A Short Review of Nitric Esters and Their Role in Energetic Materials

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ABSTRACT: A review of energetic materials based on the nitric ester functionality is presented. Examined are materials that are classified as primary explosives, pressable secondary explosives, melt-castable secondary explosives, and rocket- and gun-propellant materials. Disclosed are the molecular structures, physical properties, performances, and sensitivities of the most important legacy nitric esters, as well as the relevant new materials developed within the past several years. Where necessary, discussions of the synthetic protocols to synthesize these materials are also presented.

1. INTRODUCTION

The field of energetic materials encompasses the areas of explosives, propellants, and pyrotechnics. In designing suitable materials, the incorporation of nitro groups represents the classic way to increase density and energetic power of a given energetic material. Nitro groups can be added to nitrogen atoms to form nitramines, aromatic carbons to form nitro-aromatics, aliphatic carbons to form nitroalkanes and polynitroalkanes, and alcohols to form nitric esters.1a−d The nitric ester moiety is not only of high medicinal importance,2 but also one of the most useful explosives in designing rational energetic materials.1a Conversion of hydroxyl functionalities to the nitric ester can be achieved by several means and is an appealing way to significantly increase the density, oxygen balance, and energetic power of a molecule. Nitric esters are commonly found in materials that can be classified as primary explosive, secondary explosive, and propellant ingredients. While there are hundreds of nitric ester-based energetic materials that have been synthesized to date, this review will focus on materials that are of interest from an application standpoint.

2. NITRIC ESTER EXPLOSIVES

2.1. Primary Explosives. A primary explosive material is characterized as a material that has a high sensitivity to impact, friction, and electrostatic discharge. It is typically present in small amounts and is used as part of an ignition train to initiate a more powerful secondary explosive in a weapons system. Legacy primary explosives include the highly effective but also toxic mercury fulminate, lead azide, and lead styphnate, to name a few.3 However, there are nitric ester materials that also fall into the primary explosives category and are thus “greener” due to their heavy-metal-free nature. Officially classified as a “borderline” primary explosive due to its respective impact and friction sensitivity of 3 J and 60 N, pentaerythritol tetranitrate4 (PETN) is a common ingredient in many pyrotechnic percussion primer mixtures, blasting caps, and detonation cord due to its high performance, coupled with its sensitivity values. Highly nitrated sugars have also been prepared and, because of their high sensitivities to impact, friction, and shock, are firmly classified as primary explosive materials (Figure 1). This includes xylitol pentanitrate (XPN), sorbitol hexanitrate...
XPN has sometimes been characterized as a viscous liquid material, but this is due to impurities that arise during nitration. Pure XPN is a white, crystalline solid. XPN possesses an explosive power that is similar to RDX. However, unlike the secondary explosive nature of RDX, XPN is classified as a primary explosive material, because it possesses a significantly higher impact and friction sensitivity as compared to PETN. A primary explosive material, because it possesses a significant primary explosive-like sensitivity to friction, and borderline primary explosive impact sensitivity. However, the ((S,S)- and (R,R))-diastereomers were found to be liquids, with evidence of a glass transition temperature at −50 °C. Interestingly, the latter two diastereomers were found to exhibit very insensitive friction sensitivities, yet very high impact sensitivity values. While it is expected that the ETN materials will exhibit similar calculated performance values, the physical properties of energetic materials are demonstrated to change based on the orientations of the explosophores in space.

A rather distinct class of nitrated sugars that is worthy of discussion is the erythritol tetrinitrate (ETN) series of nitric esters. Although the ((R,S)-meso diastereomer of ETN was isolated in high purity by recrystallization. Nitration of cyclohexane 1 was not the major product. Instead, the fused tricycle 2 was the major product, and was isolated in high purity by recrystallization. Nitration of 2 yielded trinitrate 3.
sensitivities, triazole 6 possessed a lower friction sensitivity than the monoazide and diazide. While this may seem counterintuitive, it is to be expected, given that 4 and 5 are solids, and 6 is a liquid.

2.2. Secondary Explosives. A secondary explosive, unlike a primary explosive, has a lower sensitivity to impact, friction, and electrostatic discharge, but yields higher detonation velocities and detonation pressures.8 Due to their relatively insensitive nature, secondary explosive materials are usually present in large quantities in munitions such as mortar and artillery rounds and are thus referred to as “main fill” materials. Some of the most common secondary explosives include the pressable materials RDX and HMX.3 CL-20 also fits within the pressable secondary explosive category, but finds little practical application due to its expensive cost. Interestingly, despite the large number of nitric ester molecules that have been synthesized to date, it is difficult to find such a standalone material that fits into the secondary explosive profile. However, several secondary explosive formulations containing PETN have been developed, in which these formulations feature a high performance but a reduced sensitivity.

One of the most common PETN-based formulation classes is Semtex. The Semtex series of explosives is currently produced in the Czech Republic and has many variants, including 1A, 1H, 10, 10-SE, and S 30.12a They are all classified as plastic explosives with the capability to be shaped into charges. Semtex mixtures contain large amounts of PETN and/or RDX as the main fill, inert binders/plasticizers to reduce sensitivity, and a small amount of stabilizer to prolong shelf life. Semtex 1A, 1H, and 10 are used mainly for demolition and underwater blasting, and can also be used as an initiator. SEMTEX 10-SE is used for the explosive hardening of metal materials, while the S 30 variant is used for explosive cladding and welding of metals. Some physical and performance properties of the aforementioned Semtex formulations are given in Table 5.

| Table 3. Performance, Physical Properties, and Sensitivities of Trinitrate 3 |
|-----------------|---------|---------|
| data category   | 4       | 5       | 6       |
| \(T_m\) [°C]    | 115     | 115     | 115     |
| \(T_{decomp}\) [°C] | 155     | 155     | 155     |
| \(\Omega_{CO2}\) [%] | −13     | −13     | −13     |
| \(\rho'\) [g cm\(^{-3}\)] | 1.73    | 1.73    | 1.73    |
| \(V_{det}\) [ms\(^{-1}\)] | 8000    | 8000    | 8000    |
| \(\Delta H^f\) [kJ mol\(^{-1}\)] | −649.2  | −649.2  | −649.2  |
| IS\(^\circ\) [J] | 2       | 2       | 2       |
| FS\(^\circ\) [N] | 50      | 50      | 50      |

\(a\)\(T_m\) = onset temperature of melting. \(b\)\(T_{decomp}\) = onset temperature of decomposition. \(c\)\(\Omega_{CO2}\) = CO\(_2\) oxygen balance. \(d\)\(\rho'\) = derived density from X-ray data. \(e\)\(V_{det}\) = detonation velocity. \(f\)\(\Delta H^f\) = molar enthalpy of formation. \(g\)IS\(^\circ\) = impact sensitivity. \(h\)FS\(^\circ\) = friction sensitivity.

Table 3 provides a comprehensive overview of the performance, physical properties, and sensitivities of trinitrate 3.

Figure 3. Molecular structure of azido nitrate derivatives 4–6.

Table 4. Performance, Physical Properties, and Sensitivities of Azidonitrates 4–6

| data category   | 4       | 5       | 6       |
|-----------------|---------|---------|---------|
| \(T_m\) [°C]    | 82      | 32      | −24     |
| \(T_{decomp}\) [°C] | 180     | 172     | 175     |
| \(\Omega_{CO2}\) [%] | −27     | −46.4   | −68.7   |
| \(\rho'\) [g cm\(^{-3}\)] | 1.67    | 1.59    | 1.53    |
| \(P_j\) [GPa]   | 27.8    | 24.2    | 21.2    |
| \(V_{det}\) [ms\(^{-1}\)] | 8092    | 7842    | 7740    |
| \(\Delta H^f\) [kJ mol\(^{-1}\)] | −59     | +362    | +795    |
| IS\(^\circ\) [J] | 2       | 3       | 1       |
| FS\(^\circ\) [N] | 36      | 15      | 80      |

\(a\)\(T_m\) = onset temperature of melting. \(b\)\(T_{decomp}\) = onset temperature of decomposition. \(c\)\(\Omega_{CO2}\) = CO\(_2\) oxygen balance. \(d\)\(\rho'\) = derived density from X-ray data. \(e\)\(V_{det}\) = detonation velocity. \(f\)\(\Delta H^f\) = molar enthalpy of formation. \(g\)IS\(^\circ\) = impact sensitivity. \(h\)FS\(^\circ\) = friction sensitivity.

As the nitrate moiety was replaced with the azide explosophore, the density, detonation pressure, and detonation velocity declined, while the heat of formation, as expected, rose significantly (Table 4). Addition-

ally, the melting point was observed to decrease significantly as the number of azide groups increased, culminating with triazole 6 exhibiting liquidous behavior. As expected, impact sensitivities were in the primary explosive range for all materials, with sensitivities to impact increasing with higher azide content. Although 4–6 exhibited high friction
Table 6. Physical and Performance Properties of Formex P1, Sprängdeg m/46, and EPX-1 Plastic Explosives

| data category | Formex P1 | Sprängdeg m/46 | EPX-1 |
|---------------|-----------|----------------|-------|
| $\rho'$ [g cm$^{-3}$] | 1.53 | 1.52 | 1.55 |
| $V_{\text{det}}$ [ms$^{-1}$] | 7544 | 7520 | 7636 |
| $P_d$ [GPa] | 20.0 | 19.3 | 21.1 |
| % PETN | 89 | 86 | 86 |
| IS$^i$ [J] | 13.5 | 14.2 | 13.9 |
| FS$^i$ [N] | 194 | 183 | 176 |

Table 7. Performance, Physical Properties, and Sensitivities of Tetranitrate SMX

| data category | SMX |
|---------------|-----|
| $T_m$ [°C] | 85–86 |
| $T_{\text{det}}$ [°C] | 141 |
| $\Omega_{\text{CO}}$ [%] | 0 |
| $\Omega_{\text{CO}}^i$ [%] | +38.1 |
| $\rho'$ [g cm$^{-3}$] | 1.912 |
| $V_{\text{det}}$ [ms$^{-1}$] | 9100 |
| $P_d$ [GPa] | 40.0 |
| $\Delta H^\text{m[det]}$ [kJ mol$^{-1}$] | −371 |
| IS$^j$ [J] | 3 |
| FS$^j$ [N] | 60 |
| ESD$^j$ [N] | 0.625 |

Table 8. Physical and Performance Properties of Melt-Castable Nitric Esters BIDN, BITN, BODN, and TNT

| data category | TNT | BIDN | BITN | BODN |
|---------------|-----|------|------|------|
| $T_m$ [°C] | 80.4 | 92 | 121.9 | 84.5 |
| $T_{\text{det}}$ [°C] | 295 | 189.2 | 193.7 | 183.4 |
| $\Omega_{\text{CO}}$ [%] | −74 | −62 | −37 | −33.3 |
| $\Omega_{\text{CO}}^i$ [%] | −24.7 | −16.8 | 0 | 0 |
| $\rho'$ [g cm$^{-3}$] | 1.65 | 1.605 | 1.76 | 1.832 |
| $P_d$ [GPa] | 20.3 | 19.3 | 27.1 | 29.4 |
| $V_{\text{det}}$ [ms$^{-1}$] | 6950 | 7060 | 7837 | 8180 |
| $\Delta H^\text{m[det]}$ [kJ mol$^{-1}$] | −59.3 | −139 | −395 | −79.4 |
| IS$^j$ [J] | 15 | 11.2 | 30 | 8.7 |
| FS$^j$ [N] | 240 | >360 | 60 | 282 |
| ESD$^j$ [N] | 0.25 | 0.25 | 0.0625 | 0.125 |

because of the latter, the prospect of SMX being a melt-castable material is likely very limited.

More recent work has demonstrated that nitric ester materials can exhibit low sensitivities, high performance, and optimal melting points and decomposition temperatures to be classified as melt-castable. Three such materials, summarized in Scheme 2, were derived from the common intermediate diazodiaminoglyoxime (7).

Scheme 2. Synthesis of Melt-Castable Nitric Esters BIDN, BITN, and BODN

![Scheme 2](image-url)

Table 8. Physical and Performance Properties of Melt-Castable Nitric Esters BIDN, BITN, BODN, and TNT

| data category | TNT | BIDN | BITN | BODN |
|---------------|-----|------|------|------|
| $T_m$ [°C] | 80.4 | 92 | 121.9 | 84.5 |
| $T_{\text{det}}$ [°C] | 295 | 189.2 | 193.7 | 183.4 |
| $\Omega_{\text{CO}}$ [%] | −74 | −62 | −37 | −33.3 |
| $\Omega_{\text{CO}}^i$ [%] | −24.7 | −16.8 | 0 | 0 |
| $\rho'$ [g cm$^{-3}$] | 1.65 | 1.605 | 1.76 | 1.832 |
| $P_d$ [GPa] | 20.3 | 19.3 | 27.1 | 29.4 |
| $V_{\text{det}}$ [ms$^{-1}$] | 6950 | 7060 | 7837 | 8180 |
| $\Delta H^\text{m[det]}$ [kJ mol$^{-1}$] | −59.3 | −139 | −395 | −79.4 |
| IS$^j$ [J] | 15 | 11.2 | 30 | 8.7 |
| FS$^j$ [N] | 240 | >360 | 60 | 282 |
| ESD$^j$ [N] | 0.25 | 0.25 | 0.0625 | 0.125 |

$^aT_m$ = onset temperature of melting. $^bT_{\text{det}}$ = onset temperature of decomposition. $^c\Omega_{\text{CO}}$ = CO$_2$ oxygen balance. $^d\Omega_{\text{CO}}^i$ = CO oxygen balance. $^e\rho'$ = derived density from X-ray data. $^fV_{\text{det}}$ = detonation velocity. $^gP_d$ = detonation pressure. $^h\Delta H^\text{m[det]}$ = molar enthalpy of formation. $^i$IS = impact sensitivity. $^j$FS = friction sensitivity. $^k$ESD = electrostatic discharge sensitivity.

one that is able to be melted with steam at ambient pressure. 3,3’-Bisoxazole-4,4’,5,5’-tetra(methylene) tetranitrate (BIDN) was higher performing than BIDN due to its higher density, and more favorable oxygen balance. However, BITN also exhibited a PETN-like sensitivity to impact, friction, and electrostatic discharge because of these reasons, coupled with the presence of more nitric ester functionalities. The higher melting point of BITN also eliminates it as a standalone melt-castable material. However, BITN can serve as a potential melt-castable eutectic compound. Melt-castable eutectics are materials that exhibit melting points slightly above 100 °C, but whose melting point can be lowered into the standalone melt-castable range when formulated with other materials.
Bis(1,2,4-oxadiazole)-bis(methylene) dinitrate (BODN) exhibits very promising properties as a standalone melt-castable material, with a detonation pressure ca. 50% higher than TNT, and a low sensitivity. The high performance is owed to the presence of a higher nitrogen content as compared to BIDN, its higher density, and favorable oxygen balance. The low sensitivity of BODN likely stems from its crystal structure, in which the nitric ester moieties engaged in intramolecular hydrogen bonding with the methylene hydrogen atoms.

Standalone melt-castable material 10 was recently synthesized, in which the well-known furoxan ring16 was inserted between the 5-nitroxyethyl isoxazole rings (Figure 5). When comparing 10 to BIDN, introduction of the furoxan ring was observed to significantly increase the density, heat of formation, detonation velocity, and detonation pressure (Table 9).17 Interestingly, the melting and decomposition temperatures remained largely unchanged, meaning that 10 also exhibits standalone melt-castable behavior.

| data category | TNT | 10 |
|---------------|-----|----|
| $T_m$ [°C]   | 80.4| 91 |
| $T_{dec}$ [°C] | 295 | 194 |
| $\Omega_{CO}$ [%] | −74 | −56.2 |
| $\Omega_{CO}$ [%] | −24.7 | −13 |
| $\rho$ [g cm$^{-3}$] | 1.65 | 1.72 |
| $P_f$ [GPa] | 20.5 | 25.1 |
| $V_{dec}$ [m s$^{-1}$] | 6950 | 7374 |
| $\Delta H^f$ [kJ mol$^{-1}$] | −59.3 | +49.5 |
| IS [°C] | 15 | 7.8 |
| FS [N] | 240 | 240 |
| ESD [J] | 0.25 | 0.125 |

$^{a}T_m$ = onset temperature of melting. $^{b}T_{dec}$ = onset temperature of decomposition. $^{c}\Omega_{CO}$ = CO$_2$ oxygen balance. $^{d}\Omega_{CO}$ = CO oxygen balance. $^{e}\rho$ = derived density from X-ray data. $^{f}P_f$ = detonation pressure. $^{g}V_{dec}$ = detonation velocity. $^{h}\Delta H^f$ = molar enthalpy of formation. $^{i}$IS = impact sensitivity. $^{j}$FS = friction sensitivity. $^{k}$ESD = electrostatic discharge sensitivity.

Recently, several stereo- and regioisomeric cyclobutane tetranitrates were synthesized (Figure 6).18 Although the energetic performances were found to be similar, the physical properties of the compounds were found to be significantly different. Of the six compounds synthesized, 11 and 13 were classified as melt-castable eutectic materials, as evidenced by the melting and decomposition temperatures of these materials (Table 10). 14 can be classified as a standalone melt-castable explosive due to its 85.9 °C melting point. Unsurprisingly, the impact sensitivity of 14 is higher, which is likely due to the nitric ester moieties being in closer proximity to one another. However, the impact sensitivity is still lower than PETN. 12 and 15 are classified as explosives, but their undesirable melting points make them unappealing for practical applications.

### 2. NITRIC ESTER PROPELLANTS

As the name implies, the purpose of a propellant is to provide the energy for a projectile, vehicle, or object to fly a specified distance. Propellants that contain nitric esters include double-base (nitrocellulose and nitroglycerin) and triple-base (nitrocellulose, nitroglycerin, and nitroguanidine) mixtures (Figure 7). NG is typically synthesized using mixed acid at cold temperatures. When producing NG in mass, ensuring that the material is free from acid is critical to ensuring its long-term stability. Acid buildup of nitroglycerin mixtures is well-known to exothermic autocatalytic decomposition, which can lead to severe explosions.14

NC is prepared by nitrating high-quality cellulose (derived from wood pulp or cotton linters) with mixed acid. By controlling the concentration and ratios of mixed acid used, various degrees of nitrated NC can be obtained. The degree of nitrination is measured by determining the nitrogen content of the product. The percent nitrogen content for NC is typically 10.3–13.5%. NC that possesses a nitrogen content between 10.3% and 12.3% typically finds applications as lacquers.

![Figure 5. Molecular structure of standalone melt-castable nitric ester 10.](image)

![Figure 6. Structure of stereo- and regioisomeric cyclobutane tetranitrates 11–15.](image)

![Figure 7. Molecular structure of nitrocellulose (NC), nitroglycerin (NG), and nitroguanidine (NQ).](image)

![Table 9. Physical and Performance Properties of Standalone Melt-Castable Nitric Ester 10](table)

| data category | TNT | 10 |
|---------------|-----|----|
| $T_m$ [°C]   | 106 | 47.5 |
| $T_{dec}$ [°C] | 198.5 | 199.7 |
| $P_f$ [GPa] | 24.5 | 22.9 |
| $V_{dec}$ [m s$^{-1}$] | 7438 | 7544 |
| $\Delta H^f$ [kJ mol$^{-1}$] | −510.1 | −535.9 |
| IS [°C] | 6.2 | 6.2 |
| FS [N] | 240 | 240 |
| ESD [J] | 0.125 | 0.125 |

$^{a}T_m$ = onset temperature of melting. $^{b}T_{dec}$ = onset temperature of decomposition. $^{c}\rho$ = derived density from X-ray data. $^{d}P_f$ = detonation pressure. $^{e}V_{dec}$ = detonation velocity. $^{f}\Delta H^f$ = molar enthalpy of formation. $^{g}$IS = impact sensitivity. $^{h}$FS = friction sensitivity. $^{i}$ESD = electrostatic discharge sensitivity.

![Table 10. Physical and Performance Properties Cyclobutane Tetranitrates 11–15](table)
The ability to gelatinize helps to reduce the overall sensitivity of propellant mixtures. Although EGDN, DEGDN, and TEGDN are not considered NG replacements due to their lower performances and oxygen balances, they do possess the ability to depress the freezing temperature of NG. Butanetriol trinitrate (BTTN) not only gelatinizes well with NC, but also has been explored as a potential replacement to NG. At low temperatures, NG has been found to crystallize in double-base formulations, causing the propellant grain to crack, thus rendering a formulation unusable. Partial replacement of NG with BTTN has been found to solve the cracking problem. BTTN has been found to possess a higher thermal stability, a lower shock sensitivity, and a lower freezing point, and it is six times less volatile than NG. Despite this, NG remains the plasticizer of choice on the basis of cost. Currently, on a pound basis, BTTN costs $60 to produce, while NG costs $2. There are recent efforts, however, to employ directed evolution/microbe technologies to manufacture butanetriol (the precursor to BTTN). If successful, this could significantly reduce the cost.

Due to the presence of only primary nitric ester functionality, its low volatility, and because of its lower oxygen balance, trimethyloltrinitrate (TMETN) is one of the more stable and less sensitive nitric esters commonly encountered in propellant mixtures. Unlike the aforementioned plasticizers, TMETN gelatinizes NC only to a moderate extent, and due to the presence of only primary nitric ester functionalities, it can signiﬁcantly reduce the cost. While TMETN does not gelatinize well with NG, it does only limited applications as a plasticizer in propellant mixtures. It has, however, been found to be a favorable plasticizer for glycyl azide polymer (GAP).

Nitroxyethyl nitrates (NENAs) are of high interest to the rocket and especially gun propulsion community. Two of the most popular NENAs are n-butyl nitroxyethylnitramine (BuNENA) and dioxynitrolylmethylnitramine dinitrate (DINA). NENAs are typically prepared with a mixture of ArO and HNO₃ in the presence of ZnCl₂ as a catalyst. ZnCl₂, which forms the transient chlorine intermediate, is critical in obtaining high yields of product. Like many in the NENA class, BuNENA and DINA have been shown to plasticize cellulose-based polymers. This includes NC, GAP, polyglycidyl nitrate (poly GLYN), and poly(3-nitratomethyl-3-methyl) oxetane (poly NMMO) (Figure 9). BuNENA and DINA are characterized as having a low impact sensitivity and low glass transition temperatures. They are capable of forming eutectic mixtures, exhibiting lower melting points than conventional nitric esters, and thus preserving optimal low-temperature mechanical properties. NENAs have been found to impart high

Table 11. Performance and Sensitivity Values of Some Commonly Encountered Ingredients in Double- and Triple-Base Propellant Formulations

| data category | NC | NG | NQ | EGDN | DEGDN | TEGDN | BTTN | TMETN | BuNENA | DINA |
|---------------|----|----|----|------|-------|-------|------|-------|--------|------|
| $T_{m}$ [°C]  | 14 | 16 | 27 | -26  | -19   | -19   | -27  | -3    | -9     | 51.3 |
| $T_{dec}$ [°C] | 192–209 | 150 | 248.9 | 175 | 160 | 170 | 182 | 180 | 177.5 |
| $\Omega_{CO}$ [%] | -28.7 | 3.5 | -30.7 | 0 | -40.8 | -66.7 | -16.6 | -34.5 | -104.3 | -26.6 |
| $\Omega_{CO}$ [%] | 24.7 | -15.7 | -21 | -8.2 | -26.7 | -10.5 | -3.5 | -57.9 | 0 |
| $\rho$ [g cm⁻³] | 1.67 | 1.59 | 1.71 | 1.48 | 1.38 | 1.335 | 1.52 | 1.46 | 1.22 | 1.488 |
| $V_{det}$ [ms⁻¹] | 7300 | 7600 | 8200 | 7300 | 6600 | 2000 | 7050 | 7580 |
| $\Delta H_f$ [kJ mol⁻¹] | -1435.1 | -370.1 | -93 | -244.8 | -436.8 | -629.9 | -406 | -425.2 | -192.5 | -448.2 |
| IS [°C] | 3 | 0.2 | >49 | 0.2 | 0.2 | 12.7 | 1 | 9.2 | 6 | 6 |
| FS [N] | >353 | >353 | >353 | >353 | >353 | >353 | >353 | >353 | >353 | >353 |

$^aT_m$ = onset temperature of melting. $^bT_{dec}$ = onset temperature of decomposition. $^c\Omega_{CO}$ = CO₂ oxygen balance. $^d\Omega_{CO}$ = CO oxygen balance. $^e\rho$ = derived density from X-ray data. $^fV_{det}$ = detonation velocity. $^g\Delta H_f$ = molar enthalpy of formation. $^hIS$ = impact sensitivity. $^iFS$ = friction sensitivity.

Figure 8. Molecular structures of commonly encountered nitric ester plasticizers in double- and triple-base rocket propellant formulations.
burning rates in formulation, with reduced flame temperature. BuNENA and DINA has been used as a replacement for NG in the development of insensitive, low vulnerability (LOVA) double-base rocket and triple-base gun propellants.23b The Navy has produced DINA on large scales for the development of insensitive, low vulnerability (LOVA) double-base rocket propellants, and more recent work has demonstrated that DINA can be employed successfully in CL-20- and HMX-based double-base rocket propellants.24b

Despite the positive characteristics of NENA plasticizers, they suffer from long-term aging issues, and formulations containing these plasticizers have difficulty maintaining a 10 year service life. Although NENAs possess excellent plasticizing effects initially, their low molecular weights and high volatility allow these materials to move readily from polymeric binder systems in formulation.24a

Although their utility has been well demonstrated, the aforementioned nitric ester liquid propellant materials are relatively historical materials, and there have been very few new materials synthesized in this area. However, some recently synthesized liquid nitric esters were found to have potential energetic plasticizer properties. (Figure 10). Cyclobutane tetranitrate 16 was one of the family of materials synthesized in Figure 6, but was the only one in that family that exhibited liquid behavior, with a freezing point of $< -40 \, ^\circ C$, a high decomposition temperature, a good specific impulse (240 s), and a low sensitivity to impact, friction, and electrostatic discharge (Table 12).18 Another class of materials recently disclosed were energetic 1,2,3-triazole nitric ester materials, synthesized using click chemistry between azidoethanol and propargyl alcohol or 1,4-butyne diol, followed by nitrization to give 17 and 18.25 With a low decomposition temperature of 120 $^\circ C$, 17 is likely not to find application as a propellant plasticizer material. The fully substituted nature of 18 evidently increased the decomposition temperature significantly, and this material therefore has the potential to find use in propellant formulations.

**CONCLUSION**

In summary, not only does the nitric ester functionality contribute significantly to the overall energy of energetic molecules, but its presence also spans the many classes of energetic materials. Disclosed in this review are nitric ester materials that have the potential to serve as ingredients in primary explosives, pressable secondary explosives, melt-castable secondary explosives, double-base rocket propellants, and triple-base gun propellants. Although believed to be linked to a high degree of sensitivity, with unpredictable chemical and thermal stability, many of the newer nitric ester materials disclosed over the past 5 years were found to exhibit a significant degree of insensitivity and chemical/thermal stability. The nitric ester moiety—one of the earliest discovered and known explosophores—still plays an important role in the discovery of new energetic materials, across many potential energetic applications and platforms.

| Table 12. Performance and Sensitivity Values of Energetic Liquid Plasticizers 16–18 |
|---------------------------------|---|---|---|
| data category | 16 | 17 | 18 |
| $T_m$ [°C] | $< -40$ | - | - |
| $T_{de}$ [°C] | 186.8 | 120 | 155 |
| $\Omega_{CO}$ [%] | $-44.9$ | $-51.5$ | $-36.4$ |
| $\Omega_{CO}_2$ [%] | -9 | $-17.2$ | $-5.2$ |
| $\rho$ [g cm$^{-3}$] | 1.543 | 1.44 | 1.73 |
| $P_d$ [GPa] | 24.5 | 19.9 | 26.3 |
| $V_{de}$ [m s$^{-1}$] | 7577 | 7170 | 7950 |
| $\Delta H_{det}$ [kJ mol$^{-1}$] | $-512$ | $-70.9$ | 36 |
| IS [J] | 9 | 5.7 | 9 |
| FS [N] | >360 | - | - |
| ESD [J] | 0.125 | - | - |

$T_m$ = onset temperature of melting. $T_{de}$ = onset temperature of decomposition. $\Omega_{CO} = CO_2$ oxygen balance. $\Omega_{CO}_2 = CO$ oxygen balance. $\rho$ = derived density from X-ray data. $P_d$ = detonation pressure. $V_{de}$ = detonation velocity. $\Delta H_{det}$ = molar enthalpy of formation. IS = impact sensitivity. FS = friction sensitivity. ESD = electrostatic discharge.

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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■ ABBREVIATIONS

PETN, pentaerythritol tetranitrate; XPN, xylitol pentanitrate; MHN, mannitol hexanitrate; SHN, sorbitol hexanitrate; RDX, hexogen; NG, nitroglycerin; NQ, nitroguanidine; EGDN, ethylene (1,2,4-oxadiazole)-bis(methylene) dinitrate; NC, nitrocellulose; BIDN, 3,3′-biisoxazole-5,5′-bis(methylene) dinitrate; BTBN, 3,3′-biisoxazole-4,4′,5,5′-tetra(methylene) tetrinitrate; BODN, bis(1,2-oxidiazole)-bis(methylene) dinitrate; NC, nitrocellulose; NG, nitroglycerin; NQ, nitroguanidine; EGDN, ethylene glycol dinitrate; DEGDN, diethylene glycol dinitrate; TEGDN, triethylene glycol dinitrate; BTBN, butanetriol trinitrate; TMETN, trimethyl trinitrate; BuNENA, n-butyl nitroxyethynitrinate; DINA, dicyclohexynitrinate dinitrate; GAP, glycidyl azide polymer; Poly GLYN, polyglycidyl nitrate; poly NMMO, poly(3-nitratomethyl-3-methyl) oxetane

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