state. A peculiarity of these materials is their capability of releasing significant amount of accumulated chemical energy instantly *via* highly exothermic intra- or intermolecular redox reactions initiated by external stimuli. Key energetic components of EMs must possess nearly incompatible properties. They must have high density, balanced elemental composition, and acceptable enthalpy of formation and at the same time be thermally and chemically stable, safe in handling, transportation, storage, *etc*. Hypergolic fuels[7] and high-energy-density hydrocarbons[8] which are responsible for high specific impulse of liquid bypropellants used in aero and space vehicles also belong to the EM category. At present, energetic and operating resources of existing chemical energetic kit are nearly exhausted. Evidently, synthesis of basically new energy rich molecules or essential improving properties of known ones are urgent tasks.

Another challenge is originated from ecological issues.[9,10] Existing technologies for production of energetic compounds (ECs) and EMs, in particular those based on nitration reactions, are explosion risky and do not meet contemporary ecological standards because of enormous amount of harmful wastes demanding energy-consuming utilization.[11]

In this focus article, we overviewed recently proposed strategies for targeted design and rational synthesis of ECs containing nitro groups and/or other active oxygen rich or high enthalpy structural fragments and briefly discussed potential directions of their application as components of advanced energetic materials (for pharmacology oriented applications of nitro compounds see recent reviews[12–14]).

## 2. Energetic nitro compounds

A majority of practically used ECs contain nitro groups as powerful source of accumulated chemical energy.[6,15–18] Active

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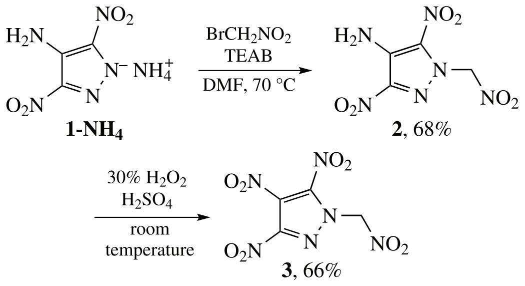
† Deceased.

oxygen atoms incorporated into the nitro group oxidize hydrogen and carbon atoms of the same or other molecules under the action of external stimuli resulting in instant explosion or burning. Nitro groups can be attached to carbon, nitrogen or oxygen atoms of the energetic molecule backbone. The structural core exerts a significant impact on the EM efficiency. For better performance it should contain optimal amount of C and H atoms disposed to oxidation and, in some cases, heterocyclic fragments bearing high enthalpy N–N and N–O bonds. The main challenge in the discovery and development of novel ECs is the trade-off between sensitivity, thermal stability, and explosive performance.

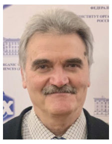
### 2.1. *C*-Nitro compounds

*C*-Nitro compounds are considered as the first generation of ECs. Most prominent representative of these ECs is 2,4,6-trinitrotoluene (TNT), which is traditionally used in energetic compositions as available, thermally stable ($T_{dec}$ 285 °C) and nearly insensitive melt-castable explosive (mp 80 °C).[17] Syntheses of novel, more powerful than TNT, *C*-nitro compounds with azole-based (mainly, unique nitro-compatible pyrazole-based) backbone, has attracted considerable attention of researchers.

Shreeve with co-authors[19] developed synthetic approach to 3,4,5-trinitro-1-(nitromethyl)-1*H*-pyrazole **3** which is based on reaction of ammonium 4-amino-3,5-dinitropyrazolate **1-NH$_4$** with bromonitromethane in the presence of tetraethylammonium bromide (TEAB) as phase transfer catalyst (10 mol%) and subsequent oxidation of resulting 3,5-dinitro-1-(nitromethyl)-



**Scheme 1**



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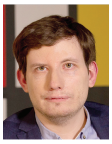

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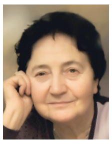

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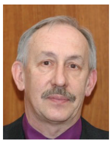

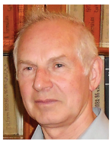

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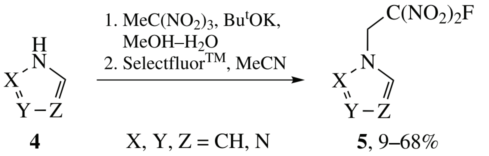
Professor **Vladimir A. Tartakovsky**, Full Member of the Russian Academy of Sciences, is the head of the Laboratory of Chemistry of Nitro Compounds at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. He is an expert in the areas of theoretical and practical implications of nitro and nitrogen-oxygen heterocyclic compounds as well as in industrial organic synthesis (the synthesis of universal ingredients for multi-purpose composite materials and environment-friendly ingredients of propellants).

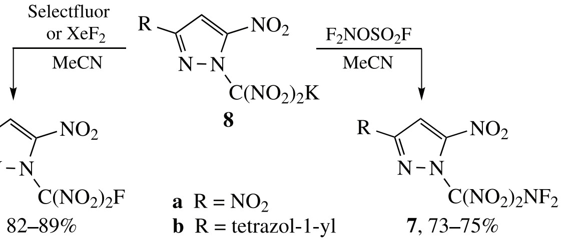
1*H*-pyrazol-4-amine **2** with a sulfuric acid–30% $H_2O_2$ mixture (Scheme 1). Product **3** has good oxygen balance (+18.3%) and exhibits detonation velocity ($V_D = 8858$ m s$^{-1}$) and detonation pressure ($P = 35.1$ GPa) higher than hexogen (RDX). It is concomitantly characterized by high thermal stability ($T_{dec} = 202$ °C) and acceptable impact and friction sensitivities (IS = 14 J, FS = 120 N). This combination of properties makes it a promising chlorine-free high energy density oxidizer and a potential candidate for replacement of ammonium perchlorate.

An original two-step synthesis of pyrazole, imidazole, triazole, and tetrazole based ECs **5** bearing dinitrofluoroethyl group *via* a two-step dinitrofluoroethylation of corresponding NH-azoles **4** was developed by Sheremetev *et al.*[20] The one-pot tandem reaction included Michael addition of NH-azoles **4** to 1,1-dinitroethene, generated *in situ* from 1,1,1-trinitroethane and a base, followed by electrophilic fluorination of *N*-dinitroethyl intermediates formed (Scheme 2). Synthesized compounds **5** are considered as important components of energetic materials for metallized solid propellant formulations and explosive compositions.



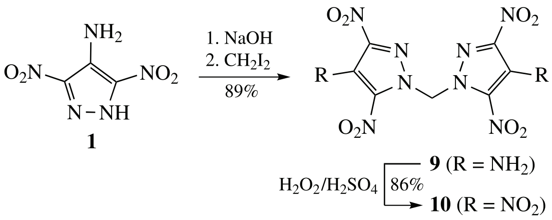
**Scheme 2**

Synthesis of more energetic dinitropyrazole derivatives **6a** and **7a** bearing dinitrofluoromethyl or (difluoroamino)dinitromethyl group attached to a nitrogen atom of the heterocycle was achieved by the same research team *via* treatment of 1,1-dinitro-1-(3,5-dinitropyrazol-1-yl)methanide **8a** with electrophilic fluorinating or difluoroaminating agents (Scheme 3).[21] Estimated and measured densities of compounds **6a** and **7a** (*d* 1.931 and 1.920 g cm$^{-3}$, respectively) and calculated detonation parameters ($V_D = 8570$–$8721$ m s$^{-1}$, $P = 33.1$–$36.3$ GPa) are notably high. However, moderate thermal stability ($T_{dec} = 113$ °C for energetically superior compound **7a**) prevents practical application of **7a** in energetic compositions. Similar methodology was applied later to synthesis of analogues **6b** and **7b** in which substituent-free high-enthalpy tetrazol-1-yl fragment rather than nitro group is attached to the pyrazole unit at position 3.[22]



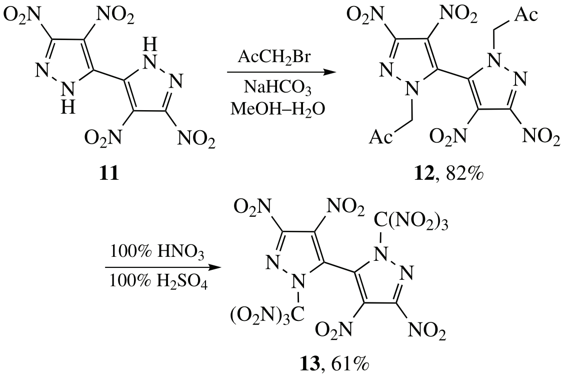
**Scheme 3**

Compounds bearing two pyrazole rings linked to each other or fused with another polynitrogen heterocycle are considered as perspective energetic targets. Klapötke with co-authors reported preparation of very promising ECs with bis-pyrazolyl core by the reaction of available 3,5-dinitro-4-aminopyrazole **1** sodium salt with diiodomethane (Scheme 4).[23] The alkylation product **9** produced in this reaction in excellent yield possesses very high thermal stability ($T_{dec} = 310$ °C) and impact sensitivity (11 J) compatible with those of benchmark hexanitrostilbene (HNS) and pentaerythritol tetranitrate (PETN). Moreover, the amino groups in bispyrazole **9** could be oxidized to the nitro groups with a 50% $H_2O_2$–$H_2SO_4$ mixture affording bis(3,4,5-trinitropyrazolyl)methane **10**, a novel nitrogen and oxygen rich secondary explosive with theoretical and estimated experimental detonation performance ($V_D$ 9304 and 9910 m s$^{-1}$, respectively) in the range of that of CL-20. Importantly, it exhibits promising thermal stability ($T_{dec}$ 205 °C). Though, impact sensitivity of compound **10** is rather high (4 J).



**Scheme 4**

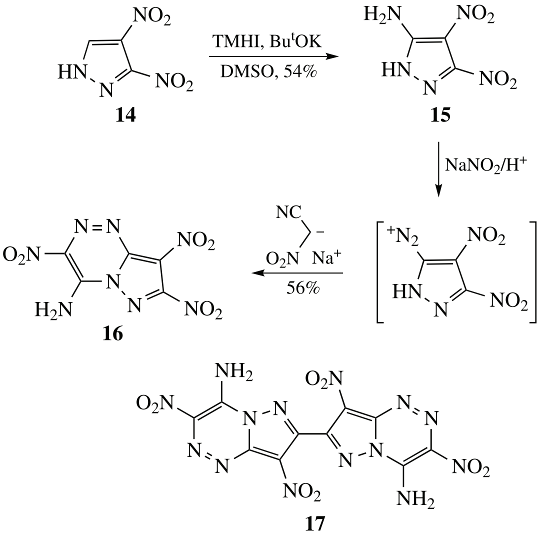
Sheremetev and Dalinger with co-authors[24] synthesized an oxygen-rich energetic oxidizer bearing four aromatic and six aliphatic nitro groups by alkylation of tetranitrobipyrazole **11** with bromoacetone followed by destructive nitration of *N*-acetonyl derivative **12** (Scheme 5). Bipyrazole **13** has outstanding density ($d = 2.021$ g cm$^{-3}$), positive oxygen balance to $CO_2$ (+10.5%) and exhibits very good detonation performance ($V_D = 9320$ m s$^{-1}$, $P = 40$ GPa) far beyond those of commonly used oxidizers ammonium perchlorate and ammonium dinitramide (ADN). However, insufficient thermal stability ($T_{dec} = 125$ °C) complicates application of this compound in solid propellant formulations and other EMs.



**Scheme 5**

Significant attention has been focused on energetic C-nitro compounds containing pyrazole core fused with another high-enthalpy polynitrogen heterocycle. It is expected that flat geometry of fused polycyclic explosive molecules would result in π–π interactions and N–H···O type hydrogen bonding, which reduce their sensitivity and enhance thermal stability. Chavez with co-authors[25] developed rational synthesis of high density pyrazolo-triazine explosive **16** which was first synthesized in seven steps and 10% overall yield by Shevelev and coworkers.[26] Vicarious nucleophilic amination of 3,4-dinitropyrazole **14** with trimethylhydrazinium iodide (TMHI) afforded 5-amino-3,4-dinitropyrazole **15**, which was converted to pyrazolo-triazine **16** in 56% yield *via* diazotization and subsequent condensation with the sodium salt of nitro-acetonitrile (Scheme 6). The high-density compound **16** ($d_{exp}$ 1.946 g cm$^{-3}$) has positive heat of formation (+88.44 kcal mol$^{-1}$) and, according to calculations, should exhibit HMX-like performance with lower sensitivity and good vacuum thermal stability.

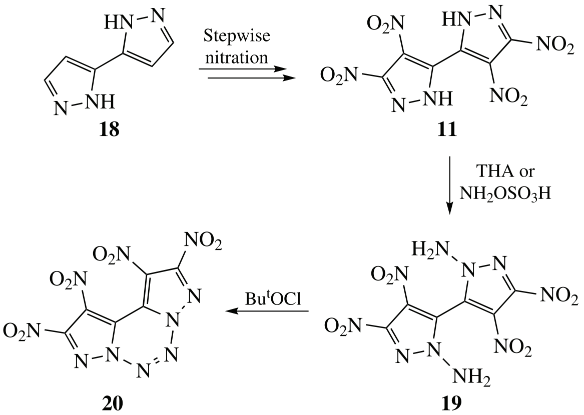
Similar diazotization approach was applied for the preparation of more complex molecule **17** containing two pyrazolo-triazine fragments linked to each other by the C–C bond (see Scheme 6).[27] Compound **17** possesses useful combination of properties: excellent thermal stability



**Scheme 6**

($T_{dec}$ = 315 °C), very low sensitivity to impact and friction (>60 J and >360 N, respectively) and promising detonation performance ($V_D$ = 8572 m s$^{-1}$, $P$ = 31.4 GPa) and has potential as a high-temperature EM.

Shreeve with co-authors synthesized novel hydrogen-free dinitropyrazole fused 1,2,3,4-tetrazine **20** starting from bipyrazole **18**.[28] The reaction sequence included stepwise nitration of compound **18** to 4,4′,5,5′-tetranitro-2*H*,2′*H*-3,3′-bipyrazole **11** followed by amination of the latter with *O*-*p*-toluenesulfonylhydroxylamine (THA) or hydroxylamine-*O*-sulfonic acid and the intramolecular N-azo coupling reaction of the diamine **19** to the desired tricyclic fused ring **20** (Scheme 7). The EC **20** exhibits unexpectedly high thermal stability with the decomposition point 233 °C. It has a remarkable density of 1.955 g cm$^{-3}$ measured at room temperature and shows excellent detonation performance ($V_D$ = 9631 m s$^{-1}$). These parameters along with lower impact and friction sensitivities of **20** compared to those of CL-20 make it very attractive candidate for further testing as a key energetic ingredient in high performance compositions.



**Scheme 7**

## 2.2. *N*-Nitro compounds

*N*-Nitramines constitute a very important class of ECs. Basic powerful explosives such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) with crystal density up to 2.04 g cm$^{-3}$ and velocity of detonation up to 9380 m s$^{-1}$ and one of the most efficient oxidizers ammonium dinitramide (ADN) bearing a two-fold excess of active oxygen ($\alpha$ = 2.0) contain nitramine groups (Figure 1).

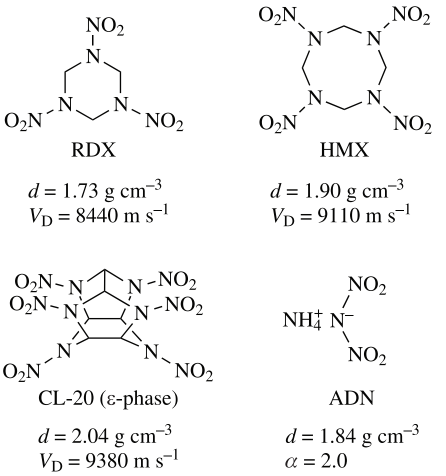
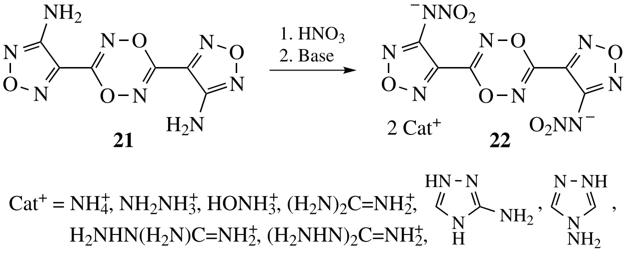


**Figure 1**

Over the past five years, several reviews on high-energy nitramines have been published,[18,29–34] which cover both covalent compounds and the *N*-nitramine salts. Different research groups tried to improve multi-step synthesis of most promising caged nitramine CL-20, in particular catalytic debenzylation[35] and nitration steps.[36–38]

To improve operational safety while retaining energetic performance of the CL-20, its co-crystals with TNT, HMX,[39] benzotrifuroxan[33] and with high-energy azoles[40] were synthesized. The CL-20/7*H*-trifurazano[3,4-*b*:3′,4′-*f*:3″,4″-*d*]-azepine (TFAZ) co-crystals in a 1 : 1 molar ratio exhibited good thermal stability ($T_{dec}$ = 242.8 °C), low sensitivity towards impact ($H_{50}$ = 42 cm) and friction ($P_f$ = 38%), high crystal density (1.932 g cm$^{-3}$), and high calculated detonation velocity (9103 m s$^{-1}$).[41]

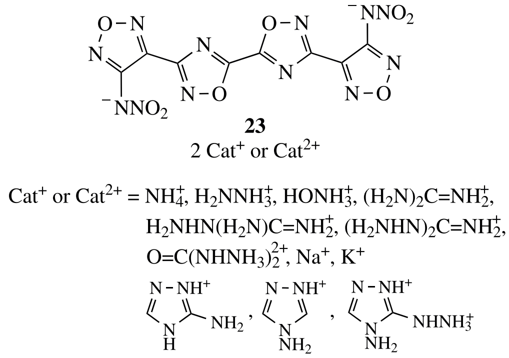
Another direction of researches has been focused on synthesis of *N*-nitramine salts as potential energetic materials. Energetic salts **22** were recently obtained by acidic nitration of 3,6-bis-(4-amine-1,2,5-oxadiazolyl)-1,4,2,5-dioxadiazine scaffold **21** followed by treatment of resulting *N*-nitramine with a base (Scheme 8).[42] The crystal densities of the salts are ranged from 1.730 to 1.914 g cm$^{-3}$. Ionic compounds **22** decomposed at 114–197 °C without melting and exhibited higher impact (1.5–4.5 J) and friction (53–144 N) sensitivities than TNT or RDX. However, detonation parameters of the hydroxylammonium salt **22** (Cat$^+$ = HONH$_3^+$) ($V_D$ = 9095 m s$^{-1}$ and $P$ = 38.1 GPa) are better than those of RDX.



**Scheme 8**

The *N*,*N*′-{[5,5′-bi(1,2,4-oxadiazole)]-3,3′-diylbis(1,2,5-oxadiazole-4,3-diyl)}-based nitramide salts **23** were prepared in a similar manner.[43] In terms of energetic properties ($V_D$ = 9030 m s$^{-1}$, $P$ = 36.0 GPa), dihydroxylammonium salt **23** (Cat$^+$ = NH$_3$OH$^+$) is superior to RDX but slightly inferior to HMX (Figure 2).

Cation nature contributes significantly to energetic performance and safety of the *N*-nitramine salts. Dihydroxylammonium salt **24** of 3-nitramino-4-(1*H*-tetrazol-5-yl)-



**23**
2 Cat$^+$ or Cat$^{2+}$

Cat$^+$ or Cat$^{2+}$ = $NH_4^+$, $H_2NNH_3^+$, $HONH_3^+$, $(H_2N)_2C{=}NH_2^+$, $H_2NHN(H_2N)C{=}NH_2^+$, $(H_2NHN)_2C{=}NH_2^+$, $O{=}C(NHNH_3)_2^{2+}$, $Na^+$, $K^+$

**Figure 2**

furazan is rather sensitive towards impact but exhibits very good velocity of detonation. On the other hand, corresponding diguanidinium salt **25** is much safer in handling, however at the expense of detonation parameters.[44] Interestingly, equimolar mixture of salts **24** and **25** obtained by careful removal of solvent from the mixed solution shows a better balance between energetic properties and safe handling (Figure 3).

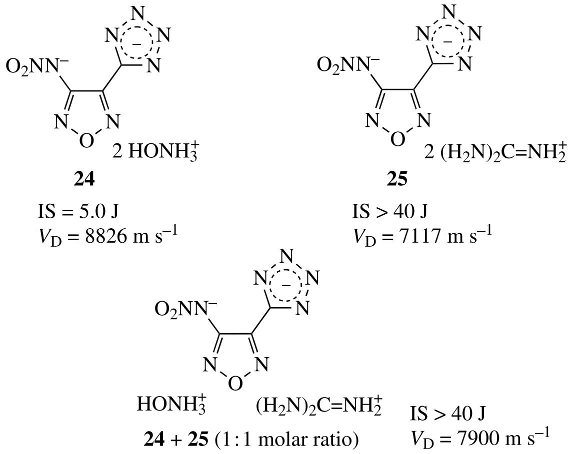
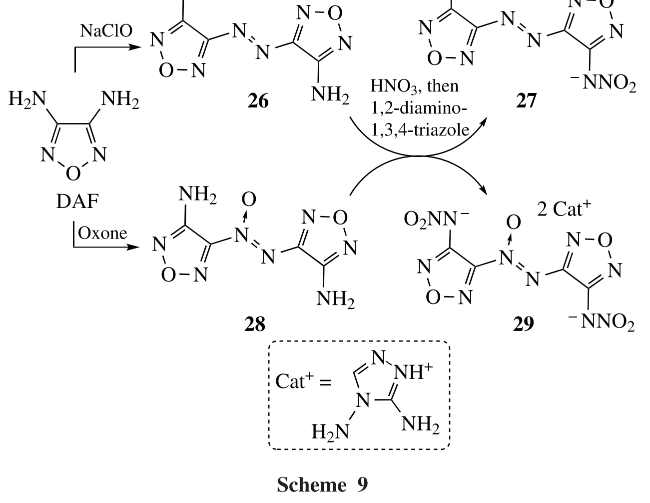


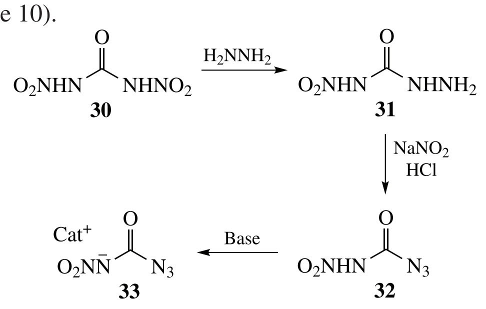
**Figure 3**

Oxidation of diaminofurazan (DAF) with sodium hypochlorite or Oxone® afforded corresponding azo- and azoxy furazans **26** or **28**, which were converted to energetic bis-*N*-nitramine salts **27** or **29** by acidic nitration reaction followed by treatment with 3,4-diamino-1,2,4-triazole (Scheme 9).[45] According to differential scanning calorimetry, salts **27** and **29** are stable up to 216 and 191 °C decomposition onset temperatures, respectively.



**Scheme 9**

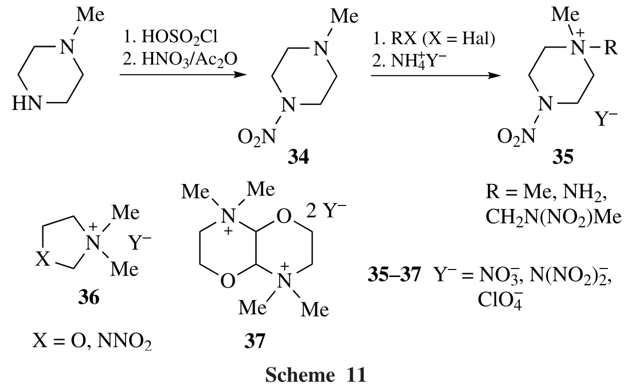
Very recently, Klapötke with co-authors proposed a synthetic approach to novel nitrocarbamoyl azide and its salts.[46] Dinitrourea **30** was converted to 4-nitrosemicarbazide **31** by treatment with hydrazine hydrate. Subsequent nitrosation of compound **31** afforded azide **32**, very sensitive to shock and friction, which was transformed to energetic salts **33** under the action of corresponding bases. However, thus obtained salts revealed unsatisfactory thermal stability ($T_{dec}$ = 80–120 °C), high sensitivity to mechanical stimuli and low density (Scheme 10).



Cat$^+$ = $Na^+$, $K^+$, $NH_4^+$, $HONH_3^+$, $(H_2N)_2C{=}NH_2^+$

**Scheme 10**

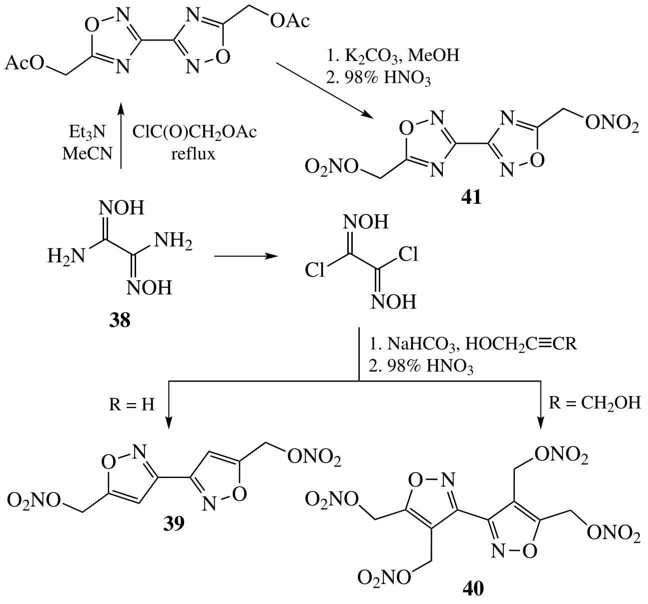
Energetic salts bearing explosive *N*-nitramine groups in both cation and anion are particularly attractive for designing novel high-performance ECs. Compounds **35** of this type were recently synthesized from *N*-methylpiperazine by successive sulfamidation and nitration reactions, followed by alkylation of *N*-methyl-*N*-nitropiperazine **34** and the anion metathesis in the resulting quaternary ammonium salt (Scheme 11). The *N*-nitroimidazolidine, oxazolidine and bismorpholine-based energetic quaternary ammonium salts **36** and **37** were prepared *via* similar synthetic approach.[47] Energetic salts **35–37** containing *N*-nitramine groups and oxygen-rich nitrate, dinitramide (DNA) or perchlorate anions possess an enhanced hydrogen content, improved oxygen balance and satisfactory (for DNA salts) heat of formation. They are stable up to 200 °C and may be considered as prospective components of propellants and powders.



**Scheme 11**

### 2.3. *O*-Nitro compounds

The nitric ester moiety is historically the first explosive group which up to now remains one of the most useful in designing EMs.[48] It is an integral part of primary or secondary explosives and is widely used in the development of modern powder and propellant ingredients. Herein, recent advances in the energetic nitric ester chemistry are briefly summarized. Sabatini with co-authors synthesized melt-castable nitric esters **39–41** basing on available diaminoglyoxime precursor **38** (Scheme 12). The 3,3′-biisoxazole-5,5′-bis(methylene) dinitrate **39** was found to have performance properties similar to TNT, while fitting into the standard melt-castable range.[49] Biisoxazoletetrakis(methyl

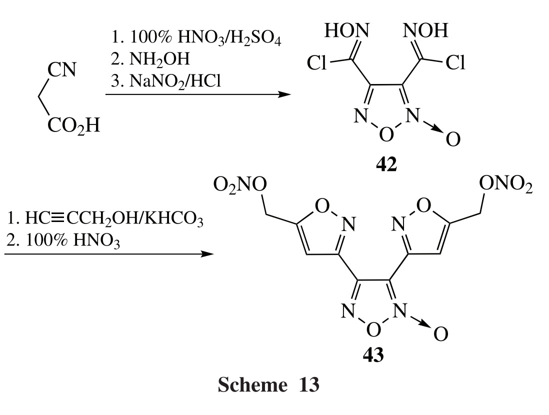


Scheme 12

nitrate) tetranitrate **40** exhibited better performance than dinitrate **39** due to its higher density (*d* 1.76 *vs.* 1.65 g cm$^{-3}$), and an enhanced content of active oxygen ($\Omega_{\mathrm{CO_2}}$ –37 *vs.* –62%).[50] However, sensitivity to friction and electrostatic discharge for **40** was also higher. Bis(1,2,4-oxadiazole)-bis(methylene) dinitrate **41** exhibits superior performance properties as melt-castable explosive and energetic propellant plasticizing ingredient with a detonation pressure *ca.* 50% higher than that of TNT along with a relatively high decomposition temperature (193 °C) that is rarely observed for nitrate-based compounds and a low friction sensitivity.[51] The unexpected thermal stability and reduced sensitivity were attributed by the authors to intramolecular hydrogen bonding between the nitrate and methylene groups in the crystal lattice of compound **41**.

An interesting melt-cast explosive **43** containing two 5-nitroxymethyl isoxazole fragments linked by the furoxan ring, was recently synthesized by successive treatment of bis(hydroximoylchlorido)furoxan **42** derived from cyanoacetic acid with propargyl alcohol and fuming nitric acid (Scheme 13).[52] Dinitrate **43** exhibits standalone melt-castable explosive properties, with a melting point of 90 °C and an onset decomposition temperature of 194 °C. Remarkably, it is nearly insensitive to friction and electrostatic discharge, with a calculated detonation pressure *ca.* 25% higher than that of the state-of-the-art melt-castable explosive TNT.

Sabatini and Baran with co-authors prepared a series of regio- and stereoisomeric tetranitrate esters **44**–**46** containing cyclobutane core.[53] All of the obtained isomers were thermally stable with onset decomposition temperatures of 192–199 °C, possess equivalent or lower friction sensitivities than TNT (240–>360 N) and exhibited similar energetic performances. However, their melting points were significantly different depending on the isomers structure (Figure 4). In accordance with this parameter, compounds **44a** and **44c** may be classified as melt-castable eutectic materials, compound **45** as a standalone melt-castable explosive and compounds **44b** and **46** as potential explosives.



Scheme 13

Another recently disclosed sub-class of energetic *O*-nitro compounds are 1,2,3-triazole-based nitric esters **47**–**49**, synthesized from β-hydroxyazides (polyazides) and 1,4-butynediol *via* azide–alkyne condensation followed by exhaustive nitration of hydroxyl groups (Scheme 14).[54] Formation of the 1,2,3-triazole core was achieved with excellent yield (>95%) and purity under green and industrially companionable copper-free conditions including microwave activation. Among the prepared compounds, trinitrate **47** exhibited superior energetic performance and has the potential to find use in propellant formulations.

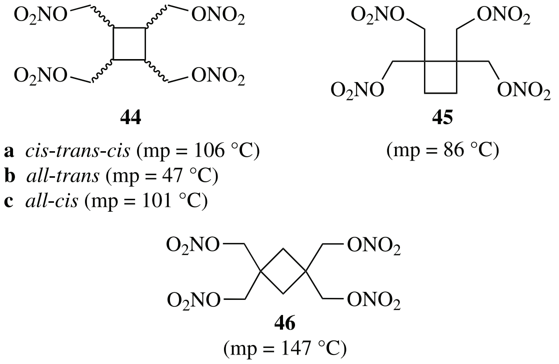
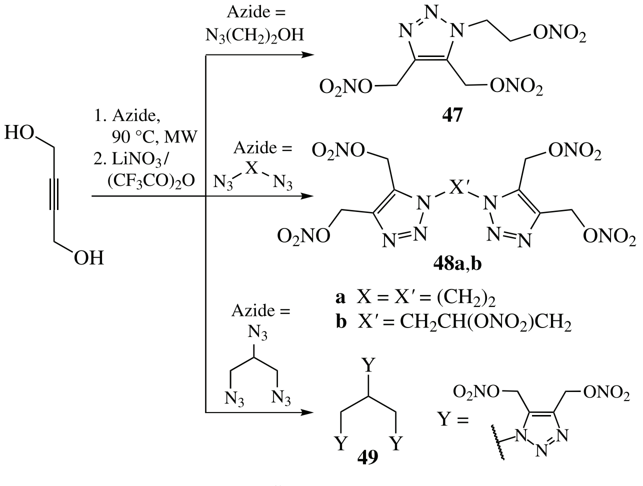


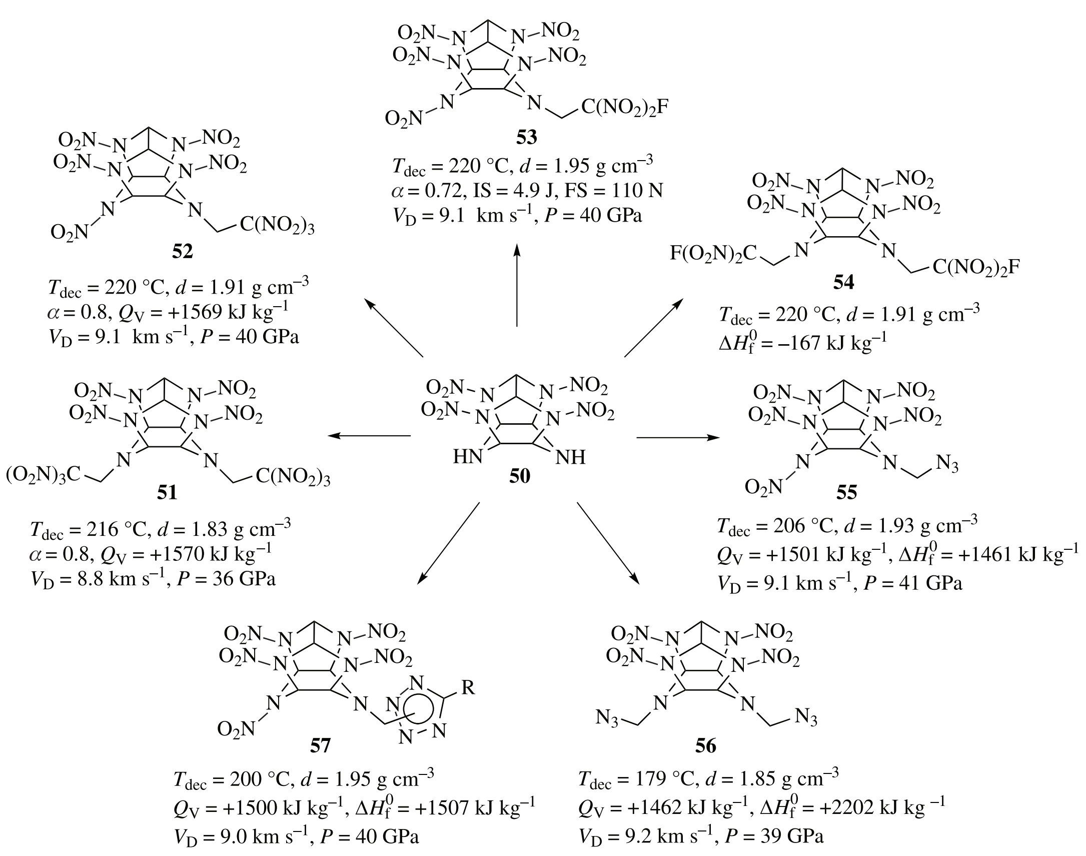
Figure 4



Scheme 14

## 2.4. Compounds bearing several nitro groups of different types

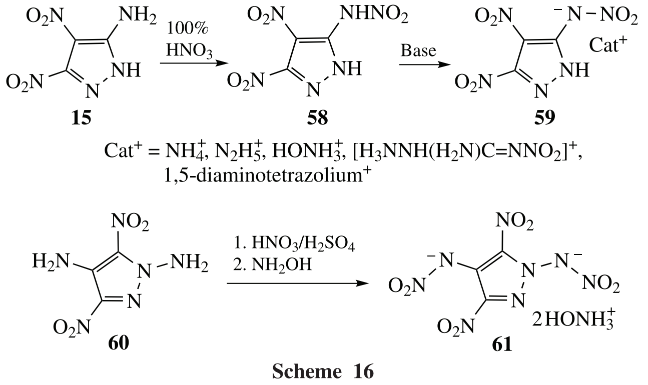
In some cases, introduction of several nitro groups of different types into a single molecule allows for accurately tuning properties of the EC to attain an optimal combination of high energetic performance with safety of handling. Novel high-energy analogues **51**–**57** of powerful explosive CL-20 bearing trinitroethyl, fluorodinitroethyl, tetrazolomethyl and azidomethyl groups have been recently synthesized from available tetranitro hexaazaisowurtzitane **50** (Scheme 15).[55–57] Experimental data on density, enthalpy of formation, decomposition temperature and sensitivity to impact and friction as well as theoretically calculated detonation parameters of compounds **51**–**57** allow



**Scheme 15**

one to rank them as powerful thermally stable explosives and propellant components compatible with or even surpassing HMX. Among substances **51**–**57** trinitroethyl derivatives **51** and **52** possess the highest content of oxygen. The dinitrofluoroethyl derivatives **53** and **54** have relatively low impact sensitivity while retaining promising density. Azidomethyl (**55**, **56**) and tetrazolylmethyl (**57**) derivatives have high enthalpies of formation.

Shreeve with co-authors synthesized a family of energetic pyrazole derivatives bearing nitro and nitroamino groups *via* the nitration of corresponding aminonitropyrazoles, in particular compounds **15** and **60** with nitric and mixed acids.[58] Most promising of the prepared compounds are 5-nitramino-3,4-dinitropyrazole **58**, its salts **59a–e** with nitrogen rich bases and bis-hydroxylammonium salt of 1,4-bis-nitramino-3,5-dinitropyrazole **61** (Scheme 16). Due to the formation of multiple hydrogen bonds between the nitramino group, the nitro group and an NH-bond rich counter ion, these compounds possess remarkable densities (up to 1.97 g cm$^{-3}$). Favorable elemental composition and high enthalpies of formation result in excellent detonation pressures and velocities ($P$ = 35.6–41.6 GPa, $V_D$ = 8880–9430 m s$^{-1}$). Surprisingly, impact and friction sensitivities of the salts (IS = 4–30 J, FS = 40–240 N) are also generally acceptable for advanced energetic applications.



**Scheme 16**

Later, the same research team reported synthesis of energetic bis-nitramine salts **62** and **63** with nitropyrazole and dinitrobipyrazole cores using similar methodology (Figure 5).[59] Furthermore, this versatile strategy appeared useful for facile preparation of the nitramine salts of pyrazole-based polynitrofunctionalized fused heterocycles, such as pyrazolo[4,3-*c*]pyrazoles **64**[60] and dipyrazolo-1,3,5-triazinanes **65**.[61] Thus, prepared ionic ECs are thermally stable and reveal energetic performance and sensitivities to mechanical stimuli similar to compounds **59** and **61**.

A series of high-enthalpy nitrogen heterocycle-based nitrate esters were synthesized from fused-ring and coupled-ring nitrated precursors using a simple and efficient nitrogen-functionalization approach.[62] Mannich reactions of 3,6-dinitropyrazolo[4,3-c]pyrazole **66** or 3,3′-dinitro-5,5′-bis(1*H*-1,2,4-triazole) **68** with formaldehyde in the presence of the acid catalyst (10% $H_2SO_4$) followed by the nitration of the resulting

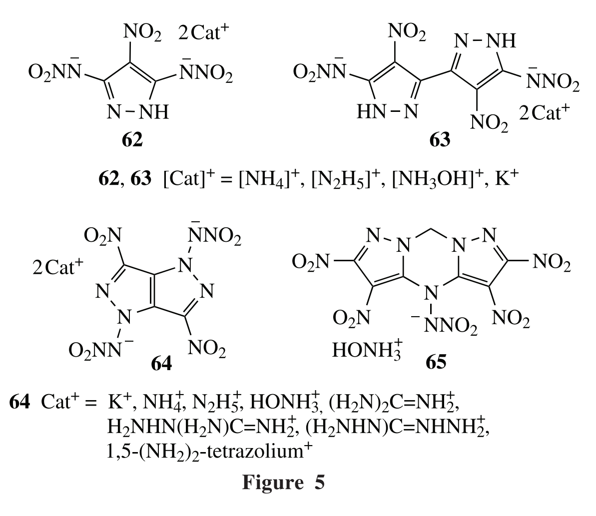
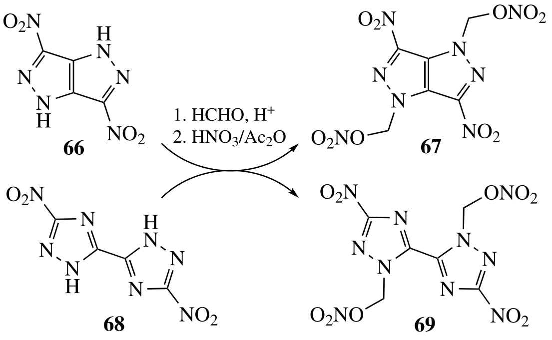


**Figure 5**

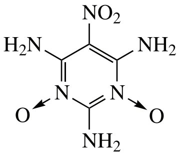
diols with fuming nitric acid–acetic anhydride nitrating system provided the corresponding dinitrate esters **67** or **69** in good yields (Scheme 17). Products **67** and **69** are rather stable compounds ($T_{dec}$ is 206 and 176 °C, respectively) exhibiting a pentaerythritol tetranitrate (PETN)-like detonation performance while having a somewhat lower impact sensitivity than this traditional nitrate ester explosive (10 and 6 *vs.* 3 J).



**Scheme 17**

## 2.5. Nitro compounds bearing other energetic groups

A prospective strategy to achieve high-energy-density materials with good detonation performance is based on optimal combination of several different nitrogen-rich explosive groups, which would act cooperatively.[63,64] The *N*-oxide group is a powerful instrument in the energetic kit for attaining this goal. The presence of the *N*-oxide group in a heterocyclic system improves oxygen balance of the molecule and often enhances crystal densities and detonation performance.[65] In some cases, energetic compounds bearing this group exhibit reduced mechanical sensitivity and provide an increase in thermal stability.[66] In particular, *N*-oxide groups are presented in energy-rich compound ICM-102 (Figure 6) with balanced detonation performance, thermal stability and mechanical sensitivity ($d = 1.95$ g cm$^{-3}$, $V_D = 9169$ m s$^{-1}$, $T_{dec} = 284$ °C, IS > 60 J, FS > 360 N) recently designed by a materials genome approach.[67]



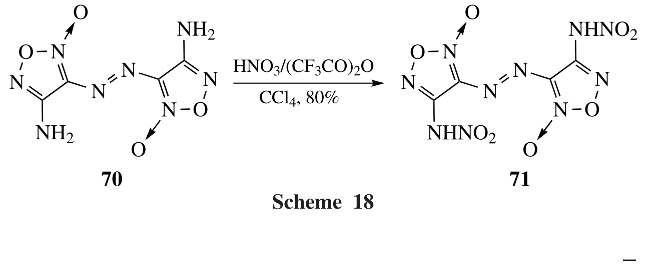
ICM-102

**Figure 6**

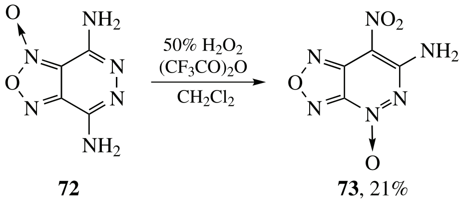
Nitro compounds bearing *N*-oxide group (groups) can be attained by nitration reactions, by oxidation of a nitrogen heterocycle nitro derivative with strong oxidants such as peroxytrifluoroacetic acid or hypofluorous acid (HOF) or *via* intramolecular cyclization reactions. Several recent examples of these strategies are presented below.

Nitration of 4,4′-diamino-3,3′-diazenofuroxan **70** with a $HNO_3$–$(CF_3CO)_2O$ mixture (5 : 1) afforded bis-nitramine **71**, a promising precursor to new furoxan-based high-energy *N*-nitroamine salts (Scheme 18).[68]

Shreeve with co-authors reported unusual synthesis of furazano[3,4-*c*]pyridazine 4-oxide **73** by oxidation of 4,7-diaminopyridazino[4,5-*c*]furoxan **72** with a 50% $H_2O_2$–$(CF_3CO)_2O$ mixture (Scheme 19).[69] The authors do not discuss mechanism of this interesting transformation in details and speculate that compound **73** may result from complex oxidation reactions with the concomitant rearrangement of the furoxan ring. It may be ranked as insensitive explosive with detonation performance better than triaminotrinitrobenzene (TATB).

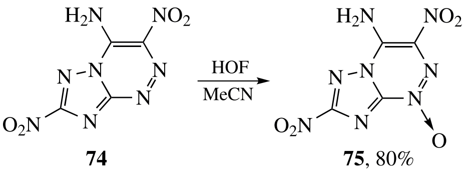


**Scheme 18**



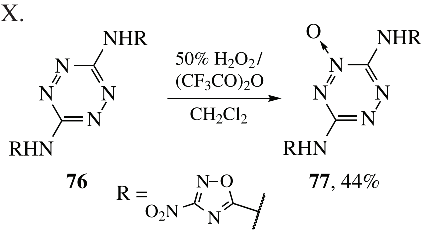
**Scheme 19**

Oxidation of triazolotriazine **74** with hypofluorous acid (HOF), a powerful oxidizing agent, afforded *N*-oxide **75** (Scheme 20) which displayed slightly better performance than RDX and showed lower sensitivity to mechanical stimuli.[70]



**Scheme 20**

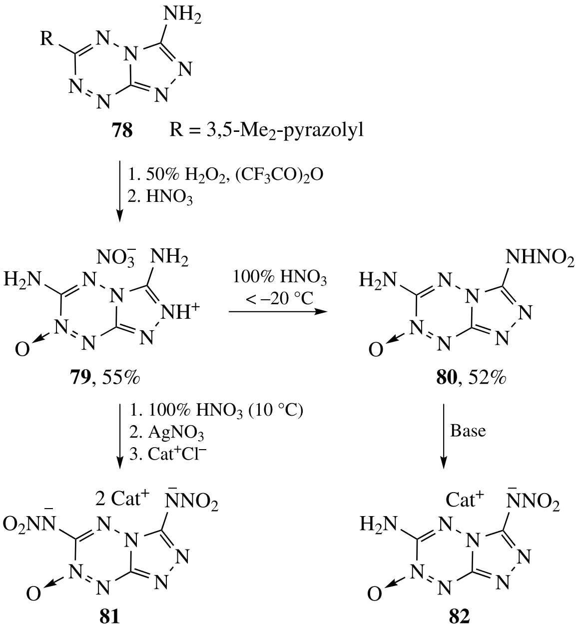
A lot of energetic 1,2,4,5-tetrazine mono- and di-*N*-oxides have been reported over the past 5 years. Tetrazine *N*-oxide **77** was obtained in 44% yield by oxidation of compound **76** with 50% $H_2O_2$ and $(CF_3CO)_2O$ in methylene chloride as a solvent (Scheme 21).[71] *N*-Oxide **77** turned to be insensitive (IS > 40 J, FS > 360 N) like TATB and it was estimated to have detonation performance ($V_D = 8926$ m s$^{-1}$, $P = 34.8$ GPa) compatible with that of RDX.



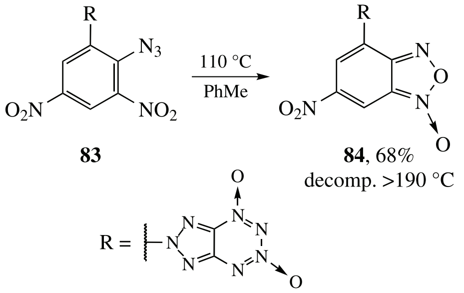
**Scheme 21**

Energetic *N*-oxides based on 1,2,4-triazolo[4,3-*b*][1,2,4,5]-tetrazine backbone were obtained from the key precursor **78** (Scheme 22). Oxidation of compound **78** with 50% $H_2O_2$ and $(CF_3CO)_2O$ followed by treatment with nitric acid led to mono-*N*-oxide nitrate **79**.[72] Nitramine **80** was obtained in 52% yield by nitration of the salt **79** with 100% $HNO_3$ at –20 °C.[73] Treatment of **80** with bases furnished corresponding nitramine salts **82** (Cation$^+$ = $NH_4^+$, $N_2H_5^+$, $NH_3OH^+$). Nitration of the nitrate **79** with 100% $HNO_3$ at 10–15 °C followed by successive treatment of the nitration product with $AgNO_3$ and appropriate chloride salts gave dinitramine salts **81** [Cation$^+$ = $NH_4^+$, $C(NHNH_2)_3^+$, $K^+$].[74] Compounds **80–82** exhibit energetic performance similar to that of HMX, but have lower sensitivity.

Intramolecular cyclization is also a useful pathway to heterocyclic *N*-oxide nitro derivatives. 1,2,3,4-Tetrazine 1,3-dioxide (TDO) **84** linked with nitrated benzofuroxan unit is generated from 2-azidodinitrophenyl-1,2,3-triazolo-fused TDO **83** at 110 °C in toluene (Scheme 23).[75] The cyclization occurs in this case with participation of the nitro group rather than the triazole ring.

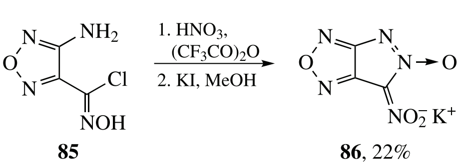


**Scheme 22**



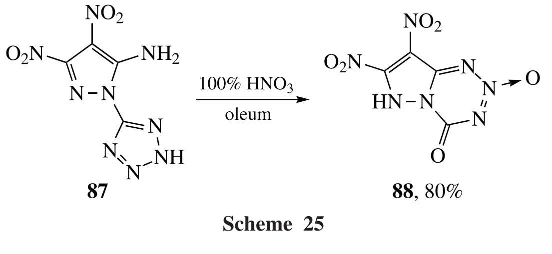
**Scheme 23**

An interesting cyclization of 3-amino-4-(chloroximino)furazan **85** to the pyrazolo[3,4-*c*]furazan *N*-oxide potassium salt **86** occurred under the action of HNO$_3$–(CF$_3$CO)$_2$O followed by the reduction with KI (Scheme 24).[76] Several energetic salts with nitrogen-rich cations [*e.g*. NH$_4^+$, NH$_3$OH$^+$, (NH$_2$)$_2$CNHNH$_2^+$, H$_2$NC(NHNH$_2$)$_2^+$, C(NHNH$_2$)$_3^+$, *etc*.], obtained from product **86**, displayed excellent detonation properties but high sensitivity to impact and friction.



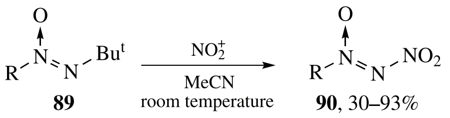
**Scheme 24**

7,8-Dinitro-4-oxo-4,6-dihydropyrazolo[5,1-*d*][1,2,3,5]tetrazine 2-oxide **88** was prepared by nitration of aminopyrazole **87** with a HNO$_3$/oleum mixture (Scheme 25)[77] and converted to energetic salts with nitrogen-rich cations [*e.g*. NH$_4^+$, NH$_3$OH$^+$, N$_2$H$_5^+$, H$_2$NC(NHNH$_2$)$_2^+$, C(NHNH$_2$)$_3^+$, *etc*.]. The hydroxylammonium salt of compound **88** exhibited promising detonation properties and low sensitivity. The authors did not rationalize the formation of fused heterocycles **86** and **88**, but it could be expected that both ring-closing reactions are initiated by *in situ* generated oxodiazonium cations [–N=N=O]$^+$.



**Scheme 25**

Compounds bearing the oxygen-rich nitro and azoxy groups linked to each other are of particular interest. The nitro-*NNO*-azoxy group [–N(O)=N–NO$_2$] designed by Churakov and Tartakovsky in 1984 is characterized by higher content of active oxygen and high enthalpy of formation. The most convenient methodology for synthesis of the nitro-*NNO*-azoxy compounds (NAC) **90** is nitration of corresponding *tert*-butyl-*NNO*-azoxy compounds **89** with NO$_2$BF$_4$, N$_2$O$_5$ or HNO$_3$/TFAA in MeCN (Scheme 26).[78–81]



R = Alk, Ar, Hetaryl
NO$_2^+$ = NO$_2$BF$_4$, N$_2$O$_5$, HNO$_3$/TFAA

**Scheme 26**

Unfortunately, aliphatic NACs exhibit moderate thermal stability.[78] Compounds **91** and **92** decompose slowly at room temperature, NAC **93** is characterized by decomposition point of 104 °C (Figure 7).

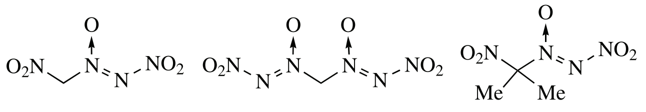


**Figure 7**

Recently, furazan-derived energetic NACs **94**–**99** (Figure 8) were synthesized by a similar scheme.[79] Theoretical calculations predict superior detonation performance of these compounds ($V_D$ = 8.07–9.40 km s$^{-1}$, $P$ = 27.4–43.4 GPa) compared with corresponding nitrofurazans. Furthermore, replacement of the nitrofurazans with the corresponding (nitro-*NNO*-azoxy)furazans increases the specific impulse of the model solid propellant

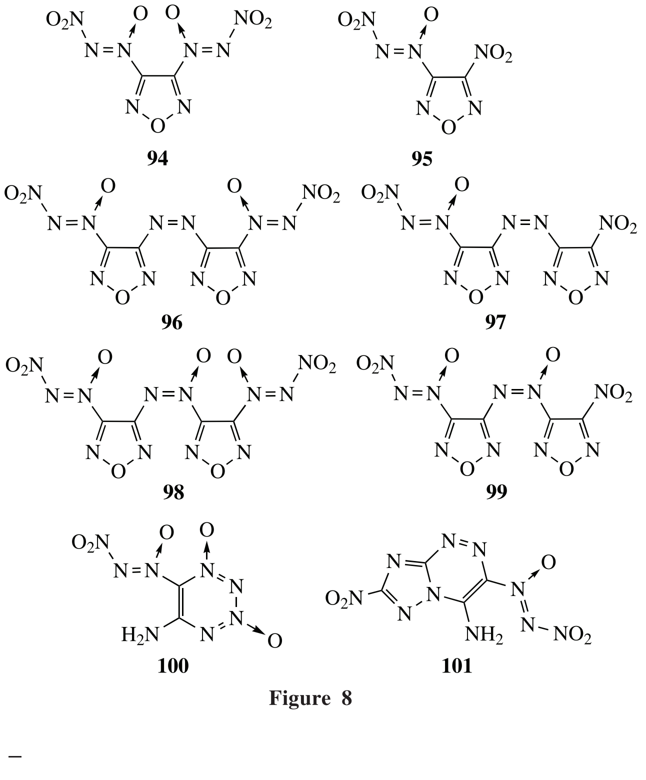
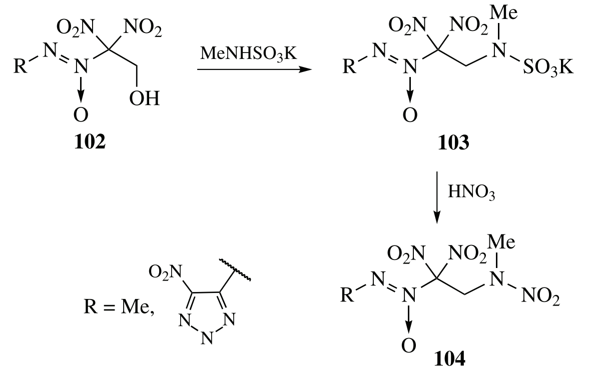


**Figure 8**

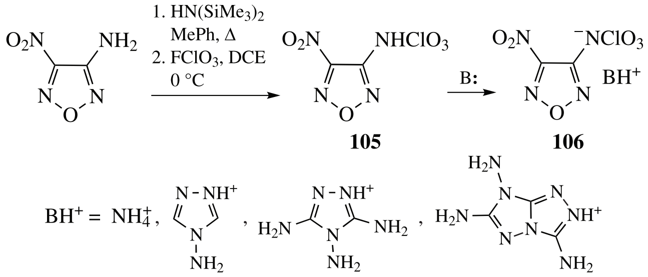
formulations by 2–10 s due to high enthalpies of formation (600–892 kcal kg$^{-1}$) and balanced elemental composition of NACs **94–99**. However, their thermal decomposition starts below 115 °C ($T_{\mathrm{dec}}$ = 83–115 °C). NAC **100** incorporating 1,2,3,4-tetrazine 1,3-dioxide cycle exhibits higher performance and zero oxygen balance,[80] but it also melts with decomposition at 110–112 °C. Compound **101**, in which the nitro-*NNO*-azoxy group is linked to the triazolo-triazine core, is characterized by higher thermal stability ($T_{\mathrm{dec}}$ = 154 °C)[81] that may be attributed to a higher melting point of the NAC **101** (170–172 °C with decomposition).

Energetic hybrid structures **104** bearing adjacent dinitromethylene fragment, azoxy group and *N*-nitramine unit have been recently prepared. The synthesis is based on condensation of α,α-dinitro diazenoxides **102** with potassium sulfamate followed by the nitration of the sulfamate precursors **103** with nitric acid (Scheme 27).[82] Further studies are needed to estimate potential of compounds **104** as components of energetic compositions.



Scheme 27

In the search of new high-energy groups, 3-nitro-4-(perchlorylamino)furazan **105** and its salts **106** comprising nitrogen-rich 1,2,4-triazol-based cations were synthesized (Scheme 28).[83] The $NClO_3$ moiety increases the enthalpy of formation compared with similar nitramines due to higher oxygen content and the presence of weak N–Cl and Cl–O bonds. However, compound **105** being dissolved in $Et_2O$ slowly decomposed at 0 °C whereas salts **106** are extremely sensitive towards heating and mechanical shock.



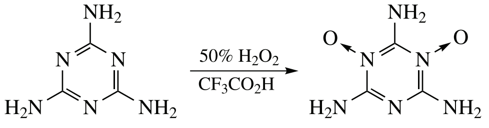
Scheme 28

## 3. Nitro-group-free energetic compounds

Sometimes, compounds that do not contain nitro groups accumulate a significant amount of chemical energy which makes them promising components of explosives, powders, and propellants. A lack of oxidizer (active oxygen) in these compounds is compensated, at least partly, by the *N*-oxide groups and/or nitrogen-rich structural fragments bearing several high-enthalpy N–N bonds.

### 3.1. Energetic *N*-Oxides

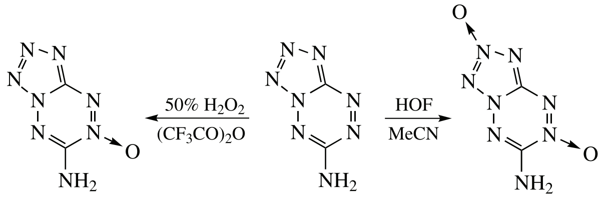
Among various *N*-oxide derivatives, compounds bearing 1,3,5-triazine- and 1,2,4,5-tetrazine-derived cores, in particular fused with other polynitrogen heterocycles, attract considerable attention as high-energy-density materials (HEDMs). Their synthesis is commonly based on oxidation and intramolecular cyclization reactions. Oxidation of melamine **107** to dioxide **108** was recently achieved using 50% $H_2O_2$ in trifluoroacetic acid (Scheme 29).[84] Perchlorate, dinitramide and nitrate salts of compound **108** turned to be practically insensitive towards mechanical stimuli.



**107** **108**, 85%

Scheme 29

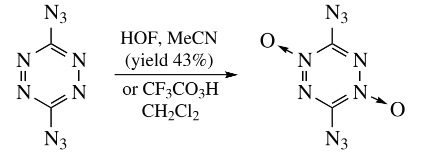
Similar oxidation of 6-aminotetrazolo[1,5-*b*]-1,2,4,5-tetrazine **109** with 50% $H_2O_2$ in $(CF_3CO)_2O$ led to mono-*N*-oxide **110** in moderate yield (Scheme 30).[85] However, with more powerful oxidizing reagent, hypofluorous acid (HOF), di-*N*-oxide **111** was generated as the main product.[86] Detonation performances of compounds **110** and **111** are superior to those of RDX and HMX, respectively, whereas mechanical sensitivity is similar to that of RDX or somewhat lower.



**110**, 42% **109** **111**, 70%

Scheme 30

Oxidation of diazido-1,2,4,5-tetrazine **112** with HOF in acetonitrile afforded 3,6-diazido-1,2,4,5-tetrazine 1,4-dioxide **113** (Scheme 31).[86] Peroxytrifluoroacetic acid also acted as effective oxidizer in this reaction. Impact and friction sensitivities of di-*N*-oxide **113** are high, but lower than those of extremely sensitive compound **112**.

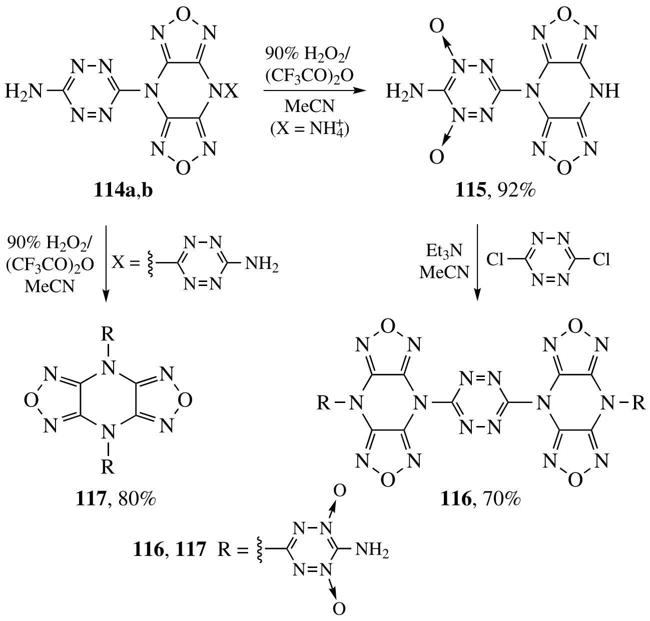


**112** **113**

Scheme 31

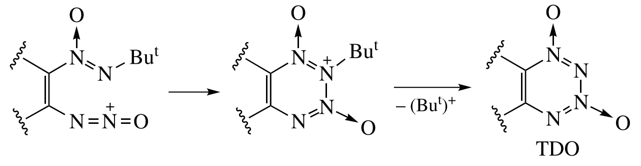
Polycyclic *N*-oxides based on 1,2,4,5-tetrazine and 4*H*,8*H*-difurazano[3,4-*b*:3′,4′-*e*]pyrazine cores were recently synthesized (Scheme 32).[87] Oxidation of the ammonium salt **114a** (X = $NH_4^+$) with 90% $H_2O_2$ and $(CF_3CO)_2O$ resulted in di-*N*-oxide **115** in high yield. Treatment of the latter with triethylamine, followed by reaction with 3,6-dichloro-1,2,4,5-tetrazine provided tetra-*N*-oxide **116**. Oxidation of diamine **114b** with 90% $H_2O_2$ and $(CF_3CO)_2O$ gave tetra-*N*-oxide **117** in 80% yield. Compounds **116** and **117** exhibit detonation performances compatible with those of RDX, but they are less sensitive. Compound **115** is almost insensitive toward impact and friction at the level of TATB.

1,2,3,4-Tetrazine 1,3-dioxides (TDOs) bearing an alternating sequence of two oxidized and two non-oxidized endocyclic nitrogen atoms are highly attractive as a new generation of HEDMs. The main approach to the synthesis of the TDO-cycle is the ring-closure reaction of the *tert*-butyl-



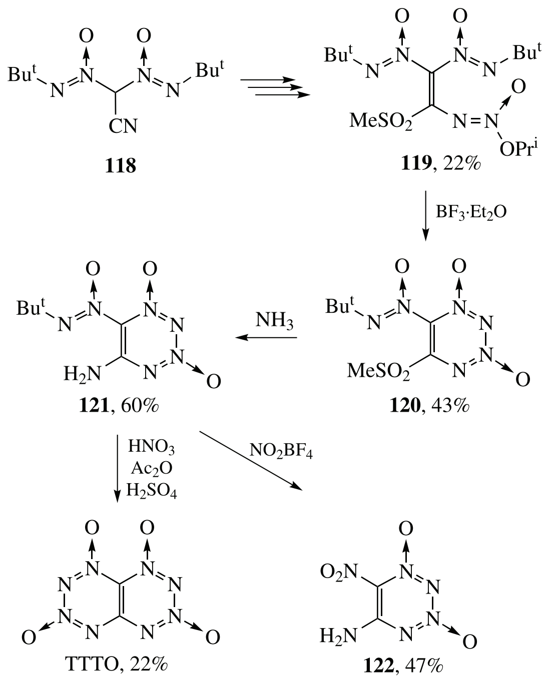
**Scheme 32**

*NNO*-azoxy group and oxodiazonium ion [–N=N=O]$^+$ followed by elimination of the *tert*-butyl cation (Scheme 33).[66] The oxodiazonium ions are commonly generated *in situ* from corresponding *N*-nitroamines and $Ac_2O$ in the presence of $H_2SO_4$.[88] Recently, new methods for the TDO synthesis have been reported involving cyclization with nitronium sulfates in organic solvents.[89]



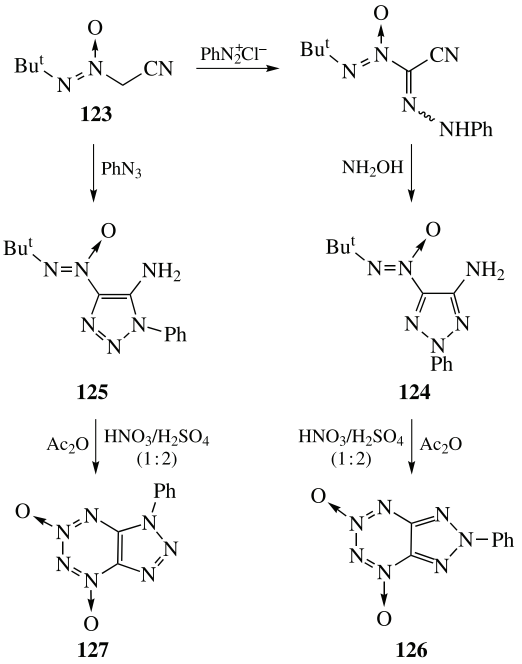
**Scheme 33**

One of the most remarkable compounds of the TDO type is tetrazino-tetrazine 1,3,6,8-tetroxide (TTTO) (Scheme 34).[90] According to theoretical studies, its heat of formation is about 206 kcal mol$^{-1}$, calculated detonation velocity 9.71 km s$^{-1}$, and detonation pressure 43 MPa,[91] which puts TTTO on a par with the most powerful EMs. The synthetic strategy for TTTO proposed by Tartakovsky, Churakov and Klenov was based on the sequential closure of two TDO rings by the generation of oxodiazonium ions [–N=N=O]$^+$ and their intramolecular coupling with *tert*-butyl-*NNO*-azoxy groups (see Scheme 34). Compound **119** was obtained from nitrile **118** in 5 steps and then cyclized to TDO **120** under the action of $Et_2O{\cdot}BF_3$. The $MeSO_2$ group of the latter was replaced by ammonia to afford TDO **121** followed by cyclization to TTTO under the action of a $HNO_3$/$H_2SO_4$/$Ac_2O$ mixture. The structure of TTTO was confirmed by X-ray analysis of its molecular complex with benzene. Energetic TDO **122** was also obtained from TDO **121** by electrophilic displacement of the *tert*-butyl-*NNO*-azoxy group with a nitro group under the action of nitronium tetrafluoroborate taken in excess (see Scheme 34).[92]



**Scheme 34**

The same research group developed a synthetic route to (*tert*-butyl-*NNO*-azoxy)acetonitrile **123**, a useful reagent with an active methylene group.[92] The reaction of nitrile **123** with phenyldiazonium chloride followed by treatment of intermediate hydrazone with hydroxylamine afforded 2-phenyl triazole **124** (Scheme 35). The reaction of the nitrile **123** with phenylazide gave 1-phenyl triazole **125**. Isomeric triazoles **124** and **125** were readily converted to appropriate TDOs **126** and **127**.[93]

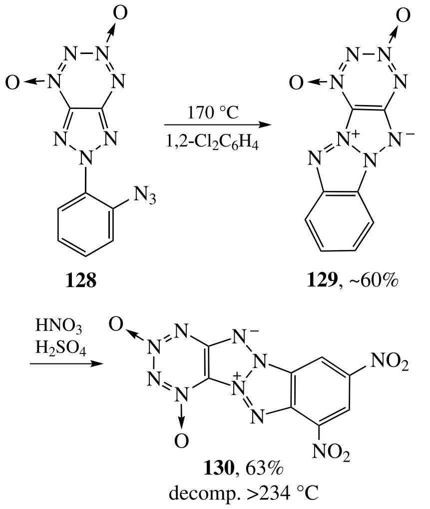


**Scheme 35**

Heating of similarly obtained TDO **128** bearing *ortho*-azido group in the aromatic ring at 170 °C in 1,2-dichlorobenzene gave 1,2,3,4-tetrazine 1,3-dioxide **129** annulated with [1,3a,4,6a]-tetraazapentalene system as the main product (Scheme 36). The latter can be used as a precursor of novel ECs, in particular dinitro derivative **130** which exhibited high thermal stability.[94]

### 3.2. Compounds bearing other energetic groups

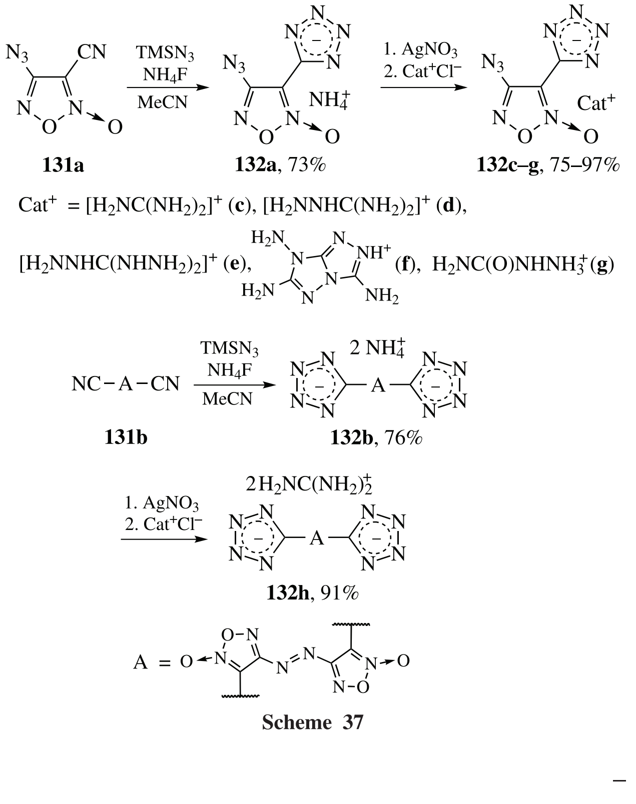
Energetic nitrogen-rich salts of azoles are among the most remarkable recent breakthroughs in the development of EMs. They have high thermal stabilities, acceptable sensitivities, and their synthesis and purification are usually based on convenient scalable procedures.[95,96] The properties of energetic salts can be diversified readily by simply changing cationic and anionic components. Moreover, the formation of energetic salts is a



**Scheme 36**

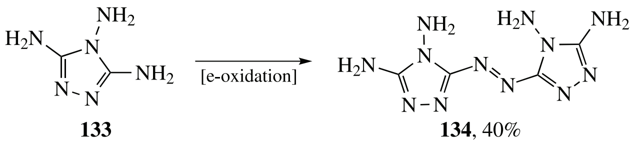
useful strategy to enhance thermal stability of a core molecule. Such advantages enable a variety of applications for these green energetic organic compounds including explosives, propellants, or pyrotechnics.[97]

Recently, a convenient synthesis of (1*H*-tetrazol-5-yl)furoxan ammonium salts **132** based on [3+2] cycloaddition of cyanofuroxans **131a**,**b** with $NH_4N_3$ generated *in situ* from $TMSN_3$ and $NH_4F$ has been developed (Scheme 37).[98] Ammonium cations in salts **132a**,**b** could be readily substituted for various poly-nitrogen cations to afford salts **132c–h**[99] which have moderate to acceptable thermal stabilities ($T_d$ = 115–173 °C) and high enthalpies of formation ($\Delta H_f^0 > 800$ kJ mol$^{-1}$). Impact sensitivities of salts **132a** (2.2 J), **132b** (1.5 J) and **132e** (2.7 J) are close to those of primary explosives, such as lead azide (~2 J) and lead styphnate (~3 J). However, they are much safer towards friction (43–129 N *vs.* 0.3–1.5 N) and guanidinium salts **132c,h** are practically insensitive (30 J, >360 N). A favorable combination of relatively high detonation performance ($V_D$ = 6850–8260 m s$^{-1}$, $P$ = 18.2–29.3 GPa) and environmental friendliness makes nitrogen-rich ECs **132** attractive for a variety of energetic applications.



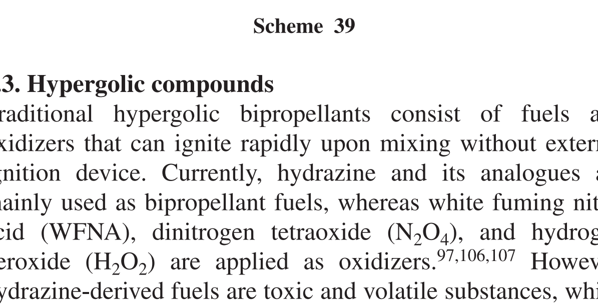
**Scheme 37**

An example of non-ionic nitrogen-rich compounds is azobis-1,2,4-triazole **134** recently synthesized through chemoselective electrochemical oxidation of triamine **133** (Scheme 38). Importantly, the synthesis of energetic material **134** is unachievable using common oxidation methods. It is completely insensitive to impact and friction, shows detonation performance comparable with that of RDX and may be used as a valuable precursor to other nitrogen-rich high-energy-density materials.[100]



**Scheme 38**

The azasydnone (1,2,3,4-oxatriazolium-5-olate) heterocyclic motif recently emerged renaissance as a valuable explosophore in design of EMs.[101] This structural fragment better contributes to crystal density and thermal stability of the molecule than nitro and azido groups. Two approaches for the synthesis of azasydnones **136** from the corresponding amines were developed. The first approach is based on intermediate formation of azotrinitromethyl derivatives **135** *via* the nitrosation/trinitromethylation sequence followed by acid-catalyzed degradative cyclization of **135** to products **136** (Scheme 39).[102] Another, more general, approach to both aryl and heteroaryl substituted azasydnones includes preparation of hydrazones **137** bearing the bromine atom at the α-position with respect to the nitro group, which upon treatment with $NH_4NO_3$ afford azasydnones **136**.[103] Incorporation of 1,2,4-triazole or tetrazole subunits to the azasydnone ring enabled a preparation of corresponding nitrogen-rich energetic salts.[104,105]

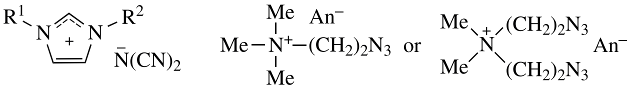


**Scheme 39**

### 3.3. Hypergolic compounds

Traditional hypergolic bipropellants consist of fuels and oxidizers that can ignite rapidly upon mixing without external ignition device. Currently, hydrazine and its analogues are mainly used as bipropellant fuels, whereas white fuming nitric acid (WFNA), dinitrogen tetraoxide ($N_2O_4$), and hydrogen peroxide ($H_2O_2$) are applied as oxidizers.[97,106,107] However, hydrazine-derived fuels are toxic and volatile substances, which create serious health and safety hazard and thereby lead to high handling and storage cost. In this minireview, two alternative types of fuels for hypergolic propellants, namely energetic hypergolic ionic liquids (HILs),[7,108–110] and 1,5-diazabicyclo[3.1.0]hexane derivatives (DABHs)[111] are considered.

The main advantages of HILs are extremely low vapor pressure, high bulk density, inflammability, resistance to thermal and mechanical stimuli and electrical shock, low toxicity, and easy handling while performing at a level with hydrazine. The first synthesized HILs were imidazolium dicyanamide (DCA) salts with WFNA as an oxidizer.[108] Unfortunately, the ignition delay (ID) time of the dicyanamide HILs **138** with allyl- and propargylimidazolium cations (170–670 ms) was far away from that of hydrazine (4.8 ms) (Figure 9). The dialkylimidazolium salt **138** ($R^1$ = Me, $R^2$ = Bu$^n$) (ID = 47 ms) better suits the requirements. Later Shreeve *et al.* reported azide-functionalized HILs **139a** and **139b** with dicyanamide (DCA), nitrocyanamide (NCA), dinitramide (DNA) or azide ($N_3$) anions which are stable up to 200 °C and exhibit the shortest ID (8–>20 ms).[112,113]



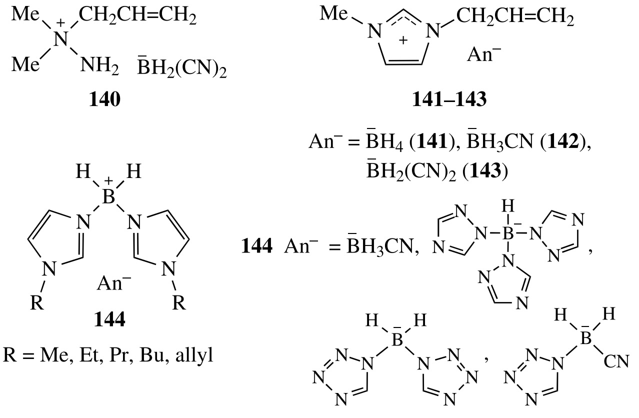
**138** **139a** **139b**

$R^1$ = Me, $NH_2$
$R^2$ = $(CH_2)_nCH{=}CH_2$,
$(CH_2)_nC{\equiv}CH$,
$(CH_2)_nMe$ ($n$ = 1–3)

An$^-$ = $\bar{N}(CN)_2$, $\bar{N}(CN)NO_2$, $\bar{N}(NO_2)_2$, $N_3^-$

Figure 9

Designing the salts with borohydride anions marked a breakthrough in the HIL chemistry.[114,115] The ID of the dicyanodihydroborate-based HIL **140** is even shorter (4 ms) than that of the DCA and NCA-based[116] HILs and the ID of borohydride salt **141** is excellent (2 ms) (Figure 10). However, the borohydride HILs are water sensitive. Recently synthesized imidazolium HILs **142** and **143** with cyanoborohydride anion and their analogues **144** bearing boronium cations and azolylborohydride anions[117–119] have remarkably low viscosity (<20 MPa s), high density (up to 1.1 g cm$^{-3}$) and ultra-short ID time (~1.4 ms) upon contact with WFNA.



**140** **141–143**

An$^-$ = $\bar{B}H_4$ (**141**), $\bar{B}H_3CN$ (**142**), $\bar{B}H_2(CN)_2$ (**143**)

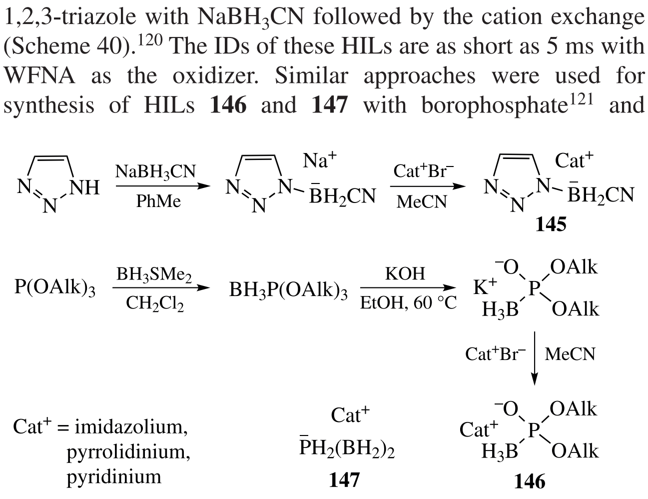
**144**

R = Me, Et, Pr, Bu, allyl

**144** An$^-$ = $\bar{B}H_3CN$,

Figure 10

HILs **145** bearing the cyano(1*H*-1,2,3-triazol-1-yl)-dihydroborate anion were synthesized *via* borocyanation of 1,2,3-triazole with $NaBH_3CN$ followed by the cation exchange (Scheme 40).[120] The IDs of these HILs are as short as 5 ms with WFNA as the oxidizer. Similar approaches were used for synthesis of HILs **146** and **147** with borophosphate[121] and bis(borano)hypophosphite anions.[122] These HILs with nitrogen heterocycle cations are also characterized by a wide liquid operating range, high density, good hydrolytic stability, and shortest ID time with WFNA as oxidizer.

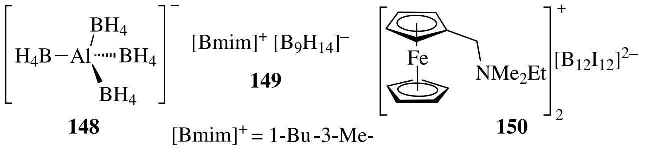


**145** **146** **147**

Cat$^+$ = imidazolium,
pyrrolidinium,
pyridinium

Scheme 40

In persistent search for efficient HILs, new boron containing anions, in particular hydrogen-rich $Al(BH_4)_4^-$ anion **148**, were designed (Figure 11).[123] When *nido*-decaborane ($B_{10}H_{14}$) was added to a dicyanamide-based imidazolium IL, the colorless precipitate of new IL **149** with cluster anion $[B_9H_{14}]^-$ was formed.[124] Generally, HILs bearing borohydride cluster anions and dialkylimidazolium cations possess high hypergolic activity (ID ~ 1 ms) both with WFNA and $N_2O_4$ oxidizers.[125] Furthermore, they are thermally and hydrolytically stable and compatible with oxygen-rich nitroxyalkyl groups which improve the combustion performance.[126] Recently synthesized HIL **150** containing ferrocene-derived cation and boron-iodine cluster anion $[B_{12}I_{12}]^{2-}$ (see Figure 11) exhibited an unprecedented ID time of 17 ms in the reaction with $H_2O_2$ (95%). This finding provides a platform for usage of commercially available $H_2O_2$ as a 'green' oxidizer for bipropellant rocket propulsion.[127]



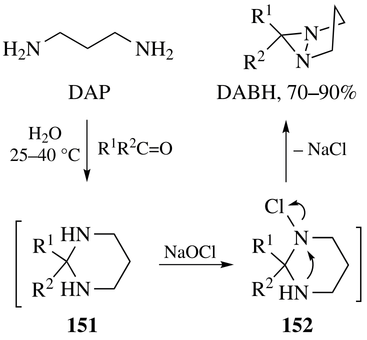
**148** **149** **150**

$[Bmim]^+$ = 1-Bu-3-Me-imidazolium

Figure 11

Theoretical studies using high level wave function theory (MP2 geometries, CCSD(T) energies) and physicochemical methods show that nitrous oxide is generated in hypergolic reactions of [bmim][$BH_2(CN)_2$] and [bmim][$N(CN)_2$] with WFNA indicating its crucial role in the hypergolic ignition process.[128–132] Both cation and anion of a HIL play important roles. As a rule, the cation is responsible for the physicochemical properties (*e.g.*, melting point, viscosity, thermal stability, *etc.*) of the HILs whereas the anion mainly contributes to the hypergolic ignition process. Moreover, the viscosity exerts a significant impact on the ID time.[133,134] The decrease of alkyl group length in dialkylimidazolium cations results in lower viscosity and shorter ID of corresponding ILs.[135]

Another promising class of hypergolic compounds are fused diaziridines, in particular, 1,5-diazabicyclo[3.1.0]hexanes (DABHs). A strained *cis*-configuration of this molecules[136] results in very short ID times (1–11 ms).[111] First DABHs were synthesized about two decades ago.[137,138] Recently, a convenient one-pot cascade process for their preparation has been proposed,[111] which includes condensation of 1,3-diaminopropane (DAP) with carbonyl compound in $H_2O$, halogenation of diazacyclohexane **151** with NaOCl and a base-initiated cyclization of labile *N*-chloro derivative **152** to DABH in



DAP DABH, 70–90%

**151** **152**

$R^1$ = H, $R^2$ = H, Me, Et
$R^1$ = $R^2$ = Me

Scheme 41

70–90% overall yield (Scheme 41). Thus obtained target compounds have low freezing points (–4 – < –50 °C), miserable toxicity ($LD_{50}$ = 1605–4865 mg $kg^{-1}$) and a higher heat of formation (129–276 kJ $mol^{-1}$) than other hydrazine derivatives.

### 3.4. Energy-rich hydrocarbons

Unlike composite solid rocket fuels, liquid rocket fuels used in the rocket and space technology contain a hydrocarbon fuel and liquid oxygen as an oxidizer. The efficiency of oxygen-hydrocarbon rocket fuels is determined by the energy content of the fuel used, the molecular masses of the combustion products, the completeness of fuel combustion and a number of other parameters that provide a high specific impulse of engine thrust. It is also important to take the specific density of the components and their cost into account.[8,139]

One of the ways to obtain hydrocarbons with high specific (mass-based) heats of combustion that determines the specific impulse $I_{sp}$ of the fuel involves incorporating strained three- or four-membered rings with high strain energies (115 or 110 kJ $mol^{-1}$, respectively) into molecules of linear or polycyclic hydrocarbons. A remarkable example of this approach is given by the 'syntin' fuel (1,2-dicyclopropyl-1-methylcyclopropane, **153**) (Figure 12) that contains three cyclopropane moieties in the molecule. This compound was first synthesized in 1960,[140] and its industrial production was later organized in the USSR. The enthalpy of the formation of syntin reaches +133 kJ $mol^{-1}$ and its freezing point is below –70 °C, which made it very attractive for application in space systems. This fuel was successfully used in Soyuz-U2 rockets, in 'D' series upper stage rockets, in particular, in the programs for the exploration of the Moon, Venus, Mars, *etc*., as well as in the combined propulsion system of the 'Buran' spacecraft. However, the scheme for syntin synthesis proved to be very complex, and as a result, its production was discontinued in the mid-1990s.

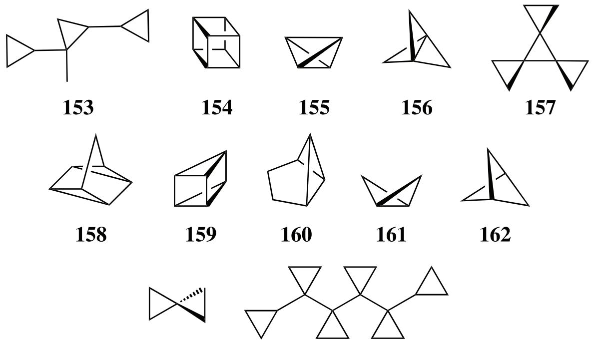
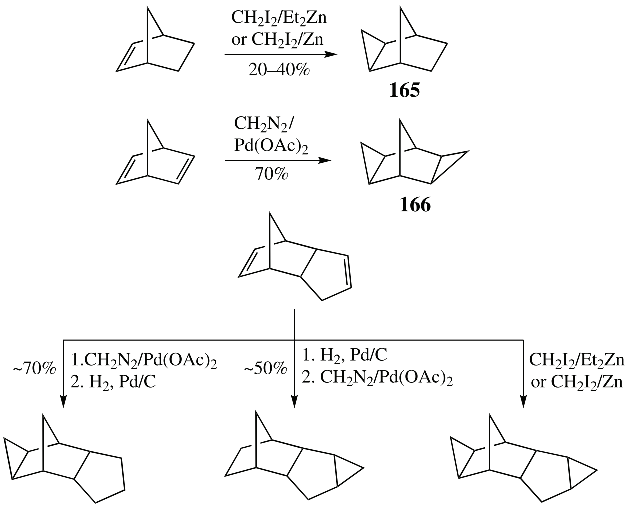

**153** **154** **155** **156** **157**
**158** **159** **160** **161** **162**
**163** **164**

Figure 12

Some other cage hydrocarbons containing strained small cycles are also promising. Of these, cubane (**154**, 695 kJ $mol^{-1}$) and tetrahedrane (**155**, 556 kJ $mol^{-1}$) have the highest strain energies. Moreover, cubane has the highest density among all hydrocarbons (1.29 g $cm^{-3}$).[141,142] However, cubane and tetrahedrane are thermally unstable. Highly strained hydrocarbons also include [1.1.1]propellane (**156**, 506 kJ $mol^{-1}$), [3]rotane (**157**, 502 kJ $mol^{-1}$), quadricyclane (**158**, 389 kJ $mol^{-1}$), prismane (**159**, 376 kJ $mol^{-1}$), dihydrobenzvalene (**160**, 330 kJ $mol^{-1}$), bicyclo[1.1.0]butane (**161**, 284 kJ $mol^{-1}$), bicyclo[1.1.1]pentane (**162**, 276 kJ $mol^{-1}$) and spiropentane (**163**, 264 kJ $mol^{-1}$). However, of these compounds, only quadricyclane **158** is used as an additive for rocket fuels.[143] The rest are not sufficiently stable and require complex methods for their synthesis.

Despite the record-high strain energy, the (mass-based) heat of cubane combustion is not the highest among hydrocarbons. This value is higher for [6]ivyane (**164**, 50.8 MJ $kg^{-1}$),[144] syntin (**153**, 46.6 MJ $kg^{-1}$), unsubstituted cyclopropane (49.7 MJ $kg^{-1}$) and some other hydrocarbons. Therefore, the search for new compounds with cyclopropane moieties that have high heats of combustion per unit mass and the creation of cost-effective methods for their synthesis remain a relevant issue. Compounds of this kind are usually synthesized by cyclopropanation of double bonds in olefins with zinc or aluminum carbenoids[145,146] obtained from expensive $CH_2I_2$ or by reactions with diazomethane.[147] The methods developed to date for the safe *in situ* generation of diazomethane in the presence of highly efficient catalysts based on palladium complexes make the second method a preferable approach.

Promising substrates for cyclopropanation include hydrocarbons containing a norbornene moiety. Products **165**–**169** of direct cyclopropanation of norbornene, norbornadiene and cyclopentadiene dimer were suggested as energetic fuels[148]. Both zinc carbenoids and the diazomethane method (Scheme 42) were used at different stages for their synthesis.



**165**
**166**
**167** **168** **169**

Scheme 42

3-Cyclopropyltricyclo[2.2.1.0$^{2,6}$]heptane **170** synthesized from 3-vinylnortricyclane in 91% yield by catalytic cyclopropanation with diazomethane[149] and 1-[2-(2,2-dimethylcyclopropyl)ethyl]-1,1′-bi(cyclopropane) **171** obtained in up to 70% yield from myrcene, a natural triene, by treatment with $CH_2I_2/Et_2Zn$ (Figure 13) are also promising components of liquid rocket fuels.[150]

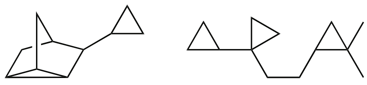
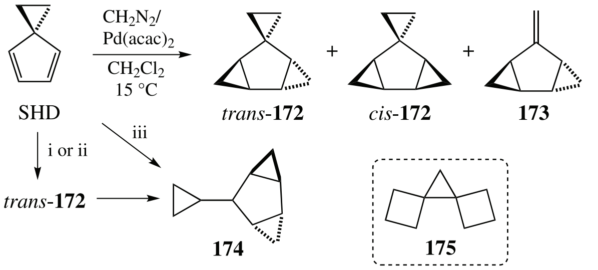

**170** **171**

Figure 13

Other high-energy hydrocarbons include spiro[cyclopropane-1,5′-tricyclo[4.1.0.0$^{2,4}$]heptane] (*trans*-**172**), 5-cyclopropyltricyclo[4.1.0.0$^{2,4}$]heptane **174** and dispiro[3.0.3.1]nonane **175** that contain three small rings per molecule. Hydrocarbon **172** is synthesized from spiro[2.4]hepta-4,6-diene (SHD) by the Simmons–Smith method (treatment with $CH_2I_2$/Zn-Cu[151] or $CH_2I_2/Et_3Al$[152]) or by catalytic cyclopropanation with diazomethane[153,154] (Scheme 43). In the latter case, the *cis*-**172** isomer and bishomofulvene **173**, a product of partial cleavage of the spirocyclopropane moiety under the action of a Pd catalyst, are also formed as minor products. The thermophysical characteristics of product **172**[155] meet the requirements. However, the reported methods for synthesizing compound **172**



**Scheme 43** *Reagents and conditions*: i, $CH_2I_2$/Zn–Cu, 50%; ii, $CH_2I_2$/$Et_3Al$/hexane, 88%; iii: $CH_2I_2$/$Et_3Al$/DCM, 71%.

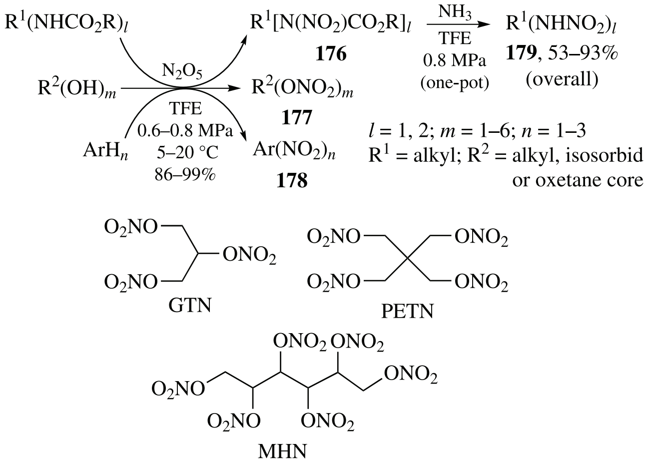
and its promising analogues **174** and **175** by reactions of SHD with aluminum carbenoids[156] generated from $CH_2I_2$, and cyclopropanation of dicyclobutylidene with diazomethane in the presence of $Et_2AlX$,[145] accordingly, are very complex and not easy to perform industrially.

## 4. Energetic materials and green chemistry

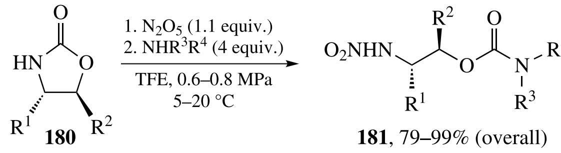
Over the past decade, a significant attention have been paid to the development of new ‘cleaner’ chemical processes for the manufacture and processing of high-energy materials (HEMs).[97] This research area is very important because hazardous chemicals and extreme conditions are commonly used in current manufacturing processes, which make them dangerous and environment polluting.[157,158] A prospective approach to meet the challenge is based on the use of chemically resistant dense gases, in liquid and supercritical (sc) state as sustainable and recyclable media for synthesis and modification of HEMs. Among them, carbon dioxide and low-molecular-weight fluorohydrocarbons are of particular interest. Carbon dioxide is an available non-toxic natural gas, which is also produced in huge amounts by combustion of hydrocarbon fuels at thermal power stations. Some low-molecular-weight fluorohydrocarbons, in particular 1,1,1,2-tetrafluoroethane (TFE) also correspond to green environmental criteria exerting no destructive effect on the ozone layer and causing no acid rains.[159–161] These gases are thermally stable, inflammable and resistant towards oxidizers, to which a majority of energetic products and corresponding reagents belong. They can be readily removed from energetic materials *via* simple decompression and do not require expensive utilization. In this focus article a few recent applications of liquid or sc-$CO_2$ and TFE for green synthesis and processing (desensitization, crystal formation, *etc*.) of energetic materials are briefly discussed.

The TFE has been recently identified as sustainable reaction medium for electrophilic nitration of carbamates,[162] alcohols[163] and arenes[164] with dinitrogen pentoxide (DNP) – a green nitrating agent taken in nearly stoichiometric amount to afford functionalized *N*-nitramines **176**, nitric esters **177** and various nitroarenes **178**, respectively, in high yields. The TFE is superior in a certain degree to liquid or sc-$CO_2$ previously applied in these reactions (see ref. 97) as it enables performing the processes at significantly lower pressure (0.6–0.8 MPa) readily attainable in industry (Scheme 44). The reactions are clean: the 100% $HNO_3$ is the only by-product, which could be directly used as a nitrating agent or the key precursor to DNP (*via* dehydration). The TFE can be readily recycled *via* evaporation/condensation (bp 20 °C at 0.3 MPa) similar to operating cycles in freezing units. This method is applicable to efficient synthesis of practically important nitroesters **177**, which are used as components of EMs and active pharmaceutical ingredients, in particular glycerin trinitrate (GTN), pentaerythritol nitrate (PETN), mannitol nitrate (MHN), *etc*.

Interestingly, thus obtained *N*-nitrocarbamates **176** could be converted without isolation to primary nitramines **179** bearing one or two nitramine groups under the action of ammonia (see Scheme 44).[162] The one-pot integrated process is safer (no manipulation with explosive intermediates **176** is needed) and greener (by-produced ammonium nitrate and ethyl carbamate are applied as fertilizers in agriculture). The reaction has a wide scope being applicable to synthesis of compounds for civil use. In particular, it enables facile conversion of cyclic carbamates **180**, derived from natural α-amino acids, to functionalized nitramines **181** studied as potential bioactive compounds (Scheme 45).[165]



**Scheme 44**



$R^1$ = Me, $Pr^i$, $Bu^i$, $CO_2Me$, $CH_2OH$; $R^2$ = H, Me
$R^3$ = H; $R^4$ = H, Et, Pr, Bu; $R^3$ = $R^4$ = Et

**Scheme 45**

The continuous nitration of alcohols with DNP in a liquefied TFE flow is also feasible.[166] The flow installation is characterized by two orders of magnitude higher performance than corresponding batch reactions. Furthermore, the continuous process is even safer as it prevents local overheat of the flowing reaction mixture and minimizes amount of the reactants located at the reactor active zone at each moment.

The increased power of practically important secondary explosives (TNT < RDX < HMX < CL-20) inevitably leads to enhanced sensitivity of material towards mechanical or thermal stimuli (IS are 30, 11, 8 and 4 J, respectively). The unfavorable tendency motivates researchers to improve operational safety of most powerful basic components, such as HMX or CL-20,[17] by the physical modification of existing samples. A promising phlegmatization method implies coating of EM particles with a polymer.[167–169] To address environmental concerns related to HMX coating with organic solvents, the supercritical carbon dioxide (sc-$CO_2$) based antisolvent process was recently employed. As a result, HMX-based composites were fabricated with common commercial polymers, polymethyl acrylate (PMA), acrylonitrile butadiene styrene rubber (ABS), ethyl cellulose (EC), polylactide (PLA), and polyethylene terephthalate glycol (PETG) taken in amount of only 1–3 wt%.[170] The coating effectively absorbed the mechanical stress, resulting in a much lower sensitivity to impact and a considerable improvement of the HMX friction sensitivity. Specifically, for HMX@3PMA composite the impact and friction sensitivities were 54 J and 240 N, as compared to 7 J and 150 N for neat HMX. In other words, the method allowed obtaining the composites that are nearly as energetic as HMX, but as low sensitive as TNT. In addition, these composites have significantly higher flowability due to a reduction of the localized charge compared to the neat HMX, thus providing a safer work environment.

Application of stable gases in liquid or supercritical state as antisolvents delivered promising results in the fabrication of micro- and nano-sized EM particles. The CL-20, one of the most promising high-energy compounds, can exist under normal conditions in the α, β, γ and ε crystal modifications (polymorphs).[171,172] Among these, ε-CL-20 is the most favorable polymorph, since it has the highest thermal stability and density values,[17,173] and the lowest sensitivity to mechanical stimuli. However, only α-phase CL-20 nanocrystals (~40 nm) were produced *via* a sc-CO$_2$-based antisolvent process due to the CO$_2$ inclusion into the explosive crystal lattice.[174] Luckily, polymorphic composition of CL-20 microcrystals can be efficiently controlled when using liquid/supercritical TFE as media for CL-20 recrystallization.[175] In particular, the desirable ε-phase or less efficient β-phase crystals selectively formed depending on the CL-20 solution concentration and the TFE flow rate at ambient temperature (Figure 14). The developed procedure for ε-CL-20 formation is characterized by mild conditions (20 °C, 0.5–0.6 MPa), tolerance to initial substrate quality (crude CL-20 is applicable), increased environmental and industrial safety, ease of product isolation (decompression), and the ability to control the particle morphology and crystalline phase. The elimination of hazardous drying stage is also an important advantage.

Nitrocellulose (NC), a basic component of explosives, powders and propellants, has been downscaled to nanosized particles with an average size of 190 nm from the nitrocellulose fibers of 20 μm in diameter *via* the CO$_2$-based supercritical antisolvent process at 10–12 MPa pressure.[176] Compared to the micron-sized powder, the obtained nano-nitrocellulose is characterized by substantially improved friction sensitivity along with the burning rate increase from 3.8 to 4.7 mm s$^{-1}$ at 2 MPa. Stable nitrocellulose composites are also prepared *via* the proposed approach. Thus, the addition of 1 wt% carbon nanotubes further improved the sensitivity of the nano-nitrocellulose up to the friction-insensitive level. Moreover, the composite containing both carbon nanotubes and nanosized iron oxide, a well-known catalyst of combustion processes, exhibited the 20% burning rate increase at 12 MPa evidenced by a high-speed filming. The proposed approach for introducing the burning rate modifiers into the EM matrices results in increasing performance, better suits the high technological and ecological requirements and may be useful for energetic composites production. From the chemical engineering prospective, the CO$_2$-based method is obviously advantageous over previously reported preparative techniques involving hydrocarbon-derived organic solvents[177,178] as it eliminates the issues of wasted solvents utilization and removal of their traces trapped inside the product.

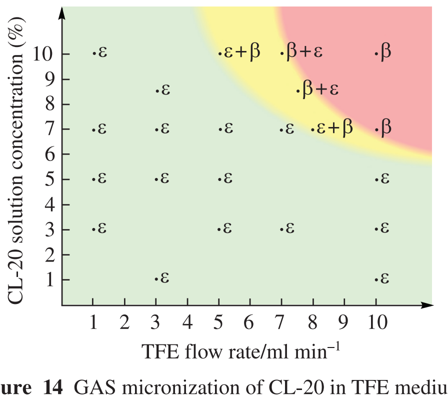


**Figure 14** GAS micronization of CL-20 in TFE medium.

## 5. Summary and outlook

In summary, efficient strategies have been developed over the past years for rational synthesis of novel high-energy density nitro compounds in which the nitro group is linked to the molecular backbone *via* N–C, N–N or N–O bonds. Particular attention was payed to targeted design of nitro compounds bearing high enthalpy azole (pyrazole, oxazole, oxadiazole, triazole, tetrazole) rings or fused heterocyclic scaffolds.

Several recently prepared energetic pyrazole, dipyrazole, pyrazolo-triazine and pyrazolo-tetrazine derivatives containing up to ten nitro groups at carbon atom exhibited remarkable density, detonation performance and have from moderate to good thermal stability. The chemistry of high-energy *N*-nitro compounds has remained an actively developing research area. Fascinating covalent and ionic ECs of this type were designed and rational synthetic approaches to them were elaborated. More powerful CL-20 derivatives, energetic DNA salts or nitramino azole salts bearing high-enthalpy nitrogen-rich cations remain most attractive targets. Ongoing researches on melt-castable nitric esters – potential substitutes of TNT in energetic formulations, resulted in preparation of novel low-melting and stable ECs containing isoxazole, furoxan, 1,2,3-triazole and cyclobutane core, which exhibit required standalone melt-castable explosive properties.

Rational installation of properly located nitro groups of different types along with other energy-rich functionalities, first of all *N*-oxide and diazene oxide fragments, into a high-enthalpy heterocyclic backbone became a powerful synthetic tool in the search of unique energetic materials. The main challenge here is attaining a subtle balance between the record energetic performance and safe operational properties of the designed EMs (thermal stability, impact and friction sensitivity, compatibility with other energetic components, *etc*.).

Research on hypergolic ionic liquids (HILs) and strained 1,5-diazabicyclo[3.1.0]hexane derivatives capable of ultrafast ignition upon mixing with an oxidizer for replacement of acutely toxic and carcinogenic methylated hydrazine derivatives in liquid rocket bipropellants occupied a priority position. However, preparation of hydrolytically stable HILs with required performance and elaboration of facile and efficient syntheses of 1,5-diazabicyclo[3.1.0]hexane derivatives applicable to industry still remain challenging tasks.

A perspective approach to large-scale production of liquid hydrocarbon fuels with strained cyclopropane fragments for high-impulse rocket propellants is based on catalytic cyclopropanation of olefins with diazomathane generated *in situ* for safety reason. Currently, palladium-based complexes are commonly used as catalysts of this process. However, novel, in particular iron-based catalysts,[179] are highly desirable to make it cheaper and more selective.

To meet environmental concerns associated with hazard of current EMs production and processing, novel methodologies have been developed based on usage of carbon dioxide or lower fluorinated hydrocarbons pressurized to liquid and supercritical state as fire and explosion safe and nearly waste-free media. Furthermore, supercritical antisolvent processes based on these media have significant potential in phlegmatization of most powerful high-energy-density materials while retaining their performance, and in the fabrication of micro- and nano-sized EM particles and energetic composites which exhibit improved performance. In some cases, organic electrochemistry also seems to be a promising tool in chemoselective preparation of high-energy substances with decreased ecological hazards and optimized production costs.

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